

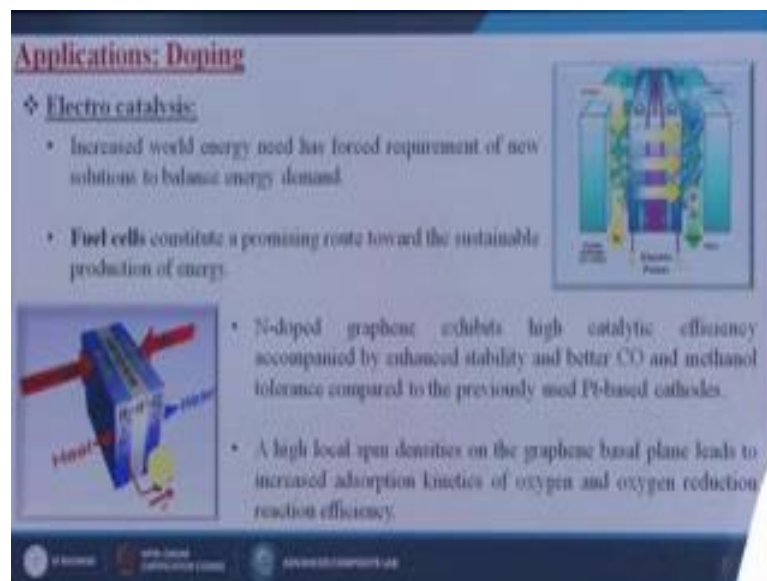
Surface Engineering of Nanomaterials
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Lecture - 39
Modified Nanomaterials: In-use for consumer products

Hello, today we are going to discuss our next lecture which actually we will discuss in brief that about the doping applications on various methods or maybe that using of doping for various applications. So, mainly we have kept our lecture title like this that modified nanomaterials in use for consumer products, so that means, whatever the products we are going to use; say suppose for the electronic purposes, for the sensing purposes, for maybe some solar cell technology or maybe for biomaterial applications, then how this doping materials can be introduced can be used for this particular applications.

First we have starting our applications on doping based on the electro catalysis techniques; that means, on electro catalysis techniques that how this doping materials is giving some better results or maybe rather we can say that how these doping materials is influencing the electro catalysis applications.

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Applications: Doping

❖ **Electro catalysis:**

- Increased world energy need has forced requirement of new solutions to balance energy demand.
- Fuel cells constitute a promising route toward the sustainable production of energy.

Graphene

- N-doped graphene exhibits high catalytic efficiency accompanied by enhanced stability and better CO and methanol tolerance compared to the previously used Pt-based cathodes.
- A high local spin densities on the graphene basal plane leads to increased adsorption kinetics of oxygen and oxygen reduction reaction efficiency.

The slide includes a diagram of a fuel cell stack and a 3D model of a graphene structure with a nitrogen atom (N) substituted for a carbon atom (C).

When you are talking about the electro catalysis, first that increased world energy need has focus requirement of new solutions to balance energy demand because when we are

talking about some kind of electro catalysis materials always we are trying to keep in mind that how we can increase the energy density at that particular material because every material is having certain limitations. So, our main motto is that; that our material should be less expensive should be cheap should be less weight, but it will store the more energy at that particular time.

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Applications: Doping

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N-doped graphene exhibits high catalytic efficiency accompanied by enhanced stability and better CO and methanol tolerance compared to the previously used Pt-based cathodes.

- A high local spin densities on the graphene basal plane leads to increased adsorption kinetics of oxygen and oxygen reduction reaction efficiency.

Same thing when we are talking about the fuel cells fuel cells is nothing, but some kind of it is coming and it is coming and some kind a renewable energy. So, renewable energy means we are not hampering the environment, it is one kind of green technology where we can make certain materials which can absorbed the maximum energy at that particular point and later when we need those energy easily we can extract that energy from that particular material and we can use that energy for our day to day life.

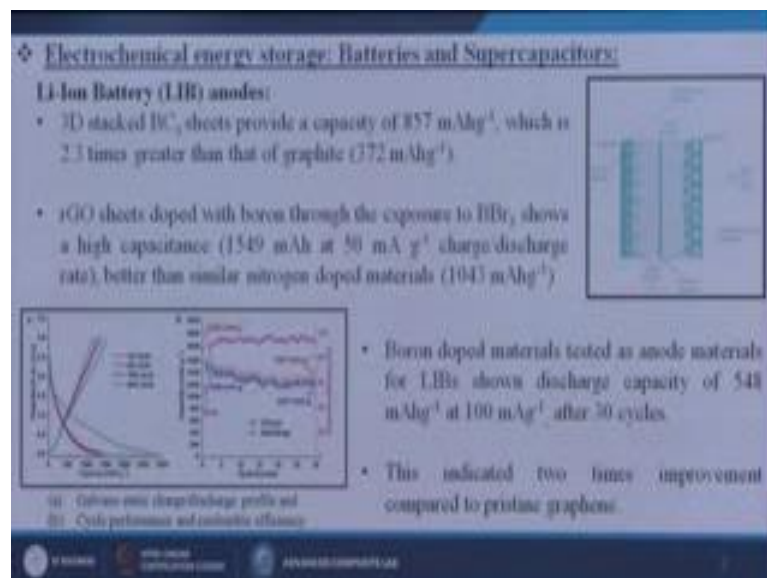
Here when we are talking about these electro catalysis mechanisms or fuel cells; say suppose some kind of the graphene materials generally that nitrogen doped graphene we are trying to utilize for these particular purpose which is giving the better properties or maybe the some enhanced properties in terms of fuel cells and the electro catalysis techniques. So, what we are going to show you that N-doped graphene exhibits high catalytic efficiency accompanied by enhanced stability and better carbon monoxide and methanol tolerance compared to the previously used platinum based cathodes.

When we are using this kind of materials, so previously we are using some materials which is generating the carbon monoxides or maybe which is generating some kind of methanol inside the system maybe that material cannot sustain or maybe some kind of toxic gases can come from the that particular techniques which can create some kind of hazardness to the environment. Nowadays we are trying to use this nitrogen doped graphene which can be readily make in our laboratory and which can tolerate this can be carbon monoxide gas or maybe some kind of toxic gases which is generating inside the systems so easily so that this material can be used for a longer time.

Also a high local spin densities on the graphene basal plane leads to increase the adsorption kinetics of oxygen and oxygen reduction reaction efficiency; that means, simultaneously, it is increasing the adsorption technology, adsorption is nothing but the attachment of the gas molecules on the substrate surface itself is not going inside. So, that adsorption of the oxygen also this kind of materials is increasing so that we can get some better properties.

Next, we are trying to discuss this kind of doping materials on best of some electro chemical energy storage, mainly for the batteries and the super capacitors.

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If we remember that nowadays, every time we are talking about the lithium ion battery or maybe we are trying to discuss about the super capacitors which is nothing but the some kind of energy storage device; that means, when I am generating these energy. So, I have

to store this energy in somehow because when I need it or maybe at the time of power cut, I have to use this kind of energy. So, for these purpose I have to make certain kind of storage tank which can absorb this energy and when I needed easily I can take out the energy from that particular materials, so that means, these kinds of materials is nothing, but a one kind of energy absorbed. So, when we are talking about this kind of materials people are also trying to use this kind of doping materials or maybe the modified nano fillers for enhancing their storage capability.

Generally we are talking about the lithium ion battery in the anodes site. So, 3 dimensional stacked BC 3 sheets provide a capacity of 857 milliampere hour per gram which is 2.3 times greater than that of graphite. So, what I am trying to tell in this particular case that when you are using this graphite, it was giving the 372 milliampere hour per gram, but when I am using this boron carbide then sheets we have when the capacity has been increased, it has gone up to 857 which is nothing, but that twice or maybe thrice of this graphitic balloon.

Then sometimes we are using the reduced graphene oxides then that sheets also doped with boron; that means, these rGO we are doping by the boron means boron doped rGO material through the exposure of boron bromide shows a high capacitance that is - 1549 milliampere hour at 50 milliampere per g charged discharge rate better than similar nitrogen doped materials which is giving only 1043 milliampere hour per gram. So, almost the result is 1.5 times better than the previous 1. So, in that particular case, what we are trying to say that when we are trying to modify this materials from the surface itself or maybe the automatically or maybe we are using some kind of dopant or impurities insided, the material electro chemical properties is totally changing.

And not only that here also that boron doped materials tested at anode materials for lithium ion batteries so as shown discharge capacity of 548 milliampere hour per gram at 100 milliampere per g after 30 cycles, these indicated the 2 times improvement compared to the pristine graphene. So, here also we are trying to pretend the same thing that when we are trying to utilize those materials the total material electro chemical properties or maybe the energy storage properties is increasing tremendously.

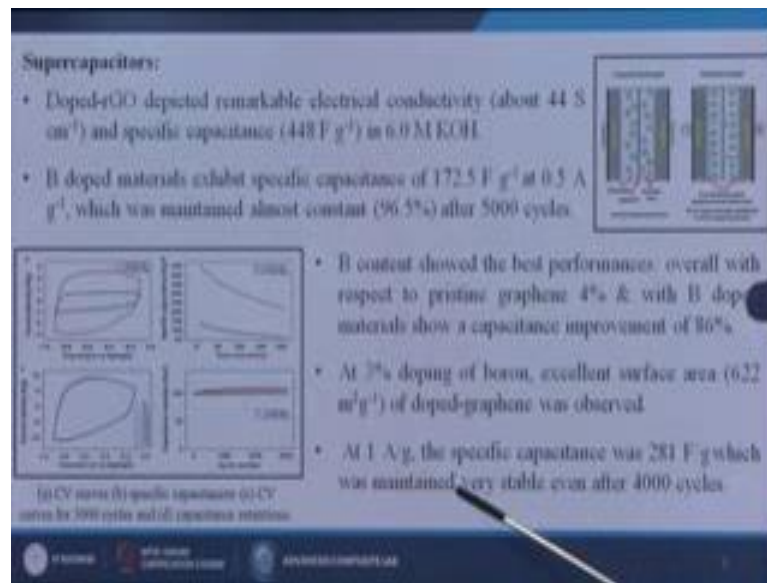
Same thing, we are showing in this particular graph also. So, here we are having the graphs irrespective of potential versus the capacity. So, here we have shown that when

we are doing for the first cycle and 5th cycle, 10 cycle 20th cycles; that means, we are trying to load this kind of energy for several cycles. That means, we are giving the energy to that particular systems for a certain time then we are trying to discharge the energy from that particular system and then we are trying to see that how much energy it is observing then how much energy it is discharging and then for a how much long period it is discharging the energy.

So, nowadays 1 important parameter I am going to tell you that when you we are using some kind of I pad or maybe I pod or maybe the laptops or maybe the mobiles, our main motto is that when you are charging this instruments that charging should be very fast, but discharging should be very less or maybe the very slow process. So, same thing here also we are trying to do that we are charging this materials for a short time, but discharging should be less. So, that I can use or maybe utilize this energy for the longer time, same thing in this particular case also we are trying to use here, it is the some kind of applications that where we are having the anode electrode in the one is the negative electrode one is the positive electrode; that means, one is the cathode, one is the anode then I am charging it in between that I am having some electro light separator or maybe that electro light membrane which will allow that one positive ion to grow from go from one side to another, but it should not be reversible. So, by this way we can do the modification of this kind of materials

Next we are trying to discuss about the super capacitors. So, super capacitors is also one kind of energy storage device, but that is for the shorter time, but still what we are trying to do? We are trying to modify the super capacitors materials so that it can store more energy than the previous one. So, in that particular case also, we are trying to dope the rGO; reduce graphene oxide which is remarkable electrical conductivity.

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About 44 Siemens per centimeter and the specific capacitance is coming 448 Fahrenheit per gram in 6.0 Mol KOH.

I am using certain kind of electro light solutions, same thing we are having 2 electrode, one is cathode, one is anode then I am trying to store the energy inside that material, this technology can be used for the super capacitor applications maybe some batteries or maybe the lithium ion batteries where I am using 1 anode materials as a lithium.

Here also we can see that boron doped materials exhibits specific capacitance of 172.5 Fahrenheit per gram at 0.5 ampere per gram which was maintained almost constant ninety 6.5 percent after 5000 cycles; that means, the longevity of the particular material or maybe the life of that particular material has been enhanced. So, when I am charging that materials and discharging that materials for a several times still that capacity of that particular material is remain same; that means, that battery life or maybe the super capacity of life it is increasing so that I can use this material for a longer period.

Also boron content showed the best performance overall with respect to pristine graphene 4 percentage with and with boron doped materials show a capacitance improvement of 86 percent. So, just you see that when we are using the simple boron in or maybe the pristine graphene that percentage is coming around 4 percent, but when we are using this boron doped materials its capacitance improvement is more than 86 percent, at 3 percent doping of boron excellent surface area like 622 meters square per

gram of doped graphene was observed at 1 ampere per gram, the specific capacitance was 281 Faraday per gram which was maintained very stable even after 4000 cycles. So, when we are collecting all these results just we are trying to establish that when we are trying to doped this kind of materials, when we are trying to improve this kind of materials by any kind of doping or maybe that surface wrappings or maybe the coatings the property; electro chemical property of that particular material is increased tremendously.

Same thing we are showing here also, when we are using that I V curve of that particular materials that current density versus potential, here the we are showing the charging and here we are showing the discharging so; that means, when I am giving the energy of that particular material, how much energy it is being absorbed by that particular material, how much energy it is depositing inside it and then how fast or how slow this material is releasing the energy. Same thing we can see that when we are going for a deference can rate, but it is the specific capacitance at that particular material, we have seen that doped reduced graphene oxide properties has been increased tremendously.

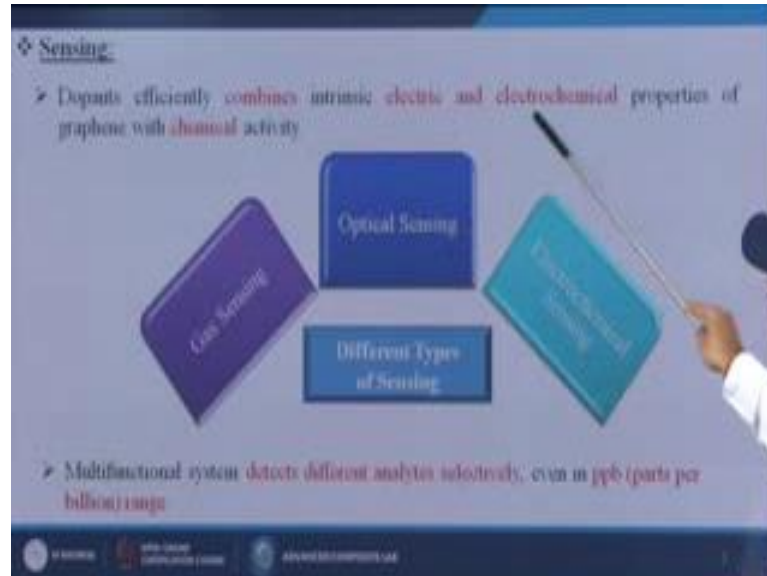
Same thing we are shown for the different cycle number and, but it is capacitance graphs also. So, here in this particular case that our boron doped or maybe that doped graphene oxide has overcome or maybe that has totally suppressed the results of pristine graphene oxides.

Then next topic is that we can use this kind of materials for the sensing applications. So, sensing means as I told in my some pervious lectures also we can use this kind of sensors for the various applications whether we can use this kind of material for the gas sensor maybe some kind of lights sensor maybe some kind of distant sensor or maybe sensing any kind of materials where maybe that human body or maybe that human being cannot reach or maybe cannot go at that particular point or maybe cannot trace some kind of trapped materials over there some kind of toxic materials over there. So, nowadays the making the sensor with this kind of materials is a tremendous challenging jobs.

When we are talking for detecting a particular gas maybe it may be easy, but when we are talking to detect some kind of duel gases or maybe mixing of several gases really really that task is still challenging. So, people are trying to use this kind of materials for the duel gas applications or maybe some kind of toxic gases applications where we can

easily detect this kind of materials or maybe this kind of gases very easily without the intervention of any kind of human being.

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Here also the dopants efficiently combine intrinsic electric and electromechanical properties are graphene with chemical activity. So, here generally different types of sensor, we are going to use, first one is called the gas sensor for the gas sensing applications, optical sensor for optical sensing applications, electrochemical sensor for electrochemical sensing applications.

Multifunctional system detects different analytes selectivity event in ppb which is nothing but the parts per billion range; that means, the main motto of these particular study is that, that detection limit should be very very high, suppose in a particular room or maybe particular area, a very little amount of gas or maybe any kind of toxic gases are present, my sensor material should be capable enough that that can easily detect those kind of materials so easily.

When we are talking about particular about the gas sensors so generally there are 2 types of gas sensors we can use, one is called the resistive type sensors, another one is called the chemical type sensors. So, when we are talking about the resistive type sensors so a resistive gas sensors have large changes in the electrical conductance after the exposure of 2 target molecules such as ammonia as a donor and the nitrogen dioxide as the

acceptor. So, for pure graphene the sensitivity of the doped device is 27 and 105 times higher for nitrogen dioxide and ammonia respectively.

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Gas Sensor:

- A resistive gas sensor has large changes in the electrical conductance after the exposure to two target molecules such as NH_3 (donor) and NO_2 (acceptor)
- For pure graphene, the sensitivity of the doped device is 27 and 105 times higher for NO_2 and NH_3 , respectively
- **Doped nanoribbons:** STM images demonstrate that NO molecules adsorb on substitutional boron atoms at the centre of the nanoribbons thus nanostuctures works as Lewis acids

The slide also features two graphs showing conductance changes over time for different gases, and two STM images showing the adsorption of NO molecules on boron atoms in a nanoribbon structure.

Here just we are going to show you that we are using 2 types of gases, one is the ammonia or maybe the ammonia environment, another one is the nitrogen dioxide or maybe the nitrogen dioxide environment. So, in this particular case, both are almost the toxic gases. So, in this particular case, what we are trying to do? We are trying to make our sensor so that easily it can detect this kind of gases. So, what we are trying to do over here.

So, when you are talking about the pristine graphene that we are trying to measure the current versus time, in this particular case and pristine graphene also we are using for the detection of the nitrogen dioxide and detection of the ammonia gases. So, what we are trying to show that, that once we are trying to make the material without any doping. So simple, we are using this materials as a film or maybe as a powder or maybe as some kind of devices, simply we are keeping into this 2 environment then we are creating some kind of potential difference in between that time, we are trying to measure the resistances of that particular material.

Then same material or maybe the same sensor then I am doing the modifications like this kind of doping maybe some kind of boron doped or maybe lithium doped or maybe some kind of rapping or maybe some kind of coatings then after modifying this materials then

again I am putting into the same environment and just I am trying to show that how the resistance of that particular materials is going to be changed.

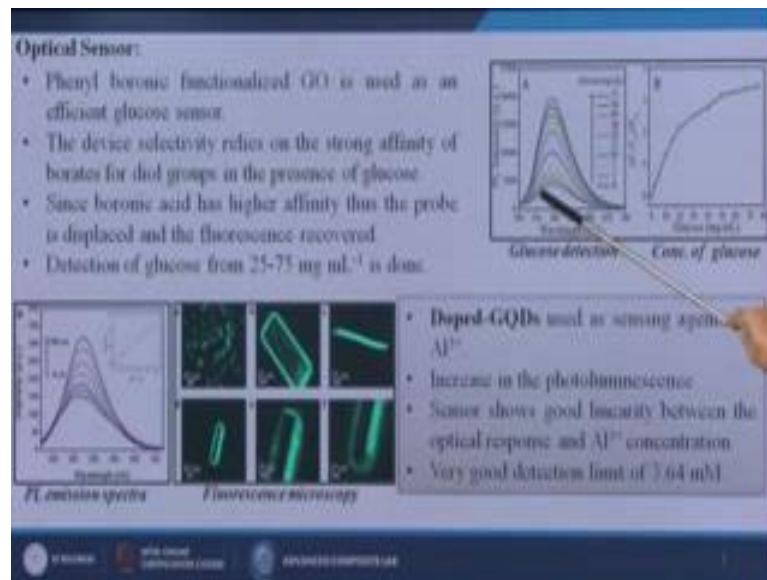
Whatever the resistance it is changing, it is actually depend upon the volume and concentration of that particular gas. So, if we train our sensor materials in such a manor, if I know that particular resistance will come for that particular gases, so when I am using this kind of sensor sensing materials into some particular environment, if my material will show the same current or maybe the same resistance at that particular point so that we can say that for that particular current or maybe the resistance, these gas is presented at that particular time. So, this is the actually whole logic behind this technology.

When we are talking about the doped nanoribbons; here doped nanoribbons also, all another type of latest kind of materials which we are using nowadays for that detection of some kind of toxic gases or maybe detection of some kind of sensing materials. So, here is the scanning tunneling microscope images that demonstrate the nitrogen oxide molecules adsorb on substitutional boron atoms at the centre of the nanoribbons, thus the nanostructures works as Lewis acids.

Here in this particular case, when we are using the boron doped graphene, generally we know that boron doped graphene is 1 kind of substitutional doping. So, boron is going to the substitutional height on that graphene sheets and then it is trying to adsorbed; that means, that nitrogen dioxide gas has been trapped on the surface of that boron doped nanoribbons and its adsorption property is going to be increased same thing, it is happening in this particular case also; ammonia gas also, the adsorption property is increasing so that the more ammonia gas or maybe the more nitrogen oxide gas can be adsorbed for these particular doping materials.

Then also these kinds of doping materials, we can use for the optical sensor purposes also.

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Here the phenyl boronic functionalized graphene oxide is used as an efficient glucose sensor. So, generally this kind of sensors, we are going to use for the biomedical applications or maybe detection of some kind of glucose sugar or for the human body.

The device selectivity relies on the strong affinity of borates for diol groups in the presence of the glucose. So, this is the main logic of this particular doping technology. Since boronic acid has higher affinity thus the probe is displaced and the fluorescence recovered detection of glucose from 25 to 75 milligram per milliliter is done. So, in this particular case, actually what we are trying to do? We are trying to modify this kind of nanofillers and then I am trying to use this kind of nanofillers for the glucose monitor. So, here also the same thing that we are measuring that glucose detections at different pH works, pH intensity versus the wavelength and just we are trying to measure that how much light actually it is adsorbing and then if it showing some kind of color or not and then how its wavelength is changing so that by changing the wavelength, we can easily detect that how much percentage of glucose is present at that particular system.

Same thing by doing this kind of techniques also we can measure that what is the concentration of that glucose for that particular systems and also sometimes we are using some doped GQDs, GQDs is nothing but the graphene quantum dots. So, this is also a one kind of modified materials, nowadays it is also having several good properties and also it is making or maybe it can be possible to make this kind of materials in our lab.

What we are trying to make? We are trying to make this kind of materials, not only that we are trying to dope this kind of materials so that its sensing property can be increased.

Here the doped GQDs are used as sensing agents for the aluminum ion, increase in the photoluminescence increasing property, what is the advantage using this kind of materials? It is increasing the photoluminescence property of that particular material, sensor shows good linearity between the optical response and aluminum, 3 plus iron concentration, very good detection limit of 3.6 micromol is being used in this particular case. So, here you can see that fluorescence microscope image. So, when we are putting this kind of material under the fluorescence microscope, it is showing some kind of light at that particular case. So, if we can see that when we are trying to increase the concentrations also automatically the light reflecting properties of that particular material is also changing.

By showing this kind of image also not only that when we are taking the intensity versus wavelength, we can see that at different intensity or maybe the same wavelength the intensity of that particular material is changing rather we can say that at different intensity is wavelength also can be changed, but in that particular case by getting this kind of fluorescence microscope results and the PL initial spectra, we can easily detect that what is the percentage of that particular metal ion into that system and then how it is behaving or maybe it is changing its sensing properties.

Then this kind of materials, we can use for the electrochemical sensor applications also. So, here that doped graphene simultaneously detect the hydroquinone and the catechol. So, if this all are the different kind of materials by doping only the graphene, we can sense this kind of materials for the electrochemical purposes. So, here in this particular case that superior electro catalytic activity compare to pristine graphene towards the redox reactions of hydroquinone and catechol having detection limits 0.3 micromol and 0.2 micromol respectively.

Here just we are trying to so that when we are using this kind of doped materials, how our sensing property is changing or maybe how our sensing property is increasing. So, in the right hand side figure just we have give shown.

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Electrochemical Sensor:

- Doped graphene simultaneously detected hydroquinone (HQ) and catechol (CC).
- Superior electrocatalytic activity compared to pristine graphene toward the redox reaction of HQ and CC, having detection limits 0.3 nM and 0.2 nM, respectively.
- Differential pulse voltammetry (DPV) also helps to investigate electrocatalytic activity of BG towards the oxidation of the two dihydrobenzene isomers.

• B-G electrode was used to detect H_2O_2 by monitoring electro catalytic reduction current at -0.4 V vs. Ag/AgCl.

• Excellent sensitivity of electrode $367 \mu A mM^{-1} cm^{-2}$ (vs. $258 \mu A mM^{-1} cm^{-2}$ for non-doped graphene).

• Good detection limit of 3.8 nM.

Some kind of time (Refer Time: 24:01) image. So, where we are showing the structure of that pristine graphene rather we can say that morphological structure of that pristine graphene and we when we are doing this boron doped graphene that how the crystal structure here may that morphological structure is changing, not only that in the below picture you can see that size of the flex has been increased. That means, it is showing certain kind of porous structure; that means, it can absorb some kind of gases so that it can increase the sensing properties of that particular material.

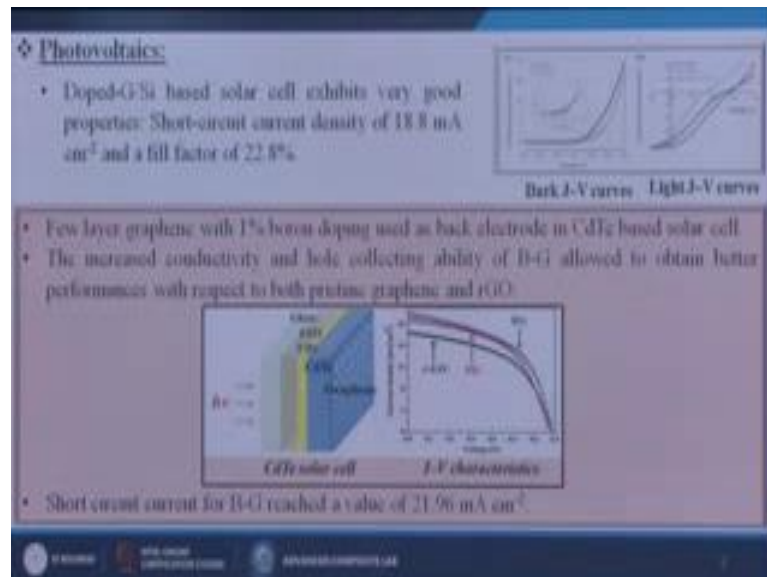
Here also the same thing, here just we are trying to show that boron doped graphene nano sheets where you can see that boron particles has been substituted the carbon atoms at that or maybe the boron atoms has been substituted the carbon atoms; that means, in this particular case, we are trying to show that boron is the substitutional actually boron doped graphene is the substitutional doping method of boron into the carbon structure.

And here also we are trying to show you the charge discharged cycle. So, how the material is sensing the materials and then how it is releasing and coming back to its original positions. Here the boron graphite electrode was used to detect the H_2O_2 the hydrogen peroxide by monitoring the electro catalytic reduction current at minus 0.4 volt versus silver and oblique silver chloride solutions, excellent sensitivity of electrode 367 micro ampere per millimol per centimeters square versus means which is more than the 258 micro ampere per millimol per centimeters square for non doped graphene. So,

from this particular case you can see that how the sensitivity property of that particular material is increasing from 258 to 367. Not only that the good detection limit of around 3.8 millimol. So, overall the sensing property of that particular material has been changed tremendously by using the boron doped graphene; by using the boron doped graphene electrode.

Next we can use this kind of doping material for the photovoltaic's applications or maybe rather we can say for the solar cell applications or maybe some kind of energy storage devices.

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Here the doped graphite or maybe doped graphene silicon based solar cell exhibits very good properties, short circuit current density of 18.8 milliamperere per centimeters square and a fill factor of 22.8 percent has been observed by doping this kind of materials.

Here also where we are trying to show that how the current density is changing with the difference in between the voltage or maybe when we are putting some kind of potential difference in that particular systems and not only that how the total current density is changing.

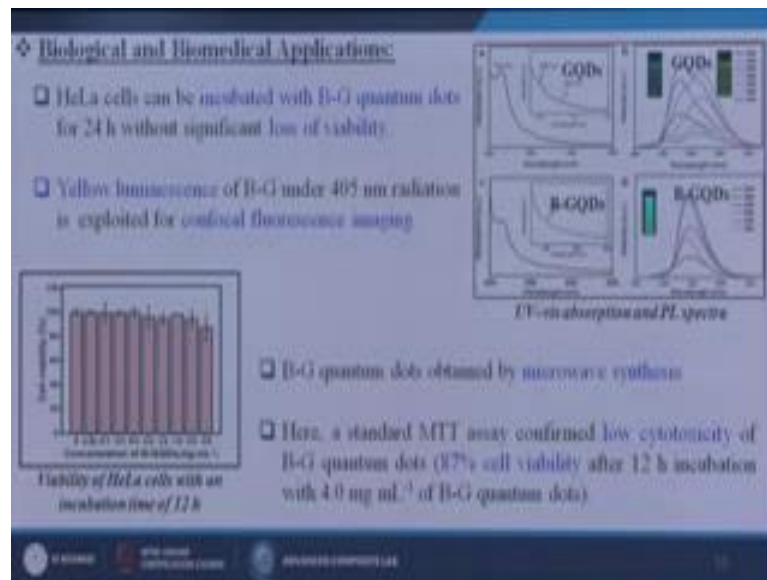
Here one is for the pristine 1; another one is called the doped graphite silicon based solar cells. So, here also what we are trying to show that few layer graphene with 1 percent boron doping used as back electrode in cadmium tellurium based solar cells, the

increased conductivity and the hole collecting ability of boron graphite or graphene allow to obtain better performance with respect to both pristine graphene and the reduced graphene oxide. So, graphene oxide, if you remember that graphene oxide first we are taking; making it from the graphite itself then when we are trying to remove some kind of function groups from it that is known as the reduced graphene oxides and the graphene is nothing, but the removing or maybe removal of all function groups from it and it is layer maybe 1 layer or maybe 2 layer or maybe 3 layers. So, that is why it is called the few layer graphene sheets.

Here this is the see cadmium tellurium solar cells which is nothing but the making it by the layer by layer techniques. So, first we are having some kind a glass then we are using the FTO over there, then on top of that we are putting the cadmium sulfide on top of that then we are trying to put the graphene and not only that this kind of materials, we are putting for the using for the photovoltaics applications and then from when you are using this kind of things, you can see that when we are increasing the voltage and the current density, you can see that boron doped graphene is giving the maximum performance at that particular level or maybe that particular conditions.

Here the short circuits current for boron graphene reach a value of 21.96 milliamperere per centimeter square. So, you can see that how the short circuit current is reaching only doping by the boron for this particular material. So, these kinds of materials we can use for the biomedical applications, maybe for the biosensors or maybe some kind of biological of the applications or maybe some kind of biomedical applications.

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Here what we are trying to see that HeLa cells can be incubated with boron graphene quantum dots for 24 hours without significant loss of viability; that means, the whatever the material or maybe whatever the medicines we are trying to make, what is our main motto? Our main motto is that when I am solving any kind of tablets or medicines or maybe the capsules inside our body, our body should accept this kind of materials or maybe I am trying to put certain kind of implants like here some elbow implants or maybe some kind of knee implants into our body. So, what that type of material generally we are choosing? We are trying to choose certain kind of materials which can be compactable with the bone structure, not only that easily our blood or maybe cells can tic that that body or maybe that accept our; that material so easily so that there are should not be any toxicity or maybe any kind of deterioration inside our body.

Here what we are trying to do that we are trying to modify this kind of graphene quantum dots, but doubt by the boron and we are trying to use this kind of materials for the biomedical applications. So, here what we are trying to show is that adsorptions in terms of that simple graphene quantum dots and the boron graphene quantum dots where we can see that adsorption spectra for the boron graphene quantum dots has been increased tremendously not only that when we are trying to characterize or material in terms of intensity versus the wavelength, we are showing that boron graphene quantum dots is showing at particular level it is increasing it is intensity; that means, these material is much better than the graphene quantum dots.

Not only that here we are tested the viability of HeLa cells with an incubation time of 12 hours and where we are trying to changes the concentration level of boron graphene quantum dots and here is the cell viability; that means, when I am preparing certain kind of materials, I am putting that materials in contact with some cells then what we are trying to see that at what time, how many cells are alive or maybe how many cells are going to be died? So, in that particular case just we are trying to see that how many how much or maybe that how many cells has been diet or maybe deported or maybe there is no deportation or maybe any kind of cell dines is not taking place so that our cells has easily accepted this foreign materials.

By choosing this one, we are trying to see the cell viability test of that particular cells here what we are trying to show that when we are increasing the concentrations also the still the cell viability is still not detecting it is into the same level; that means, this material is first of all it is not toxic our body can readily accept this materials these materials does not have any kind of side effects so that the cell can easily alive inside the systems or maybe on the surface of that particular material. Not only that boron graphite quantum dots obtained by microwave synthesis process generally by this process we have made this kind of doping of this particular graphene quantum dots and here a standard MMT assay confirmed low cytotoxicity of boron graphene quantum dots 87 percent cell viability after 12 volts incubations with 4.0 milligram per milliliter of boron graphene quantum dots; that means, when I am increasing the percentage of that particular doping material inside this cell systems still our 87 percent cells are alive.

That means I can use this kind of materials for some future biomedical applications say for some kind of implants or maybe some kind of lenses maybe some kind of stains so that it can enhance the mechanical properties of that particular material, maybe some other important parameters for that particular materials. But it will not hamper or maybe deperate our body systems, not only that it is not going to generate any kind of toxic gas or maybe toxic materials so that our blood or maybe our cells can die or maybe that can change its properties so that materials is very very acceptable to the human systems.

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Applications: Functionalization

❖ **Molecular Junctions:**

- The electrical characteristics of photochromic molecules are explored by embedding them in-between two electrodes as a molecular junction
- The electrical characteristic of this junction is governed by the structure and energetics of the two components and their interfaces, also by the ability of the chosen molecule to transport charges

Bridge two CNTs with a diarylethene molecule Two graphene point contacts with an azobenzene molecule

- The bridging of two CNTs with a diarylethene molecule occurs via amide formation and CNTs point contacts are made by electron beam lithography
- The thiophene-based devices show only one-way switching from open to closed state

Then we are trying to tell this kind of materials in terms of functionalizations till whatever the discussions we are doing that based on the doping, but now what we are trying to do? We are functionalized this kind of nanofillers and just we are going to see that where we can use or maybe where we can utilize this kind of materials for better performance.

First we are trying to use this kind of functionalized metal materials for the molecular junctions cases so the electrical characteristics of photo chromic molecules are explored by embedding them in between 2 electrodes in a molecular junctions. So, that is the basic principle that how you are going to use this kind of materials the electrical characteristics of these junctions is governed by the structure and energetic of the 2 components and their interfaces also by the ability of the chosen molecule to transport the charges. So, here same thing we are trying to use different electrode. So, what there then in between the electrodes total electrochemical reactions is going on and we are going to see that how this material is performing inside that system.

When we are talking this kind of materials so here 1 thing we are trying to use some kind of materials which can make the bridges in between the carbon nanotubes; that means, that electrolytic materials or maybe some kind of in between materials whatever that can be readily be acceptable by both the electrode, same thing we can see here in that particular case also that azobenzene bridge is forming in between these 2 materials. So,

here the bridge 2 CNTs with a diarylethene molecule, here also the bridging is taking place with 2 graphene point contacts with azobenzene molecules. So, this material is readily acceptable by both the electrode. So, that is why we are getting the better properties when we are using this kind of materials for the molecular junctions.

Then the bridging of 2 CNTs with diarylethene molecules occurs by AMIT formations and carbon nanotubes point contacts are made by electron beam lithography. So, by electron beam applying the electron beam lithography techniques, we are attaching these 2 carbon nanotubes, by this kind of materials; same the thiophene based devices show only one way switching from open to closed state.

Same thing we are trying to use this kind of functional materials for the field effect transistors or maybe in short terms we know it as FETs.

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◆ **Field-Effect Transistors (FETs):**

- FETs based on **spiropyran functionalized CNTs** could be switched from **high to low conductance**.
- **Light-driven reversible doping** of graphene by **pyrene substituted azobenzenes**.
- The **charge carrier concentration** is modulated by ultraviolet and white light illumination by $\sim \pm 1 \times 10^{12} \text{ cm}^{-2}$, preserving charge carrier mobilities of pristine graphene.
- **Azobenzenes without pyrene groups directly deposited on graphene**. The **E isomer modified graphene** shows **stronger doping effect** than that of **Z isomer** due to the **molecular conformation change**.

a
Alkane or pyrene groups were physisorbed on CNT

b
Pyrene-substituted spiropyran

FETs based on spiropyran functionalized carbon nanotubes could be switched from high to low conductance so that is the one problem over there, then light driven reversible doping of graphene by pyrene substituted azobenzenes so this kind of materials, by doing this kind of modifications or maybe the functionalizations, we can enhance the electrical properties of that particular material. Not only that the charge carrier concentration which is the vital parameter for the FETs is modulated by ultraviolet and white light illuminations by plus minus 1 into 10 to the power of 12 per centimeter square preserving charge carrier mobilities of pristine graphene.

Then also how the azobenzenes; azobenzenes without pyrene groups directly deposited on graphene, the E isomer modified graphene shows stronger doping effect than that of Z isomer due to the molecular conformation change. So, by this way this material we are trying to modify that this material can be used for the FETs.

Then we can use this kind of material for the solar thermal storage applications or maybe for the solar energy applications.

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The slide is titled "Solar Thermal Storage" and contains the following content:

- Effective conversion of light into heat is an emerging area showing great potential in solar thermal storage
- Solar thermal fuels are regarded as a closed-cycle system that only transfers energy from and to the environment by reversible transformation

Optimized intermolecular hydrogen bonding interactions and increased functionalization degree improves both the storage capacity and lifetime.

Results obtained:

- Energy density up to 138 Wh Kg^{-1}
- Long-term storage half-life exceeding 1 month
- Excellent cycle stability for 50 cycles

Photocatalytic & photochemical thermal cycling of azobenzenes covalently attached to CNTs

Each benzene covalently linked to CNTs

Effective conversions of light into heat is an emerging area showing great potential in solar thermal storage because nowadays when we are using this kind of coal and be the petroleum or maybe that thermal power plants, so always we need some kind of energy. So, we have to charge the energy from the coal into the electrical energy, but storage of this material is very very limited, maybe next few years we can finish all our coal or maybe that water can be dried out, anything can be possible. So, what we are trying to do? We are trying to use certain materials which can easily, readily available from the environment itself, not only that the sunlight will remain same for a longer time. So, why we are not using this sunlight and we can convert this sunlight into the electrical energy systems. So, same principles we are trying to utilize in this particular case.

So, here also we are trying to make certain kind of bridges in between the CNTs, not only that we are trying to make certain kind of materials which can easily observe the energy from the sun and convert that energy into the electrical energy. Not only that after

generating this electrical energy we have to store this energy for a longer time and when there will be any power cut or maybe we need some power easily we can access that power very very easily.

Not only that, some kind of optimized intermolecular hydrogen bonding interactions and increased functionalization degree improves both the storage capacity and the lifetime. So, here also we are trying to utilize some kind of materials and we are trying to functionalized these materials by the hydrogen functionalizes or maybe hydrogen bonding interactions so that its storage capacity or maybe that lifetime of that particular material can be increased. What is the result obtained from this particular study? Energy density up to 138 watt per hour per kg, long term storage half life exceeding 1 month, excellent cycles stability for the 50 cycles; that means, the stability of the particular material is increasing so that I can use that material for a longer time not only that when I will store that energy in that particular material also the discharge time will be increased not only that the material can store the same energy or maybe same amount of energy for a longer time itself.

Then we can use this kind of materials for the memory devices, so that is also one kind of technology like we are trying to use some kind of CD, DVD, some kind of USB, pen drive or maybe some kind memory devices. If you remember when we are using first time at the computer hard disc was so big because our memory devices was, so big that it was very difficult to bring that memory device from one room to another, but nowadays we are using simple one terabyte memory devices or maybe the storage systems in a pen drive itself. So, how our storage capacity is increasing, but still we are reducing the size of that particular storage capacity or maybe that storage material not only that it should be light weight it should be less expensive and not only that it can be easily make.

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◆ Memory Devices:

- A typical rewritable memory behavior with an I_{on}/I_{off} ratio of 20 and a retention time exceeding 10^4 s, which is due to the resistive switching of the azobenzene monolayer
- The non-volatile memory exhibit stability exceeding 400 cycles of write-read-erase-read.
- These devices also show good memory characteristics under bending stress, demonstrating their potential use in flexible electronic devices
- Voltage-controlled non-volatile molecular memory devices by using an azobenzene monolayer as the active layer sandwiched between two (GO) electrodes.

Voltage controlled non-volatile molecular memory device

The slide includes a schematic diagram of the device structure and a graph showing current versus voltage for the memory device. The schematic shows a cross-section of a device with two electrodes and an azobenzene monolayer in between. The graph shows a typical hysteresis loop for a memory device, with current on the y-axis and voltage on the x-axis.

Here a typical writable memory behavior with an I_{on} and I_{off} ratio of 20 and retention time exceeding 10^4 seconds which is due to the resistive switching of the azobenzene monolayer. So, here we are trying to functionalize this kind of materials by the azobenzene. The non-volatile memory exhibits stability exceeding 400 cycles of write-read-erase-read. So, here generally previous time when you are using some kind of CD, we are only that CD is having the capability that it can write on my way, we can write some materials inside that, but we cannot delete it.

But nowadays what about the storage systems we are going to use? Simply we can erase it, we can delete those materials then again we can store some kind of materials so that is the read, write or maybe erase every facility can be possible for that particular systems not only that these devices also. So, good memory characteristics under bending stress demonstrating their potential use in flexible electronic devices. So, I can use this kind of materials for certain purposes where maybe some mechanical load or maybe some mechanical pressure can be applied, but still the material will not damage also, voltage control, non-volatile molecular memory device by using an azobenzene in monolayer as the active layers sandwiched between 2 reduced graphene oxide electrodes can be possible.

Here what we are trying to show that we are trying to put certain kind of functionalized groups on this particular materials so that its memory or maybe that its storage capability

is increasing, not only that when you are talking about the current intensity in terms of time. So, one is the off time and other one is the on time then we can see that how the material properties is changing and how its storage capability is increasing. Thus we are calling it as a voltage controlled nonvolatile molecular memory device. So, by this method or maybe by this way we can make this kind of materials.

Next we can use this kind of materials for simple sensing applications. So, what we are trying to do? We are trying to make certain kind of materials which can detect the color because sensing the gas or maybe sensing some kind of thermal properties or maybe that heat or maybe some kind of distance maybe easy, but when that material is detecting some kind of color really, really this is a very challenging job. So, what we are trying to do?

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◆ Sensing:

- A nanoscale color detector based on CNTs modified with azobenzenes, where the azobenzenes serve as photo-absorbers and the nanotube as the electronic read-out.
- The amidation reaction to chemically graft spiropyrans to CNTs, and used with a hybrid system to regulate horseradish peroxidase (HRP) activity via light irradiation.
- The enhancement in the catalytic HRP activity has been used as a label-free colorimetric assay of tyrosine with a detection limit of 50 nM.

Photo/heat based nanoscale sensing

We are trying to do that in nanoscale color detector based on carbon nanotubes modified with azobenzene, where the azobenzene serve as photo absorbed and the nanotube as the electronic read-out. So, here we are trying to modify our carbon nanotubes by the azobenzene which is increasing its electro, sorry which is increasing its color detectorness or maybe that color sensing properties. Also the amidation reaction to chemically graft spiropyrans of carbon nanotubes and used such as a hybrid system to regulate the horseradish peroxidase activity via light irradiations. The enhancement in

the catalytic HRP activity has been used as a label-free calorimetric assay of lysozyme with the detection limit of 30 nano molecule or maybe that nanmole.

Here what we are trying to use that we trying to use the sensing properties of that material that. So, that it can detect the color, we can use this kind of materials for the sensing applications or say we can use this kind of materials for the biomedical applications too.

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❖ Biological Applications:

- Photochromic molecules have been used to modulate a number of important biological processes, such as protein folding, enzyme activity, membrane transport and so on.
- Carbon-based nanomaterials are also widely employed for biomedical imaging, drug delivery and cancer therapy.
- Photochromic carbon-based nanomaterials are capable of responding to a light input and behave as active building blocks for biological applications, such as fluorescent probe for diagnosis and drug carrier in drug delivery system.

The diagram illustrates the reversible photochromic transition of rGO hydrogels. It shows two states: a collapsed state (left) and an expanded state (right). The transition from collapsed to expanded is triggered by UV light, while the reverse transition is triggered by visible light. The expanded state is labeled as 'Expanded hydrogel state' and the collapsed state as 'Collapsed hydrogel state'. Below the diagram, it states: 'rGO hydrogels with acid-sphingomyelin used for in vivo fluorescence imaging.'

Next some kind of for particular biological applications also, we can use this kind of materials, when we are using this kind of materials before going to say something about this slide, just I am telling that here, 2 terms has been written, one is call the in vitro, another is called in vivo. So, in vitro is nothing, but when we are doing preparing this kind of materials and with we are testing this materials inside our lab, but when you are injecting this kind of materials into some mice or maybe some rabbits that is called the in vitro applications. So, one is called the in vivo, another one is called the in vitro. So, in vitro is nothing, but we are testing inside our lap with some cells or we some kind of characterization we are doing. In vivo simple same thing same materials we are putting to see that how that animal is reacting or maybe the how that medicines on that particular material is working.

Here the photochromic molecules have been used to modulate a number of important biological process such as protein folding enzyme activity, membrane transport and so

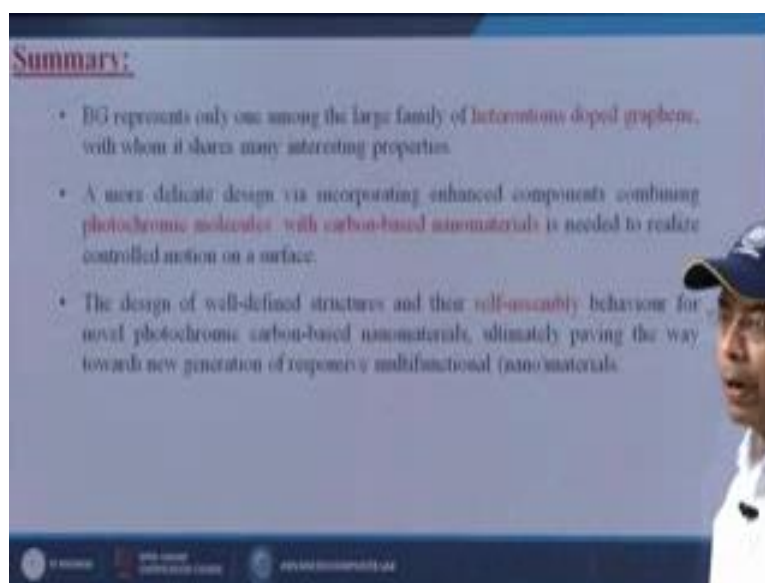
on. Carbon based nanomaterials are also widely employed for biomedical imaging, drug delivery and the cancer therapy nowadays. So, many people are working on that targeted drug delivery.

The main function of this kind of materials is that directly I can apply this kind of medicine or material to the affected zone, it will not go to the unexpected zone that side effects of this particular materials is going to be reduced and not only that from that outside simply I can locate that how the material is going on to the affected zone, how the medicine is working on the affected zone. So, these all are the added advantage of using this kind of materials. Not only that photochromic carbon based nanomaterials are capable of responding to a light input and behave as active building blocks for biological applications, such as fluorescent probes for diagnosis and drug area in drug delivery systems.

Here what we are trying to show you that when I am using some kind of materials, I am putting or maybe I am doing or maybe I am using this materials for the laboratory purpose and I am putting this kind of materials into some mice. But when I am exposing these materials into the UV light simply from the outside, I can detect that where the material is lying, how the material is behaving and then how the material is changing its characteristics. So, by these wonderful techniques, we can easily detect some kind of tumor cells or maybe some kind we can remedy some kind of tumor cells or cancer cells inside our body.

Now we have come to the last part of this particular lecture which is nothing, but the summary of this whole lecture.

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Here boron doped graphene represents only one among the last family of heteroatoms doped graphene, with whom it says many interesting properties. Already we have discussed the boron doped graphene for numerous applications. A more delicate design via incorporating enhanced components combining photochromic molecules with carbon based nanomaterials is needed to realize the control motion of a surface. The design of well-defined structures and their self-assembly that is vital parameter behaviour for novel photochromic carbon-based nanomaterials, ultimately paving the way towards new generations of responsive multi functional nanomaterials.

What we are trying to say that by using this kind of doped materials, by using this kind of functional materials, we can change the material properties so that the same material can enhance its optical properties or maybe the thermal properties or maybe the sensing properties or maybe the biomedical applications so that I can use this kind of materials for the various applications and these materials will not be harmful to the environment or maybe to the human body.

Thank you.