Nanobiophotonics: Touching Our Daily Life
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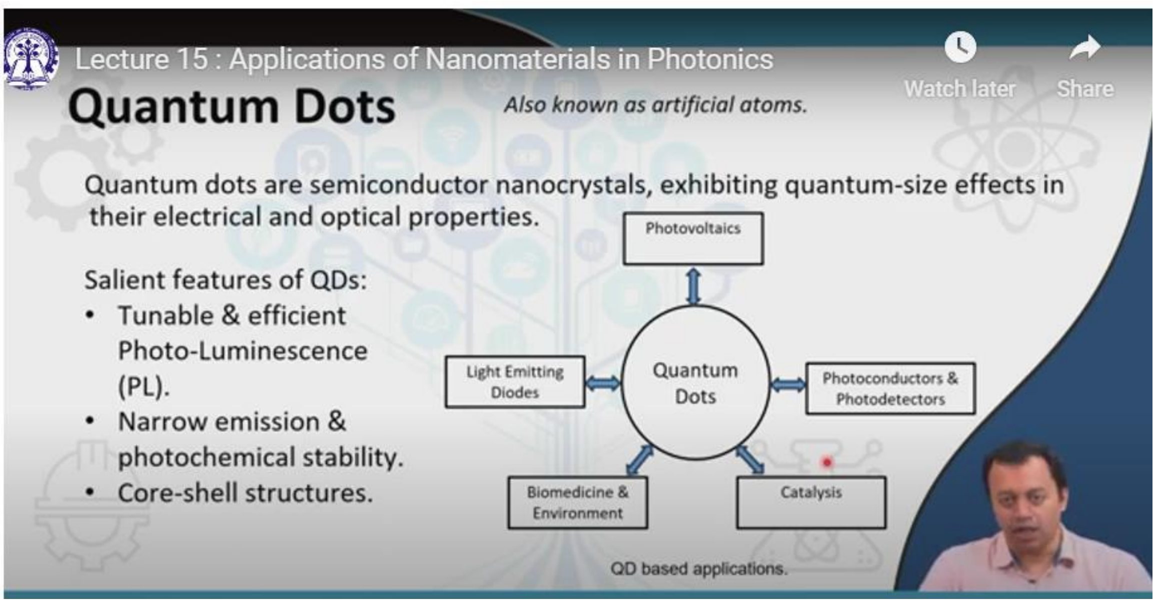
Lecture No. 15
Applications of Nanomaterials in Photonics

Welcome back. We are at the last leg of our preliminaries of this topic nanobiophotonics and we are about to conclude the chapter number 3 nanotechnology in photonics where in this lecture, this particular lecture, this particular session I am going to talk about the application of nanomaterials in photonics. So, this is the concluding part of all preliminaries. Next chapter onwards, we will go directly into the topic of biophotonics, but in this session I am going to talk about how nanomaterials are actually applied in photonics. You saw that nanomaterials previously could be made in a various different a variety of ways and they have their own magnetic properties, mechanical properties, optical properties etcetera. Here since the name suggests, we are going to look into the application part of utilizing nanomaterials in photonics.



So, whenever you talk about nanomaterials in photonics, the first thing that comes to your mind is quantum dots, QDs or quantum dots. What are quantum dots? Quantum dots could be considered as semiconductors. Semiconductor particles, nano semiconductor. However, you want, you can define it.

Some people can call it artificial atom. So, they are nanomaterials, quantum dots are nanomaterials where the band gap, since semiconductor I will use the term valence band versus conduction band, the band gap depends on the size. So, if you have a quantum dot of diameter say 100 nanometers, it is a dot. So spherical or disk like structure. So, let us use the term diameter to define it.

This is a quantum dot. So, if the diameter say is 100 nanometers, it will have a particular band gap, 1 electron fold. If the diameter increases, then the band gap decreases. Similarly, the size, higher the energy. How do we actually do it? But there is something called Bohr radius.

Bohr radius technically is the radius from when it was first derived by Bohr, it was the radius of hydrogen atom from the nucleus to the first electron. So, atom was considered spherical or circular. So, from the centre of the nucleus to the first orbital, so the first electron hydrogen atom, that was considered the Bohr radius. Later it became more and more complicated as more and more atoms and molecules etc were produced. But overall understand that if we have been able to create a size of a particular particle, smaller than the Bohr radius, then we have started to manage, started to control its band gap.

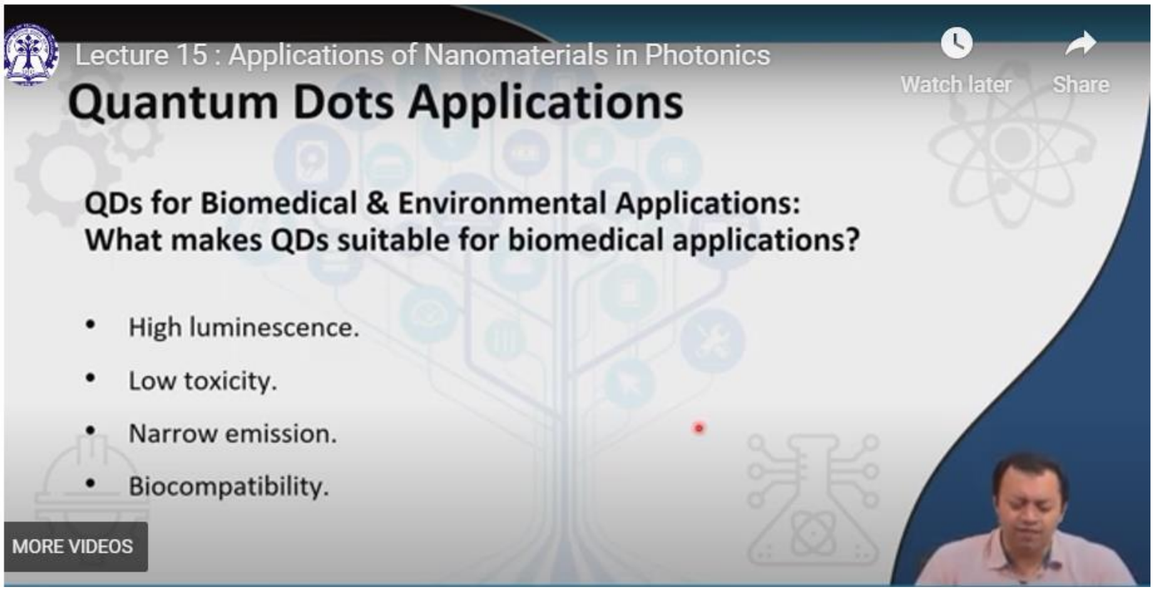
The distance, the space, the energy, I think distance or space is not the correct term. I think energy is a far more correct term. When you define the gap between valence band and conduction band, HOMO and LOMO, you do not say few nanometers, that is completely wrong. You say electron volts or energies. So if you start making the size of a material smaller than its Bohr radius, remember here the Bohr radius is not talking about hydrogen behavior, the Bohr radius is the molecular orbital of a complicated structure containing carbon, hydrogen, nitrogen, oxygen.

Here you will see cadmium sulphide, cadmium selenide, tungsten sulphide, tungsten selenide, these kinds of complicated material which has its molecular orbitals and etc which has their own HOMO and LOMO and the size has basically been reduced of such as complicated material, such a complex conjugate structure below its Bohr radius, you can control the band gap. If you can control the band gap, if you can control the energy, you can control the emission, the input energy that it will absorb for the electron which is at a lower level to go to the higher level from HOMO to LOMO, valence band to conduction band and then it is returning back from conduction band to valence band emitting a particular piece of photon out. The wavelength of the photon depends on this band gap changing the size of the structure, changing the size of the nanomaterial, you increase or decrease the band gap, increasing or decreasing the band gap will determine the energy of the photon released. The energy of the photon released can be converted into wavelength, wavelength is colour. So, the emitted photon will have a particular colour depending on the size of the nanomaterial.

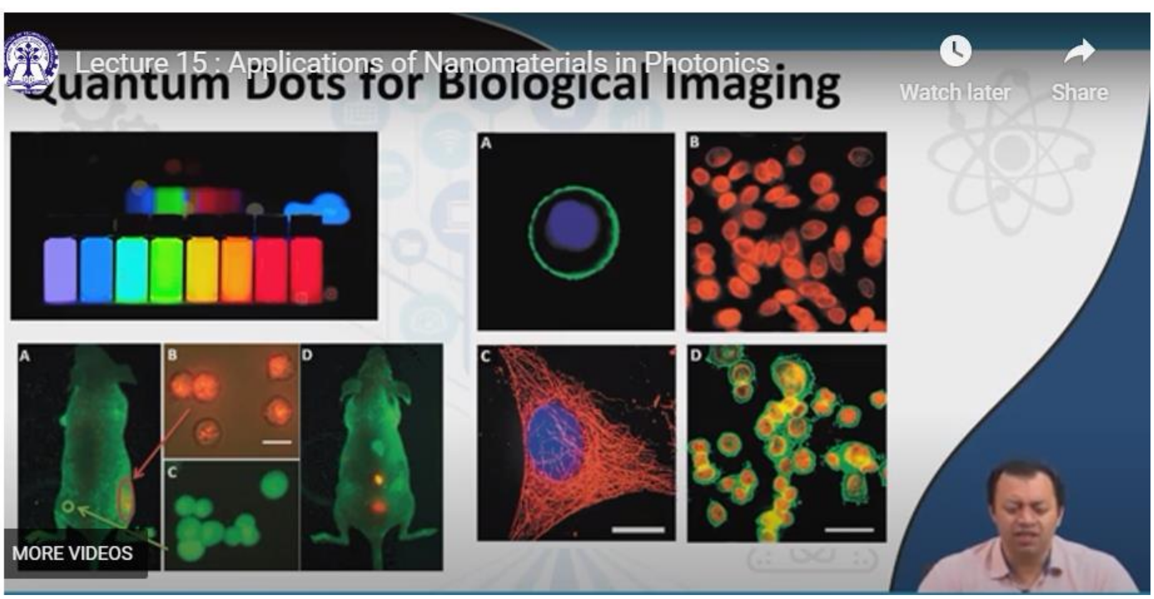
Such a nanoparticle whose size have been controlled and thereby the emission out of it is also tuned. Same material 100 nanometer, 200 nanometer, 250 nanometer, 500 nanometer, 1000 nanometer, each one of them same material, same material cadmium selenide, silicon, gallium arsenide, everything same material just the size has increased or size has decreased it will emit different wavelengths of light and that is basically quantum dots and hence it is tunable. Hence it is tunable it is size dependent band gap, size dependent output emission of the photon it has to be a direct band gap obviously, indirect band gap will not have. The emissions are pretty narrow. So, you can have a mixture of the same material of different sizes, hit them with different wavelengths, different wavelengths will come out, but the size will be, but the emission of the wavelength emission of the photon is a narrow bandwidth.

So, you have large number of colours coming out of different sizes, combine them together you basically needs red, blue and green these three colours, these three primary colours you need ah and then you mix and match them to create all different colour they can be made into light emitting diode, photo-voltage, photo-conductors, catalysis and of course, used in biomedicine and environment. Maybe you have heard quantum dot use is used in latest ah flat screen televisions right. So, they use this OLED or QLED quantum dot light emitting diodes or organic light emitting diodes materials. And another thing remember we had this ah discussion in ah last few lectures that when you make a material smaller the surface to volume ratio increases yeah surface area divided by volume if you keep on reducing it 3 by R the more the R reduces the surface to volume ratio increases meaning if you have a you by reducing the size you are comparatively getting a higher surface area. Now these surface areas can be functionalized can be added with specific specific chemical species they might alter the emission wavelength a bit, but if you are clever enough you can put specific chemical species that are very stable connected with the surface of this quantum dot not affecting the emission from the quantum dot very much and then you have put it in some sort of a solution this chemical species attaches will attach to another specific chemical species only.

You have now put these quantum dots into the into the solution it is getting attached and then you shine light you can filter out the nonattach part you can sonicate the nonattach part and you shine light wherever the attachment is it will emit a particular photon and you can you have a label you have highlighted it you have identified in a big solution where exactly is this thing located right.



It has large large applications it is very highly luminescent it has low toxicity to cadmium selenide is toxic, but these days they are making carbon quantum dots I am making carbon quantum dots so they are far less toxic narrow emission and most of the time they are biocompatible. So, you can actually put this small small nano particles semiconductors nano size semiconductors inside is carbon a semiconductor or a metal or an insulator can anyone answer me in the forum is carbon what is carbon is it metallic is it semiconductor or is it insulator what do you think tell me. So, carbon quantum dot are the semiconductors up to you is graphene a semiconductor or graphene metallic is diamond or graphite the two allotropies of carbon they are semiconductor or insulator or metal think about it let me know anyways.



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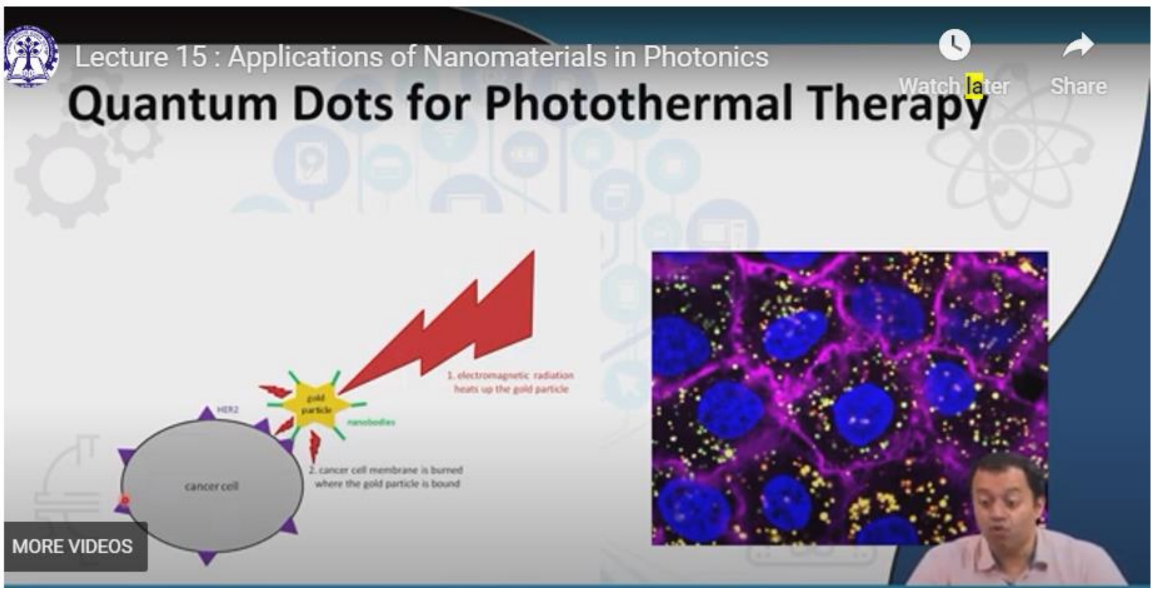
So as I said carbon dots same material different size they will emit different wavelength you combine this wavelength together you can get you can create yourself a nice flat screen television display unit etcetera or if you are more into biological imaging thing you can do both in vitro and in vivo image in vitro from the term vitruous or vitrovious its meaning glass as in cell culture in a test tube in a test tube you have different cells as I said certain quantum dots are made to infiltrate into the cells they are nano materials their size are smaller than the cell cells are usually 1 to 10 micrometers roughly typically couple of cells some types of cells you put them and shine them with light they will emit.

So this can very well act as specific specific fluorophore remember your lecture from fluorescence and you can see them you can also utilize them in vivo in vivo basically vivo is life inside a live organism suppose the organism has tumor this mouse has been made into tumor those tumor cells surface chemistry is created the core shell method in which the quantum dot the surface of the quantum dot is created with some sort of a chemical species that will only attach with the tumor part and then you shine high energy light into it enough to not kill the organism that will defeat the purpose and this will glow separate areas can glow separately. Now obviously you will ask what kind of chemical species are being used to functionalize attached on the surface of the quantum dot so they will only attach to a specific portion of the body or specific portion of particular chemical solution. Well there are several we will be discussing them in detail in coming chapters but I will give you couple of hints to go by antigen antibody complex is a very common one you know the antigen the antibodies that are produced in your body are very very specific to a particular pathogen so they will attach specific antigen in your body attacks a specific beg your pardon specific antibody in your body I keep on mixing these two terms up antigen comes from pathogen antibodies your or vice versa you tell me biologists your antibodies specific antibody attacks a particular antigen. So there is chemistry already it is a lock and key mechanism you can create that artificially all are proteins antigen is also protein antibodies also protein a protein only attach with another protein like a lock to a particular key coronavirus antibody will react or will go for coronavirus only other and other pathogens may or may not be that much attacked so you can create you can put some sort of an antibody inside attach it artificially with the quantum dot and that will attach to a specific area. What about DNA probes you know DNA's are double stranded we discussed they are made up of four pairs A T C and G adenine thiamine cytosine and guanine A will always combine with T C is always combining with G so if you have a single strand DNA with a particular sequence yeah A A T T G G C A T T so if you know one side you know the other complementary side so now you have put the single strand DNA with a particular sequence particular sets of A A T T as I said connect it single strand DNA with this and put it into the body it will attach 100 percent with only its complementary part the other part either it will not attach or only some base pairs will be attached and it will not be proper the attachment will be very weak whereas, only and only if it gets the complete proper alternate sequence it is going to attach itself completely and that is it then you shine light on it the brightest part the brightest part where most of the attachment have had happened is where most of the quantum dots are coagulating and most of the quantum dots are coagulating where a particular alternate DNA is present maybe that is the DNA of the tumor that is causing the problem so you can pinpoint locate the exact place using quantum dots they can very well act as beautiful beautiful fluoro force and other with their emetic properties right



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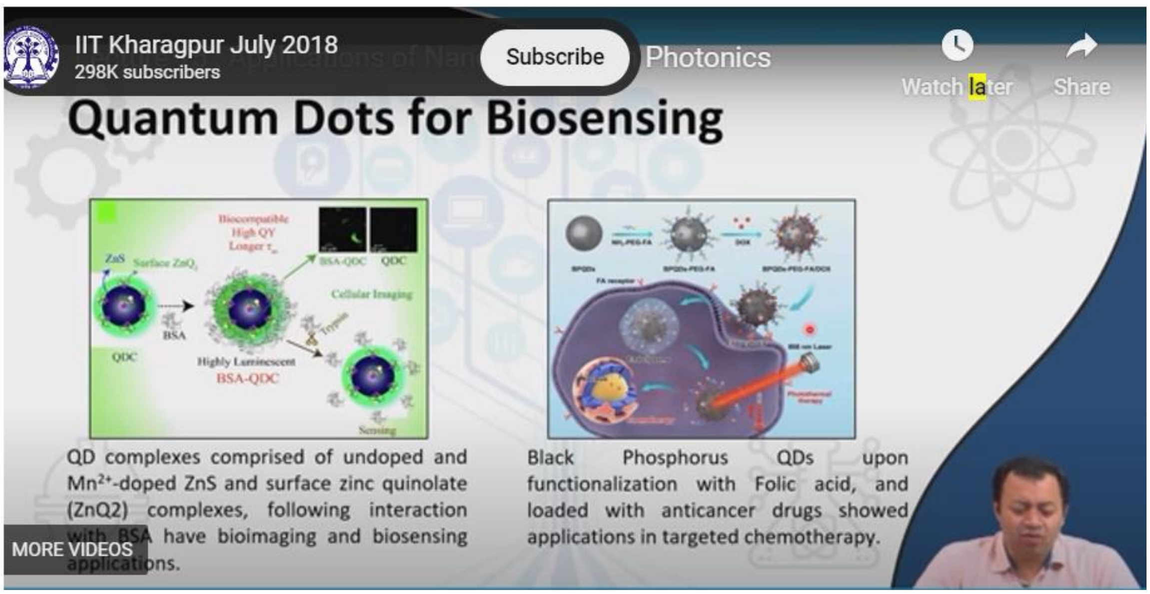
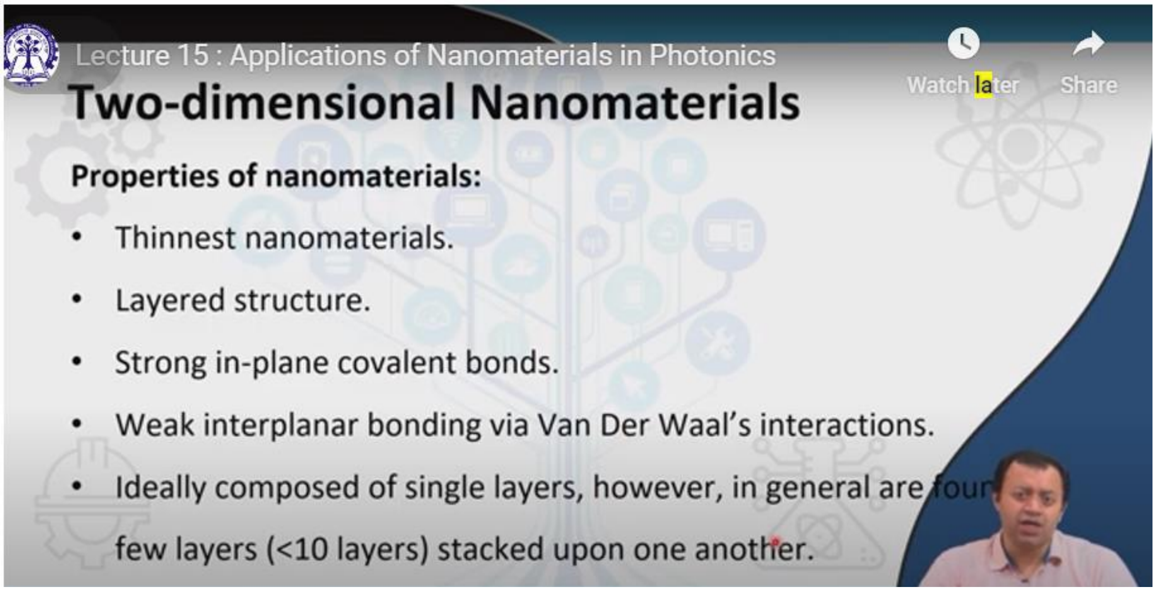
there are other ways we can utilize it we can utilize quantum dots for photo thermal therapy quantum dots can be connected with either gold nanoparticles or quantum dots by themselves which will then infiltrate inside the cells inside specific areas of the cells now as I said by changing the band gap you change the emission output now suppose instead of emission in the visible region instead of emission in any of these you have emission in infrared yeah you can do it if you can emit in blue green red yellow you can also emit in infrared what is preventing ultraviolet will be difficult very very small size and then ultra large band gap but infrared is okay infrared is possible with a nominal size of L is inversely proportional to L remember your first first class so infrared is also heat yeah so you have infiltrated these nanoparticles gold nanoparticles or quantum dots inside the cell inside a specific specific type of cell say cancer cell and then from outside your shining light into it outside your shining visible light onto it the visible light is being absorbed by the electrons in the quantum dot the electrons are going from lower level to upper level while returning the photon that is emitted is in infrared infrared is heat infrared is heat bunch of these photons creates some amount of heat some kind of kelvin change happens some amount of kelvin change happen kelvin is never in degree remember that degree kelvin is wrong Celsius and Fahrenheit are in degree kelvin is 0 kelvin yes 1 kelvin so some kelvin change takes place if you have produced enough of these enough of these photons in infrared they can heat up the cancer cell they can simply burn it out but they are burned by photons infrared photons and if you have managed to keep the quantum dots in specific specific areas only by surface chemistry then the heat is generated in those areas the heat is localized because heat is attached heat is coming from the quantum dot the quantum dot is specifically put inside the tumor.So the tumor cells are simply burned from inside so that is called what we call as photo thermal therapy this is something very very specific and very nice that I am actively looking onto research.

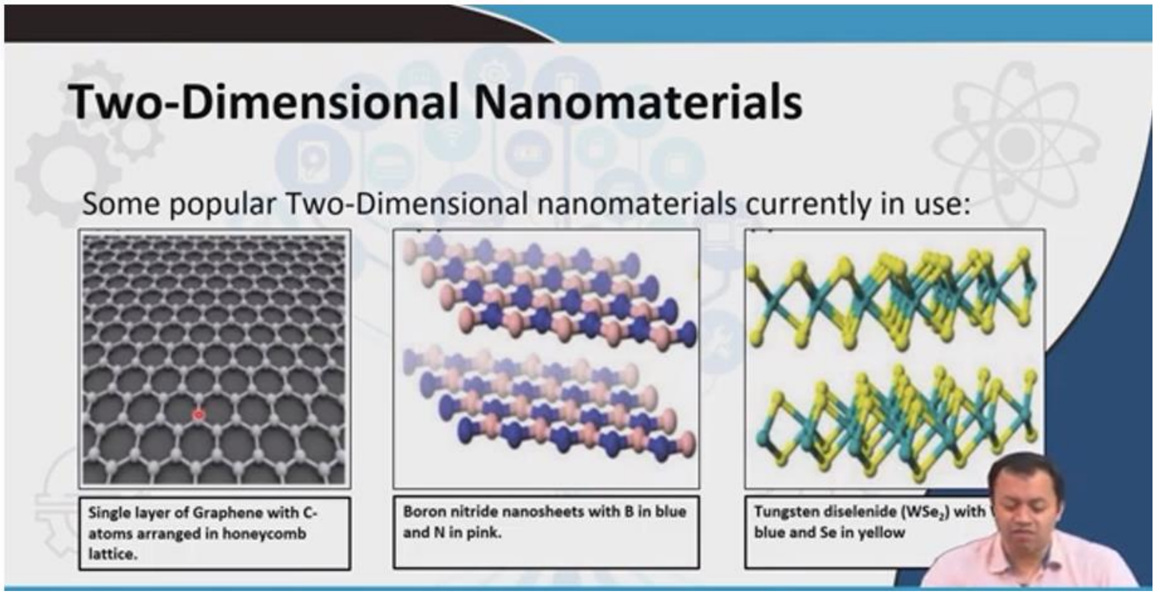


Quantum dots can be utilized for other processes as well quantum dot complexes with complicated material like zinc sulfide or other type of material zinc quantum dots complexes can detect behind serum albumin they can utilize for bio sensing basically what is happening is quenching I told you about quenching in fluorescence chapter either they do some sort of a chemical reaction this zinc selenide quantum dot they can attach with bovine serum albumin is a type of protein and because of this their emission property changes they can become highly luminescent or their luminescence reduces completely or changes into a different color. So, you have sent blue emission quantum dot now you are seeing that it has become red or yellow you can thereby say that these are the areas where a particular chemical is present the chemical reaction has taking place between that chemical and my quantum dot. So, it has converted the emission it has modified the emission profile black phosphorous is another type of phosphorous red phosphorous black phosphorous those are types of allotropes quantum dots upon functionalization with folic acid can be used for cancer detection. So those examples are there are also environmental sensing you want to sense a particular chemical type of pollutant in air water food supply food chain and that could also be utilized using quantum dot you have to make sure that your quantum dot itself is not going to pollute when you have complex material like zinc sulfide cadmium sulfide they are nice but they can sometimes start polluting themselves.

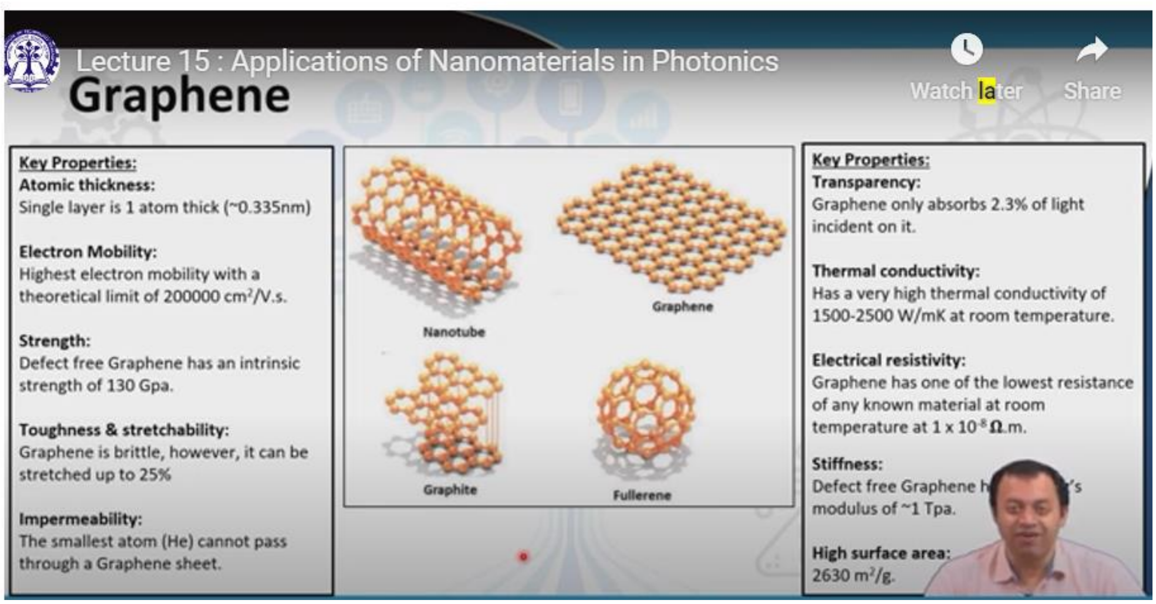
So carbon quantum dot are the new fad these days and people are utilizing carbon quantum dots for a lots and lots of functions.



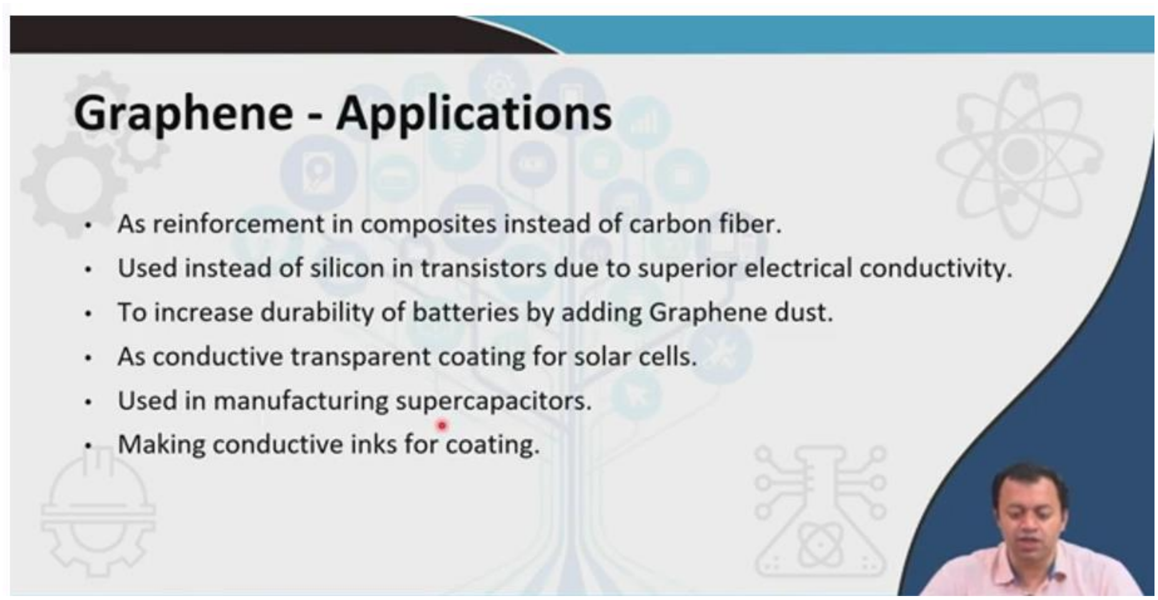
Now let us go to another type of nanomaterial that will have application in photonics these are two-dimensional nanomaterial 2D. In the previous lecture we discussed about graphene graphene was the first two-dimensional nanomaterial it comes from this layered structure. So, the strong in plane covalent bond this is very strong but these weak inter planning bonding via van der waal interaction ideally, they have single layers however in general will have difficult well not difficulty but to a large extent especially if you are doing liquid exfoliation then one layer it is not impossible it is moderately difficult let us say usually the majority will have 10 stacks together different ways. So 10 layers stacked upon one another that can also work very well you have the far there are so graphene is the first two dimensional material that was discovered and later they found out that there are several other van der waal structures which are very strongly bound in plane but very weakly browned you know in layers vertically.



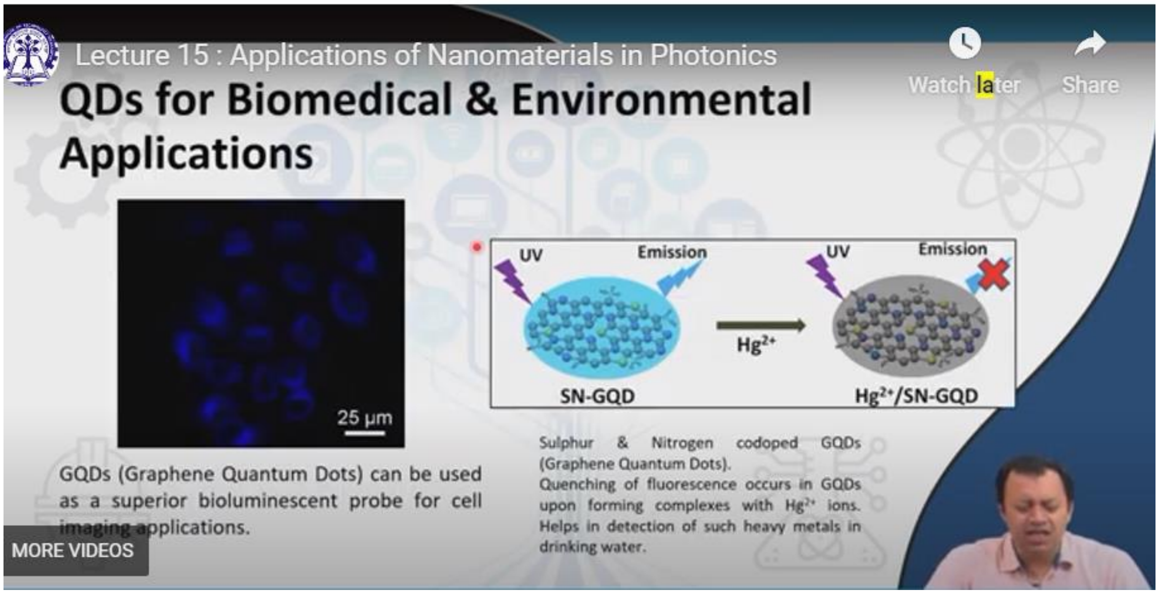
The next one was boron nitrate boron nitrate comes in different ah arrangement the one which we are talking about have a layer stripe structure is the hexagonal boron nitrate HBN or we have tungsten selenide which form TMDC transition metal dichalcogenides and they can form you know layer like structure all you have to do is break down ideally one of these layers or 10 15 of these layers from the infinite stack that you have here that makes up this material.



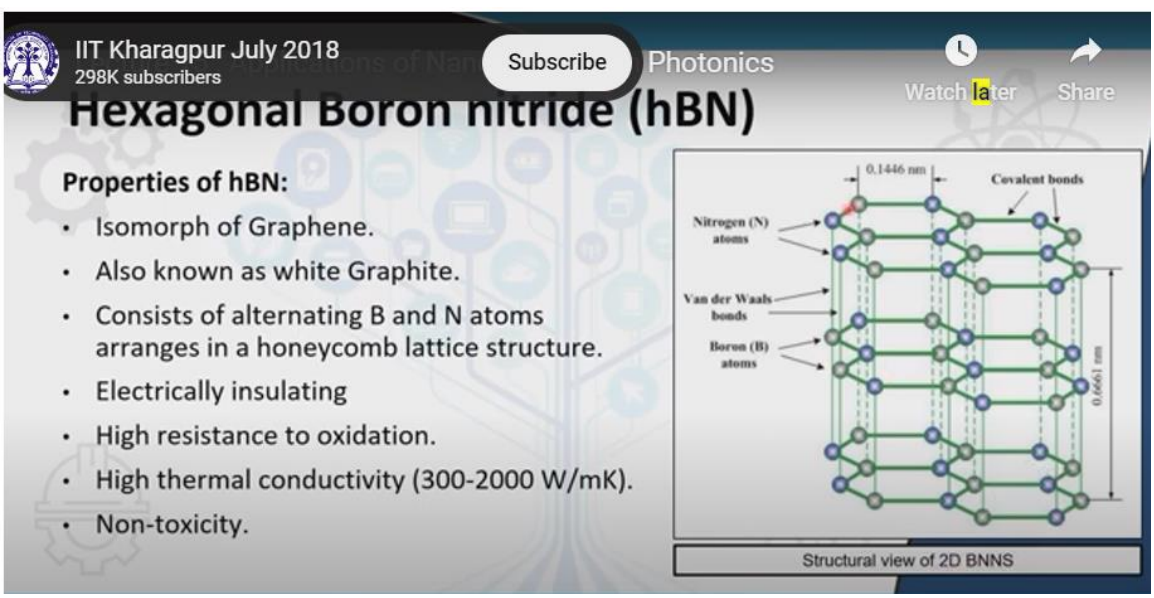
So graphene I think we have discussed in previous class but those of you who are interested in graphene I am not going to tell you whether graphene is metal or non metal you have to figure it out yourself I think it is already written here from the electrical resistivity you can figure it out, but do try to look it up as well it has an electron mobility yeah I think this is a dead giveaway what graphene is, but graphene has this several interesting properties which is not exactly found in bulk graphite you can if you have a sheet you can roll the sheet up make it some kind of a tube you can clump them together to make some kind of a ball and carbon has its own properties which allows it to form various shapes and sizes. So just use this slide as a reference to see what graphene can do, but still I want to have an answer about what do you think carbon is carbon-carbon the material carbon the element carbon whether it is dielectric metal insulator or semiconductor.



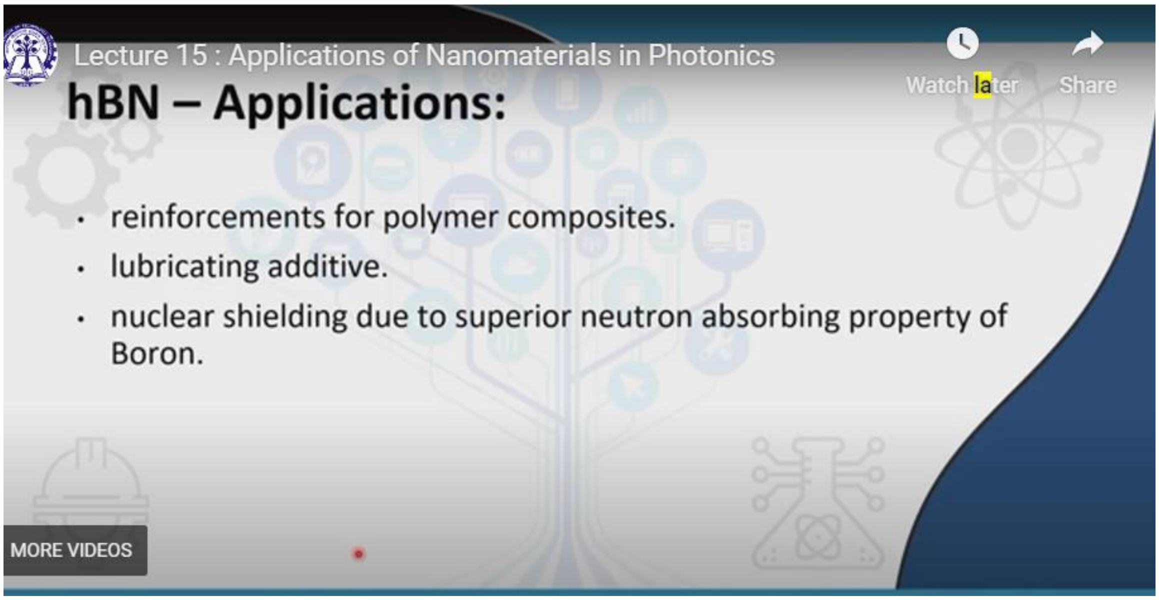
There are several several applications at this present moment graphene the graphene research is booming it has been going on for the past 10 years or so since it got Nobel Prize and at one time we heard that graphene is going to replace silicon and maybe it will someday replace silicon, but for the time being silicon is working pretty fine for us. And it has all those fantastic applications they are very strong it can be used in inks to super capacitor to solar cells to batteries to transistors and what not.



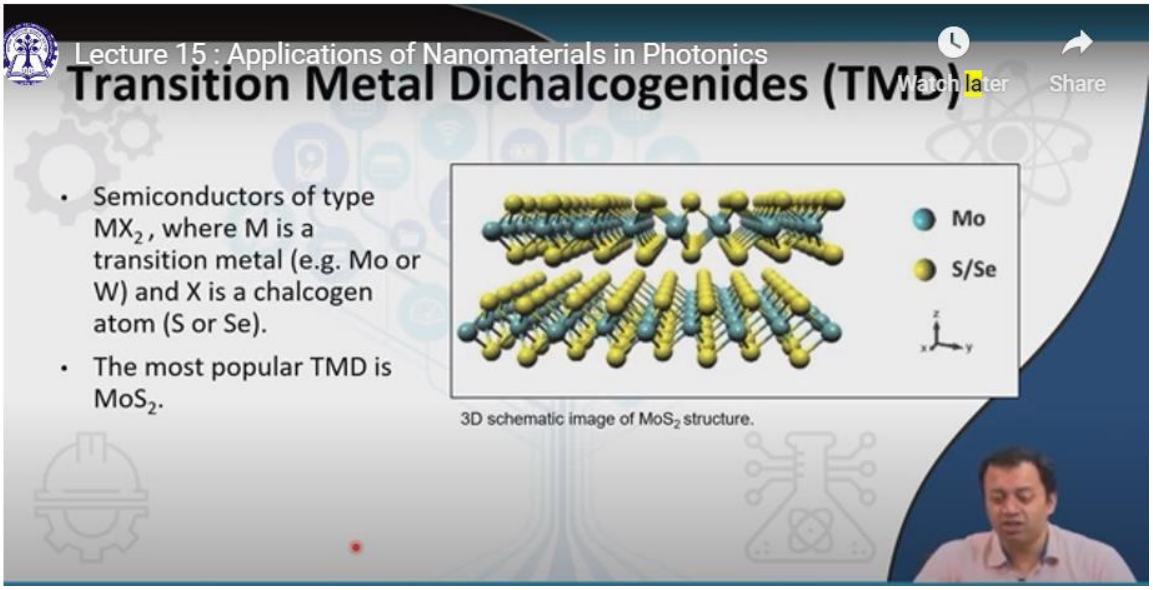
We create graphene quantum dots graphene quantum dots single sheet they can have higher superior bioluminescence and since these are just pure carbon there are two major applications you can functionalize them very easily and they are biocompatible your body is carbon based yes. So, some more amount of carbon as long as the dosage is fixed it is not going to ah cause much of a side effect much of a problem the dose has to be fixed right ah. Yeah fluorescence quenching can also occur in GQDs upon complexes like ah mercury ions helps in detection of heavy metals in drinking water as I said environmental application of quantum dots these are two-dimensional quantum two-dimensional material-based quantum dots two-dimensional material as I said layered materials which has finite length finite ah breath, but the thickness is couple of atoms thickness is within 100 nanometers or less right.



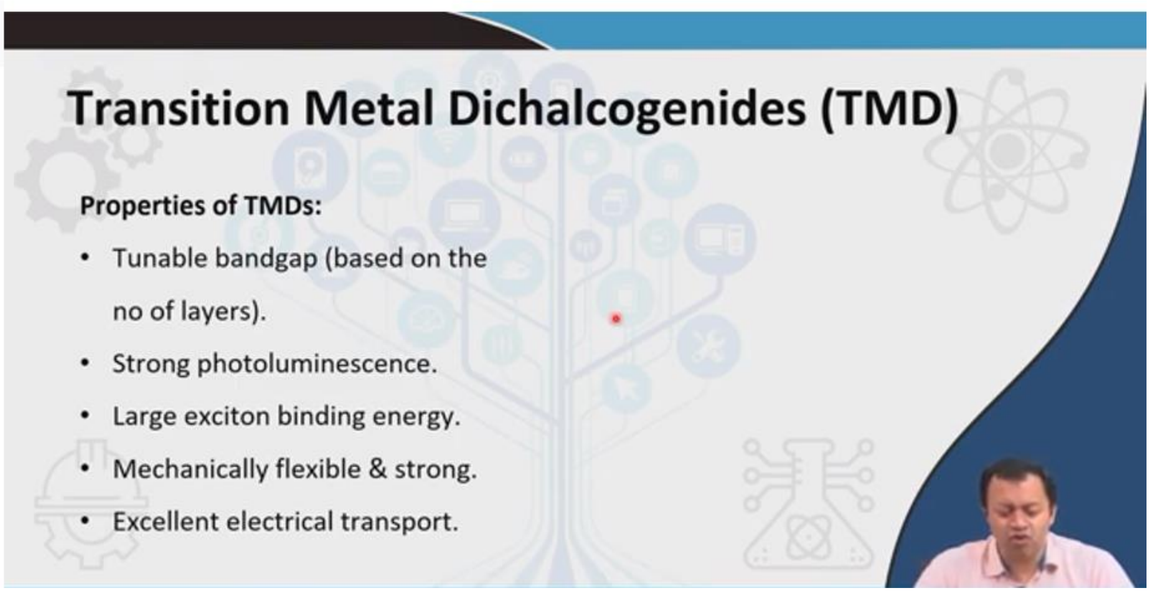
Similarly there are as I said hexagonal boron nitride a boron and nitrogen from the stack elements these bonds are very strong these bonds are very weak you break them up in you can try to get one single layer, but usually you get two or three or ten different layers also called white graphene it is highly resistance to oxidation very high thermal conductivity and it has several several applications ah nuclear shielding is one such such thing that is being done ah planning to use it in nuclear reactors.



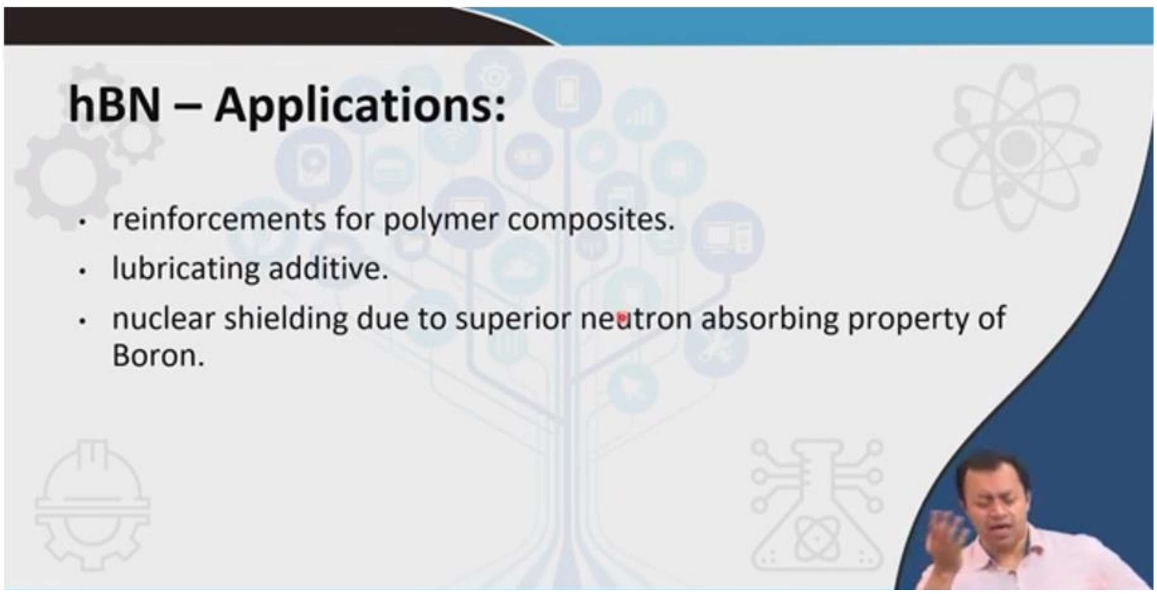
Then there is obviously, this very popular these days transitional metal dicalcogenides which usually use a transitional metal molybdenum or tungsten and x is a calcogen which is either sulfur or selenium I have seen oxygen being used I think the the very popular tmdc type is molybdenum trioxide it has fantastic optical properties it is an anisotropic medium meaning the refractive index of such material depends on the direction you are sending the light usually when you are talking about refractive index you consider it as a scalar quantity you consider it as one particular number you consider it is the number irrespective of you know direction per say, but anisotropic number these materials can have anisotropic.



So different refractive index in different materials so different direction. So, depending on which side you have shown light on the refraction will be different and then this gives rise to very ah interesting ah optical properties very very interesting optical properties their band gap as I said can be tuned it has strong photo luminescence mechanically flexible excellent electron transport the biological applications of them are still as we as I speak are being you know probed researched revealed ah they are used for bio sensing these tmds and hbn they are used for sensing other materials ah in environment as I said ah toxins in hydrogen ah toxins in water and air.

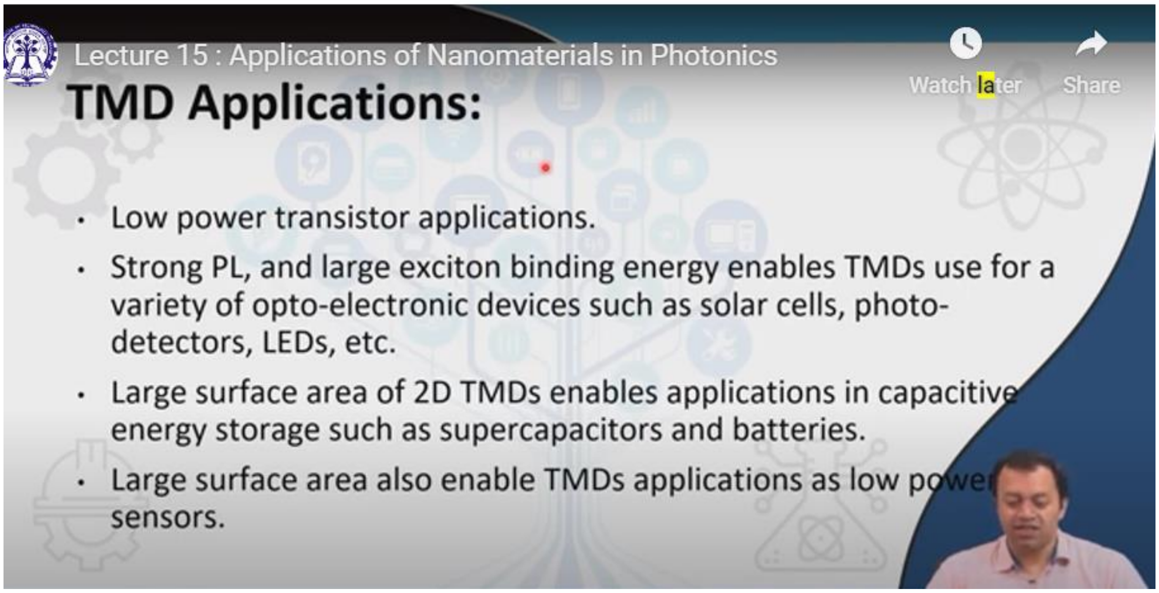


However the frankly speaking the biological application of these two specifically tmds as well as hbn are yet to be proved properly or the research is still going on yeah you have to wait few years or you have to contribute yourself on to this type of research to figure out whether there is a niche area and I am sure there is of application of ah the other type of 2D materials apart from graphene in bio sensing or bio applications there are large number of papers, but as I am someone who is directly working on it I am yet to be convinced that their bio sensing properties especially of hbn and tmdc and you can quote me on to that I am yet to be convinced that the bio sensing property bio imaging property of these 2D material hexagonal boron nitride or tmdcs are anything far superior than what we have previously seen there might be something just waiting that I have not seen or it is yet to come and it can it can change it, but till now there are biological applications of these ah, but it is an opinion it is not a fact it is my opinion that I have yet to see something extraordinary.

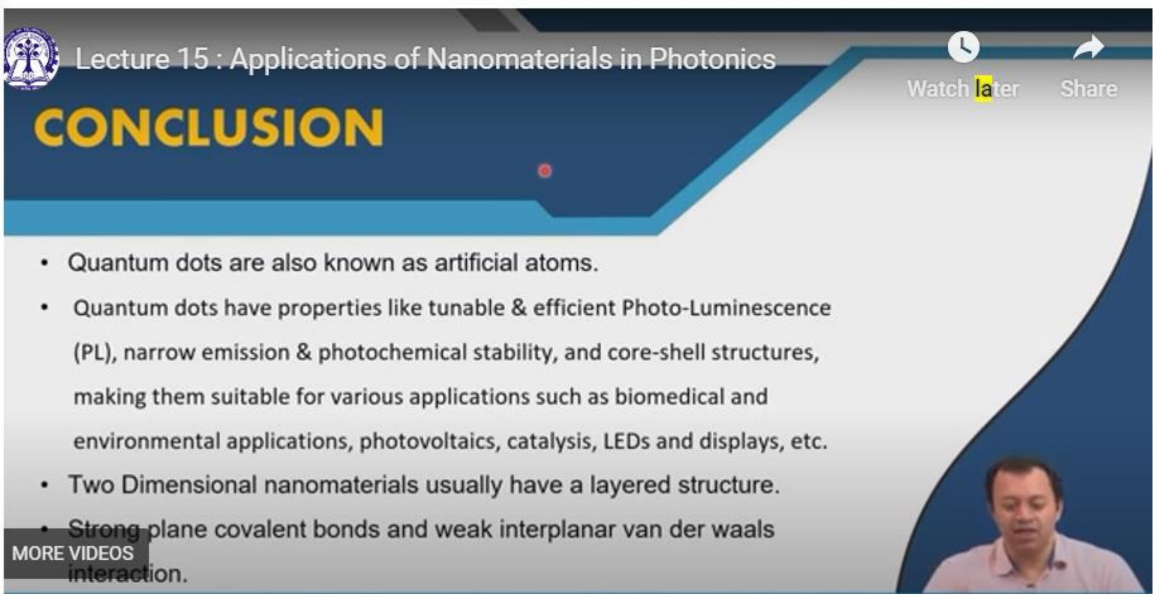


Extraordinary biological application that has come up with tmds as well as ah hexagonal boron nitride something to do with biological compatibility molybdenum selenide tungsten selenide is not something that is tremendously biological compatible I understand you make very very small amount of it very very small layer of it. So, biocompatibility still needs to be ah understood the functionalization carbon can be easily functionalized as compared to tungsten or selenide yet I am sure in the coming few years we will find something ah which is tremendously extraordinary of these materials applications biology.

As I said there are other 2D materials as well, but these 3 are the most common graphene I think all of you have heard, but then there are tmds and hexagonal boron nitride. So, again tmd are tunable band gap tmds are very nicely used in nano electronics. So, if you look into nano electronics tmds has shown something extraordinary, but when it comes to biology I am still searching for an extraordinary extraordinary paper where you have utilized it right.



They have several several applications ah you can read them at your own leisure I am not going to repeat them ah and that brings us to the end of the preliminary I think these 3 chapters are over you have sufficient background information now.



So, let us go into the actual meat of the topic from next class onwards I will be dealing with chapter 4 where our real nano biophotonics will be ok.

These are my references kindly go through them and I will see you in next chapter. Thank you very much.