Biomedical Ultrasound: Fundamentals of Imaging and Micromachined Transducers

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Lecture: 61

Characterisation of materials II

Hello everyone, I welcome you all to another lecture of characterization of materials. So, we are studying this under the course of Biomedical Ultrasound. So, I am Dr. Simranjit Singh, National Postdoc Fellow at IISC Bangalore and today we will be learning about the UV visible spectroscopy which is the second characterization under the characterization of material course. So, we will quickly go through the recap. So, in the recap section what we have learnt in the previous lecture is.

So, we talked about why we need characterization, what is characterization, and we learned about something which was called spectroscopy. Now spectroscopy is interaction of EM radiation with our materials. So, we talked about different EM radiations. So, the figure that you are seeing above is the electromagnetic radiations and we can see that we characterize the electromagnetic radiations into different segments based on the frequency and their wavelength and from right from radio waves to gamma rays we have different kinds of EM waves.

So, we have radio waves, microwaves, infrared rays, visible UV, X-rays and gamma rays and depending on the wavelength and radiation we can classify them. And then we talked about there is a relation between the terms which is wavelength, frequency and energy. So, we talked about a formula which was E is equal to h nu or which is also equal to hc by lambda. So, we have a direct relation between our wavelength, frequency and energy. So, if you want to learn about all these in detail you can refer to our previous lecture, but I will just quickly go through them.

$$E = h\vartheta = \frac{\mathrm{hc}}{\lambda}$$

So, we have something which is called frequency and the wavelength and right from radio waves when we move towards the gamma rays our energy is increasing and similarly if the energy is increasing, we would say the frequency is also increasing and our wavelength is decreasing. So, we could say that our radio waves have the least amount of energy, have highest wavelength and the frequency is also low and while in case of gamma rays it is the opposite, you can see through the relations. We talked about

the practical application of electromagnetic radiation in our day-to-day life. After talking about that we moved on to how we can use this electromagnetic different wave to for the characterization of materials. So, we talked about this table.

So, in the last lecture we could see the energy is increasing from the micro to the gamma rays as and in the last lecture we talked about something which was called infrared spectroscopy. So, we talked about the IR rays. So, and in the IR rays quickly going through it we talked about something which was called the natural resonant frequency of the materials. So, every bond has its natural resonance frequency and since the IR rays are low energy waves. Every material, every bond can absorb that particular wavelength in the IR radiation and after absorbing we can get a particular IR signal in our FTIR spectroscopy that we say.

So, if you want to learn about IR spectroscopy in detail you can refer to our previous lecture and all these kinds of vibrations are possible in every molecule when we talk about the when it absorbs the IR Rays. So, talking coming to this lecture we will go from the IR we will jump to the UV and the visible spectroscopy which is slightly higher in energy, and we talked about this earlier in brief that when we go from the IR to the UV, UV and the visible has higher energy and they can excite the spectroscopy. the valence electron in our materials and we would see this in detail when I will talk about the principle and the mechanism of the UV visible spectroscopy. Now, let us quickly talk about UV visible spectroscopy. Now, coming towards the very basic I will say that the UV region falls from 200 to 400 nanometer and the visible region will fall from the 400 to 700 nanometers.

And to slightly make it clear in the previous one this is the visible region, and this is the only portion of the light that we could visually see and the UV radiation is right beneath the visible region. So, we talk about the visible and the ultraviolet. So, the name is derived because it is just beyond the violet color and similarly infrared that we talked about in previous lecture is derived from the red because it is just beyond the red wavelength. So, talking about that we will come to the basics of UV visible spectroscopy. Now, coming to the very basic atomic model.

So, you must have studied this atomic model in your middle classes. So, in this atomic model we have something which is called nucleus in the centre which is positively charged, and we have some electron that revolves around the orbitals. Now, there are different orbitals I am labeling them KLM and further KLMN. So, there is a concept which is when a radiation of UV and the visible region falls on our material, so supposing we say that energy is equal to h nu, so a particular energy is falling on our material, so the atoms will excite. Now, what is called excitation? The inner electrons will absorb the photons that are being radiated and will be excited towards a higher energy state.

Now, from the lower shell it will be excited to a higher energy level. So, the lower one we will be called as the ground state, we will be representing as Eg and the excited one we will refer to as Ex which is the excited state. But there is a condition that the energy of the incident electromagnetic radiation or the incident UV visible radiation should match the electronic difference the difference in energy between these two levels. To better understand this, we have the energy level diagrams. So, we have this which is the ground state which is our lower energy state or the lower shell you could say to simplify it and then we have something which is called excited state represented here as Ee.

And then this is the difference of energy between these two states which is represented as delta E and whenever a energy of a particular radiation is incident on to our material and depending on the energy band gap we could say or the energy level difference between the ground and the excited state, it will absorb that particular wavelength from the UV and the visible region. After talking about this, so our every shell that we say has different vibrational and rotational energy levels as well. But when we come to the materials, we have a theory which is called the molecular orbital theory. This you might have read in your plus 2 or plus 1. So, in which we have something which are called bands.

Now, these are the band structures. So, the above region is called the conduction band. and the below one is called the valence band. So, we have the valence and the conduction band in our materials and the gap between them delta E is called the band gap of that material. So, depending on the incident radiation, our material can have certain allowed transition from the ground state or the valence band to the excited or you could say the conduction band when we talk about the materials.

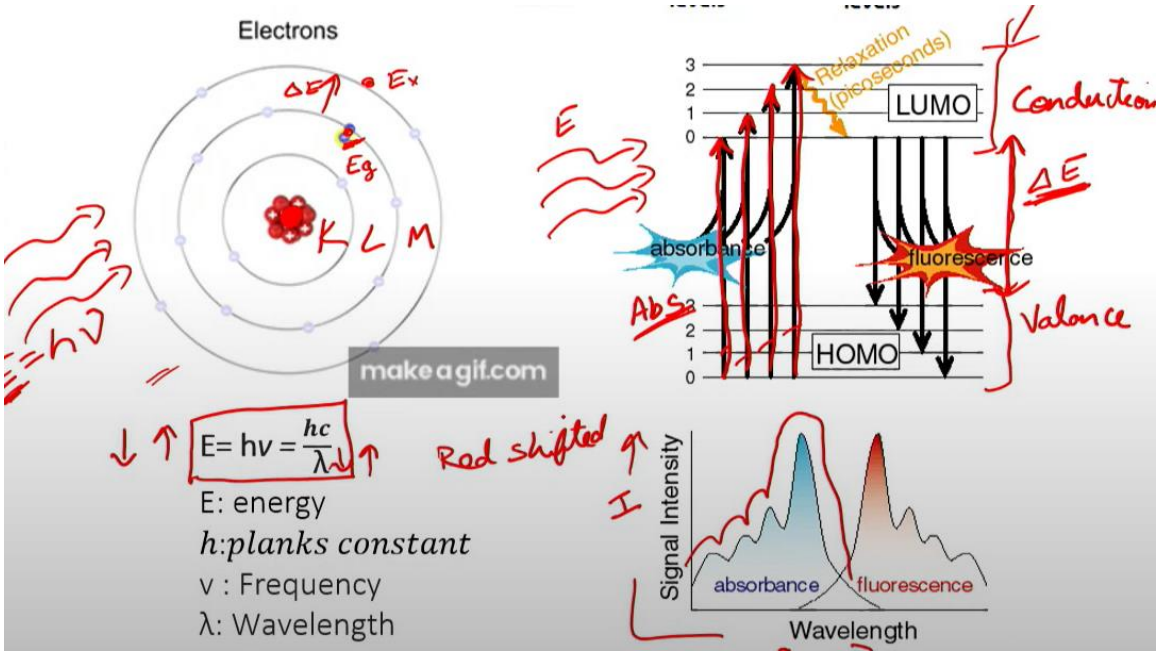
So, there are certain allowed transition because of which they absorb a certain section of the UV or the visible light. radiation and the phenomena here of the is called the absorption. So, absorption is the phenomena of the electronic absorbing of light and electronic transition which comes from the valence to the goes to the conduction level. So, coming to the lower figure we have the particular absorbance spectra and depending on the certain allowed transition. So, we have a spectrum which is called the absorbance spectra.

So, multiple peaks are possible because of the certain allowed transition and in some cases these all-peaks merge to form a broad peak. Therefore, in some cases in the UV visible we get a broad spectrum or a broad absorbance peak in case of that. So, we plot our UV visible analysis in terms of lambda and the intensity here. So, here is the example. Also, coming back to our old relation between E is equal to hc by lambda, there is something which is called red shift and the blue shift in case of our UV visible spectroscopy.

These are the very common terms that you must have heard. Now, what they particularly mean is that when we say our material is blue shifted or our material has the higher energy gap. So, if we talk about the energy gap, if our energy gap is higher our wavelength would be lower. So, based on that we would say that the lower wavelength is towards our blue region. So, if the energy band gap we say is higher, we would say that it is blue shifted.

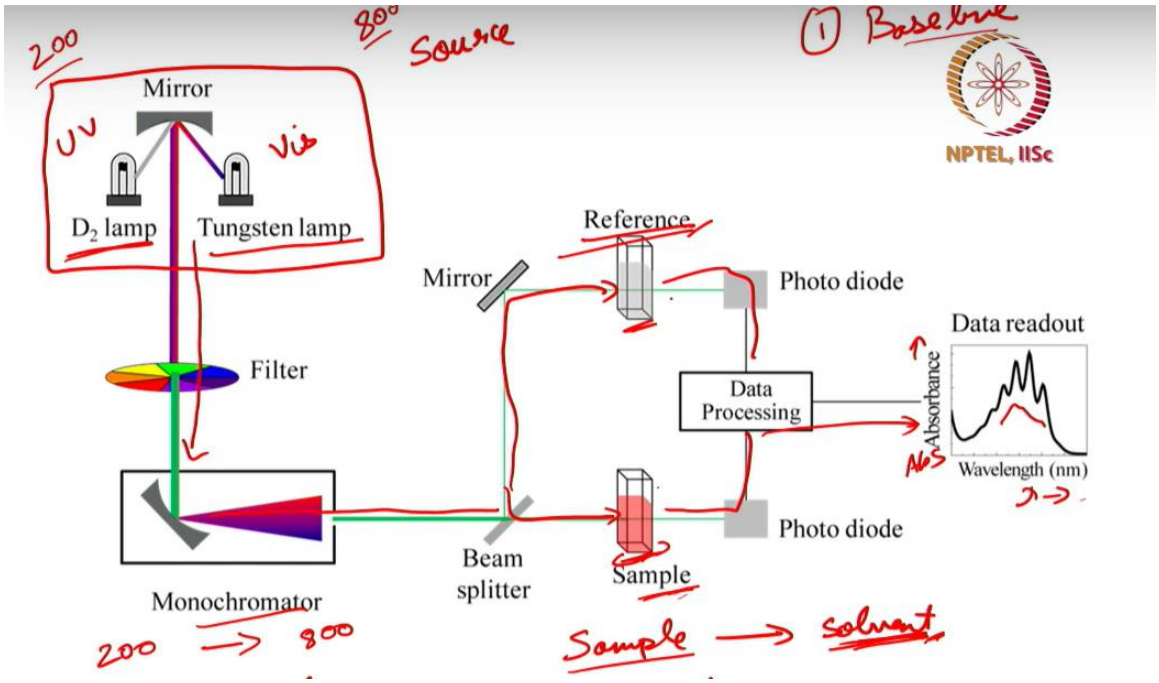
Because the wavelength that it will be absorbed is towards the blue region or towards the blue region or the UV region of the spectra, we will call it the blue shifted or there is situation number 2 in which I would probably like you to answer it. So, you could pause the video here and you could think about it. So, if our energy would be lower the band gap is lower between the of the material. So, what would be the case? It will be either blue shifted or it will be red shifted. So, you could pause the video here and think about it for a second and then I will give you the answer.

So, I guess the answer time is here. So, the answer to this is if the energy band gap is lower our wavelength would be higher. So, it would be red shifted. I hope your answer was right. So, it will be towards the red region.



So, coming talking about the very basics of the UV visible spectroscopy we will be talking about the instrumentation of that and how does it work. So, in the working mechanism in the UV visible spectroscopy the first thing that we have is the source. So, this is our source. So, this is our source of UV and the visible radiation we have something we have two lamps in this. So, we have something which is called D2 lamp which is deuterium lamp, and we have something which is called tungsten lamp.

So, a deuterium lamp is the source of UV our tungsten lamp is the source of visible. So, the UV source will produce wavelengths from 200 and the tungsten lamp will produce from around 400 to 700 and some of the UV visible it goes up to 800. So, we have the wavelength from 200 to 800. We have the source of that it moving to from the filter it falls on something which is called monochromator. Now, the role of monochromator is that it sends the radiation wavelength by wavelength towards our sample. So, right from 200 to around 800, it will send the light from wavelength to wavelength towards our sample.



So, once it passes through the monochromator. it will be splitted into 2. So, it will fall on our sample, and it will fall on our reference plate. So, after that falling the data is processed and then we get our typical absorbance versus wavelength spectrum. So, this is our graph that we obtain after the data processing.

So, here one question that may arise in your mind is what reference is and why are we using reference. Now, to explain that we need to know the basic of the UV visible. One of the basics is that it is usually done in liquid form. So, we have our sample. which is dispersed in a solvent right.

So, we have a sample suppose we take 1 or 2 mg of the sample, and we disperse it in a solvent and solvent can be any solvent, it can be distilled water, it can be ethanol, it can be toluene, it can be organic solvent, or any solvent can be there. So, our sample is dispersed in solvents and the thing is the catch is that our solvent can also have a transition in the UV and the visible region and because of that the peaks that we are

getting here may not be ideally only because of the sample it may have the interference of this solvent as well. To eliminate that we have something which is called reference. So, the first thing that we do is take a baseline. So, what is the baseline? So, we have something which is called qubits.

So, these are our two qubits in which we put our sample, or we put our solvent. So, in the baseline in both the qubits we will be taking our solvent of interest, and we will be running the baseline. What the baseline will do? It will nullify the effect of the solvent. So, if the solvent after we run the sample, we do not have the noises because of the solvent to eliminate that we take the first the baseline. Then what we do in the sample in this sample cuvette region we place our sample. So, we to placing our sample we disperse our sample into solvents.

So, that also depends on the concentration of what concentration we are taking. So, we put our sample in the sample qubit holder and then we take our analysis. So, we get the typical UV visible spectroscopy spectra which is particularly of that sample. And what is interesting is that if this is our qubit here and the length of the qubit is represented as L and the initial intensity of light if we are saying is I naught and the final intensity is I, we calculate the absorbance and transmittance. So, how do we calculate that? So, there is a relation of transmittance.

$$T = \frac{I}{I_o}$$

Transmittance I have also talked in the basics of the FTIR spectroscopy or the IR spectroscopy in our previous lecture. So, our transmittance is defined as the ratio of the final intensity divided by the initial intensity. So, this is our transmittance formula. So, what happens is that when light is falling on to our sample qubit. So, our sample is dispersed in the solvent, it will be dispersed like this and some part of it will be absorbed and some part it would be transmitted.

So, we can calculate the transmittance, and the absorbance is just the inverse of that right. And there is a relation which was given by two scientists which are called naming Beer and Lambert, they gave a relation between absorbance and concentration. They said that the absorbance is directly proportional to the concentration of the material. That means that whenever we are increasing the concentration of our material, we are increasing the absorbance value also.

$$A = \frac{1}{T} = \log\left(\frac{I}{I_o}\right)$$

$$A = \log\left(\frac{I}{I_o}\right) = \epsilon I c$$

To give you a brief example of concentration, what we call concentration, let us take an example.

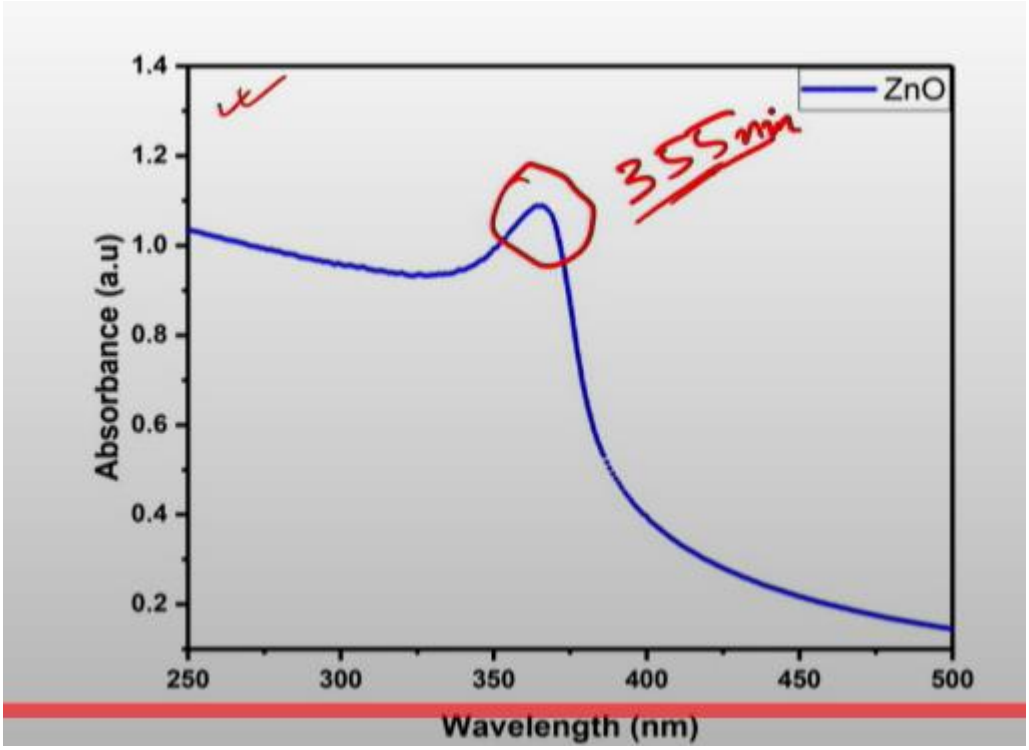
Suppose we disperse 1 mg of our sample. in 1 ml of suppose DI water distilled water you say. So, our concentration here will be 1 mg per ml. So, you can take the concentration in mg per ml or in some cases you will see that the concentration is also represented at parts per million or parts per billion. So, 1 mg per ml is actually equivalent to 1000 ppm which is either you could take the concentration in the units of mg per ml or do you take it in ppm or ppb level.

So, that depends on you. So, according to this relation if we keep on increasing the concentration suppose we take 1 mg per ml and we increase it to 5 mg per ml we take 10 mg per ml. So, similarly our absorbance value will also increase that makes sense because our amount of the material is increasing in the qubit, and it will absorb more light and thus our absorbance value will also increase. But there is a catch when we plot the absorbance versus concentration curve, we get a linear plot and after a concentration is reached, we get a saturation and after that the absorbance value does not follow the linear order. So, this is because after a point of time the concentration becomes too high, and the absorbance value does not directly follow it. And from this relation we have something which is called L.

So, L is the path length. So, usually for studies the path length is kept constant the qubit length is constant for all the analysis. So, our L is fixed. So, we can directly have a relation between absorbance and the concentration and to eliminate the proportionality sign we have a constant which is called molar absorptivity or the molar attenuation coefficient it is the ability of that material to absorb the light. So, the Beer and Lambert law is only valid in the linear region and in the linear region our absorbance and the concentration are directly proportional to each other and based on that we have a certain application in which we could use our UV visible spectroscopy.

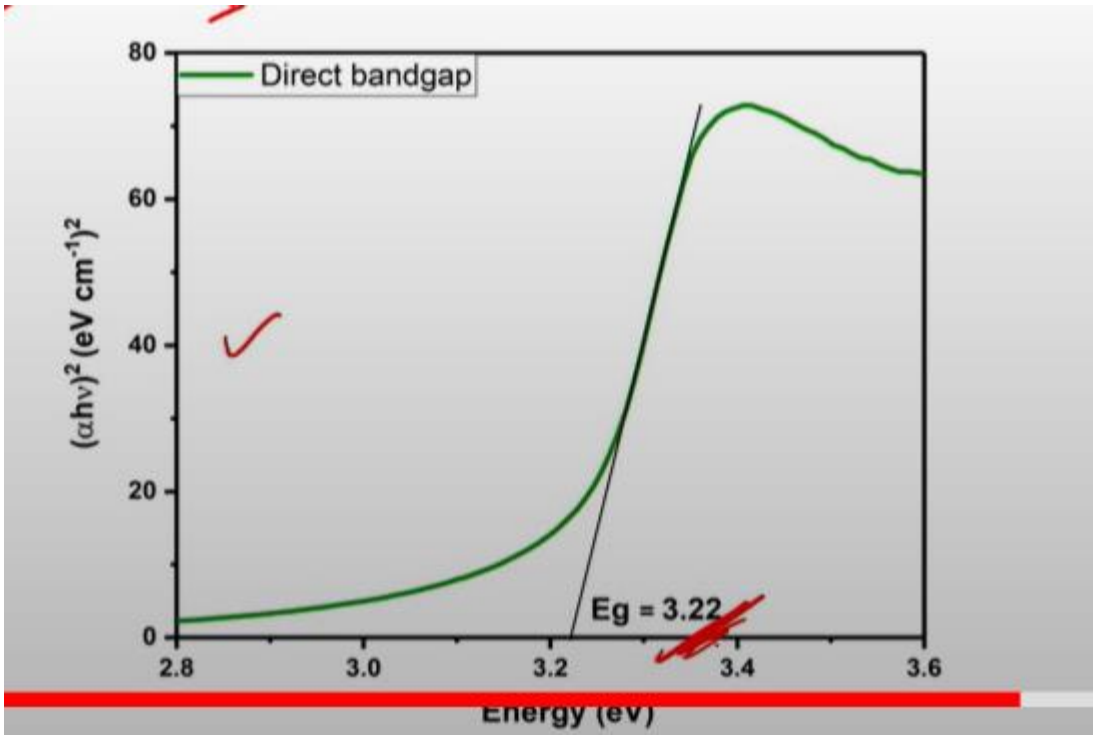
So, coming to the application part. So, there are a lot of applications that we could use with the help of UV visible spectroscopy. So, we will talk about every application in detail. So, firstly you could see that you could confirm the formation of material. So, supposedly you are a material scientist, and you are synthesizing some particles, for example, zinc oxide materials and you want to see whether your material has been synthesized or not. to see to confirm that you will run your material you will disperse it in a solvent, and you will run it through the UV visible spectroscopy.

And then you will have the typical absorption of that material and once your absorption is obtained and it matches with the literature you could say that your material has been successfully synthesized. So, supposedly you take an example of zinc oxide. So, these were the particles that I synthesized in my PhD. So, the ZNO particle has been this I synthesized the ZNO particles and wanted to confirm whether my material has been synthesized or not. So, the ZNO has a typical absorbance peak at around 355 or 360 nanometers.



I got this particular peak at around 355 nanometers for my material and from this I could conclude that my material has been successfully synthesized the ZNO material has been successfully synthesized. Also, there is another calculation I talked initially about the band gap. So, in the materials we have something which is called band gap which is the difference between the valence and the conduction band right. There is something which is called tox plot and there is something which is called tox relation. So, from that relation we could calculate the band gap of materials.

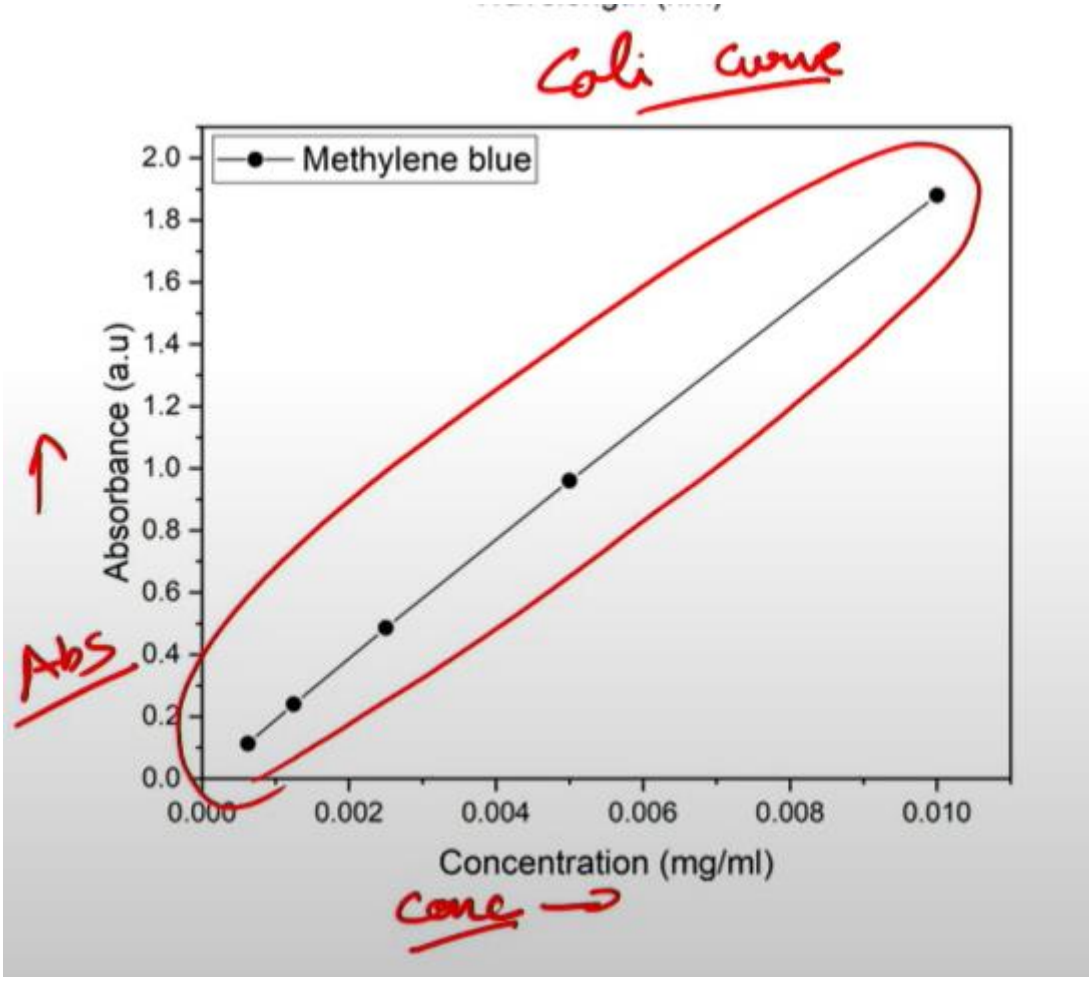
So, the band gap of these ZnO particles that I have synthesized is around 3.22 nanometers. So, it actually matches really well with the literature.



So, by measuring the UV and doing the tox plot analysis band gap analysis I could match it with the literature, and I could confirm that my material has been successfully synthesized.

So, there is another application that I would like to say that we could determine, and we could quantify the concentration of unknown concentration of some dyes or some drug or some any material.

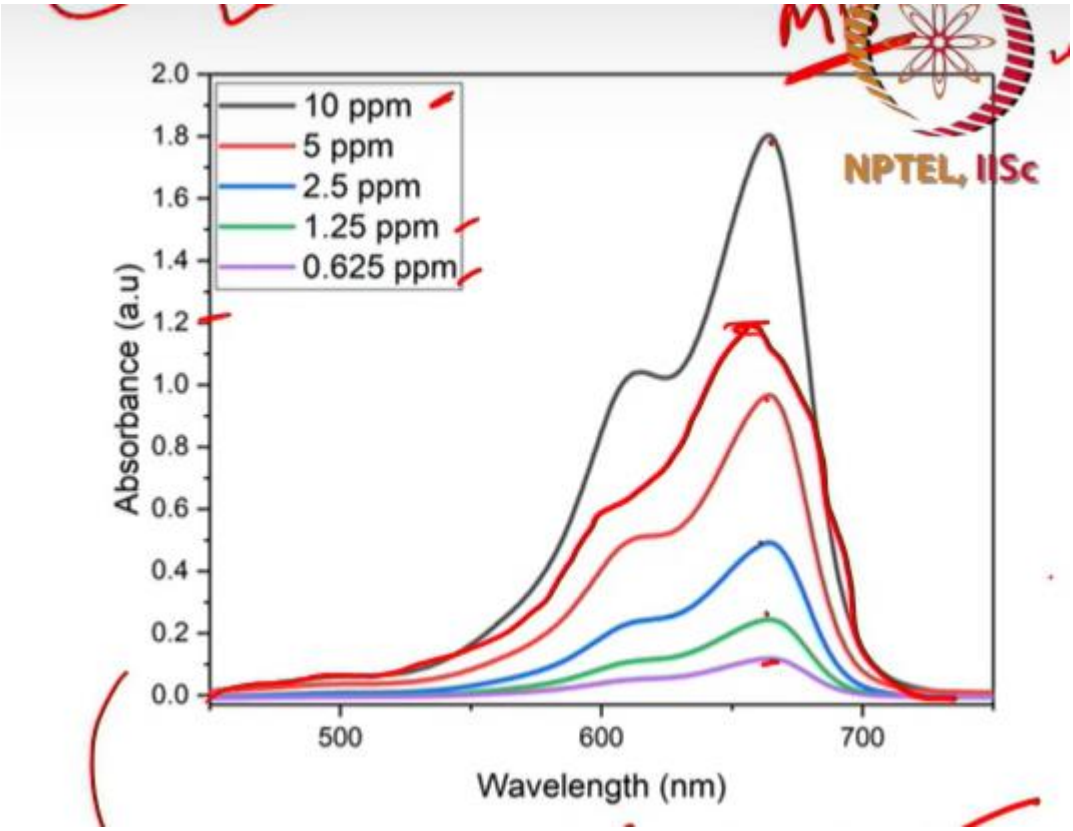
So, to understand this we will take another example. So, here on the top you are seeing is the UV visible spectroscopy of methylene blue dye I am representing as MB. So, what I have done initially is that I have taken the calibration curve. So, I will write is as the Cali curve. So, I have drawn a calibration curve from this. So, this is the Beers and Lambert's law from the Beers and Lambert's law I showed that absorbance is directly proportional to concentration.



So, I am taking the linear region of that you can see that this is the linear region obtained from the different concentrations of the dyes. So, what we have done is that we have taken known concentration of dye.

So, from 0.625 ppm. So, I have taken till 10 ppm. So, the concentration is known I have taken their absorbance value. So, we have from the UV visible spectroscopy we have the absorbance value we know the exact concentration of that methylene blue samples and we plotted the calibration curve right. So, after that suppose you have a unknown concentration of methylene blue you go to an industry and they give you a sample of methylene blue and the concentration of that dye is unknown to you. So, in that case what you will do? So, once you have the calibration curve you will run it through the UV visible spectroscopy and suppose the absorbance value falls somewhere so, that absorbance value falls somewhere around this 1.2 here absorbance. So, what you will do? You will see that where this 1.2 falls on your absorbance spectroscope on your where 1.2 absorbance falls on your calibration curve and depending on that you could identify the concentration of that particular unknown sample. So, here we have taken the example of

dye. So, instead of dye you could replace it with any drug or any material that you want to do any particular sample that for which you have the concentration dependent study.



So, this study we call it the concentration dependent study and on basis of that we plot the calibration curve, and we could find the determine the and quantify the concentration of unknown materials. So, this was our first application, confirmation of materials bandgap calculation and the third one is the determination or quantification of the unknown samples, unknown concentration of the samples. Then coming to another example, so this is a very interesting example. So, this is an environmental application.

So, for that we could also use our UV visible spectroscopy very well. So, there are something which is called degradation of the dyes. So, supposedly I took the example of methylene blue dye that was previously given. So, taking that example further there is something called degradation of these dyes. So, what we do is as researchers synthesize different kind of materials. So, supposedly we have synthesized ZnO or supposedly we synthesized TiO_2.

So, these we call as photocatalyst right. So, these are photocatalyst which means that in presence of light. in presence of light, it has the ability to produce electron and hole wear, and it will produce some raw species that will be responsible for the degradation of the dyes. So, supposedly you have this initial concentration of the dye and this concentration

will start reducing with time when you put your photocatalyst in this and you take different time intervals, you take out the sample, you take out the aliquots and you run it through UV you could see the dye degrading. So, supposedly the initial color is blue and after some time when the dye is degraded it becomes colorless. So, this is called the photodegradation of the dye which is called photocatalysis also.

So, for that you have certain photocatalyst which is known photocatalyst. So, here we are taking the example of a photocatalyst. So, in the example here. So, this was also from one of the studies that I have done. So, in this we have taken a known photocatalyst which is called MOS2, it is a 2D material.

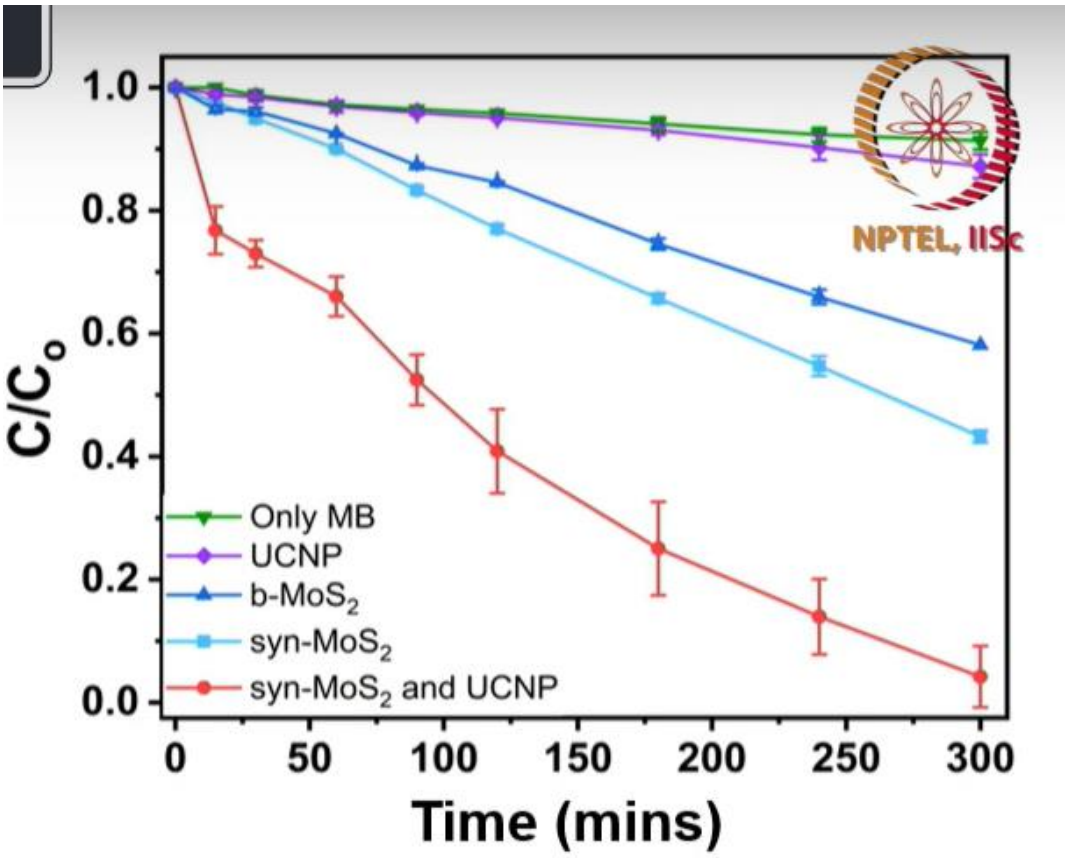
So, we took a bulk version of that which is commercially available. Now, I have synthesized MOS2 in our lab. So, this is the synthesized MOS2 and then we used it in combination with the material called up conversion particles. Now, how we could calculate the degradation efficiency of all the materials? So, to calculate the degradation or the removal efficiency we have a relation in which we have a C naught, C naught is the initial concentration of dyes right and C here is the final concentration of the dye suppose this study is till 300 minutes. So, after 300 minutes we will have the final concentration initially at 0 minutes we have the initial concentration. So, based on that we could calculate using this formula we could calculate the dye removal efficiency of that particular material.

$$\%\ Dye\ Removal\ Efficiency = \frac{C_o - C}{C_o} * 100 - \ln\left(\frac{C}{C_{eq}}\right) = kt$$

$$\%\ Drug\ Loading\ Efficiency = \frac{Initial\ Drug\ Conc. - Supernatant\ Conc.}{Initial\ Drug\ Conc.} *\ 100$$

So, after every time points, we will take out some of the aliquots and we will return it through the UV visible spectroscopy and after 5 hours we will after 5 hours or 300 minutes we will see whether our dye is degrading or not this time is not fixed for a particular thing. So, in my case I have used up to 300 minutes you could either do a 60-minute analysis or you could either take 12 hours 15 hours people take several different time points for the study. What the thing is that so, for our bulk MOS2 our degradation efficiency was around 40 percent, our synthesized MOS2 it increased to around 55 or 60 percent, while for our combination of the synthesized MOS2 with our up-conversion particle it increased to around 95 percent. So, this is what I was saying using the UV visible spectroscopy and this formula we could calculate accurately calculate the dye removal or the dye degradation efficiency of that photocatalyst material. So, this application is widely used and currently it is widely used for the wastewater treatment or

not only in case of degradation in some cases we also calculate the dye adsorption percentage.


C/C$_o$
1.0
0.8
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UCNP
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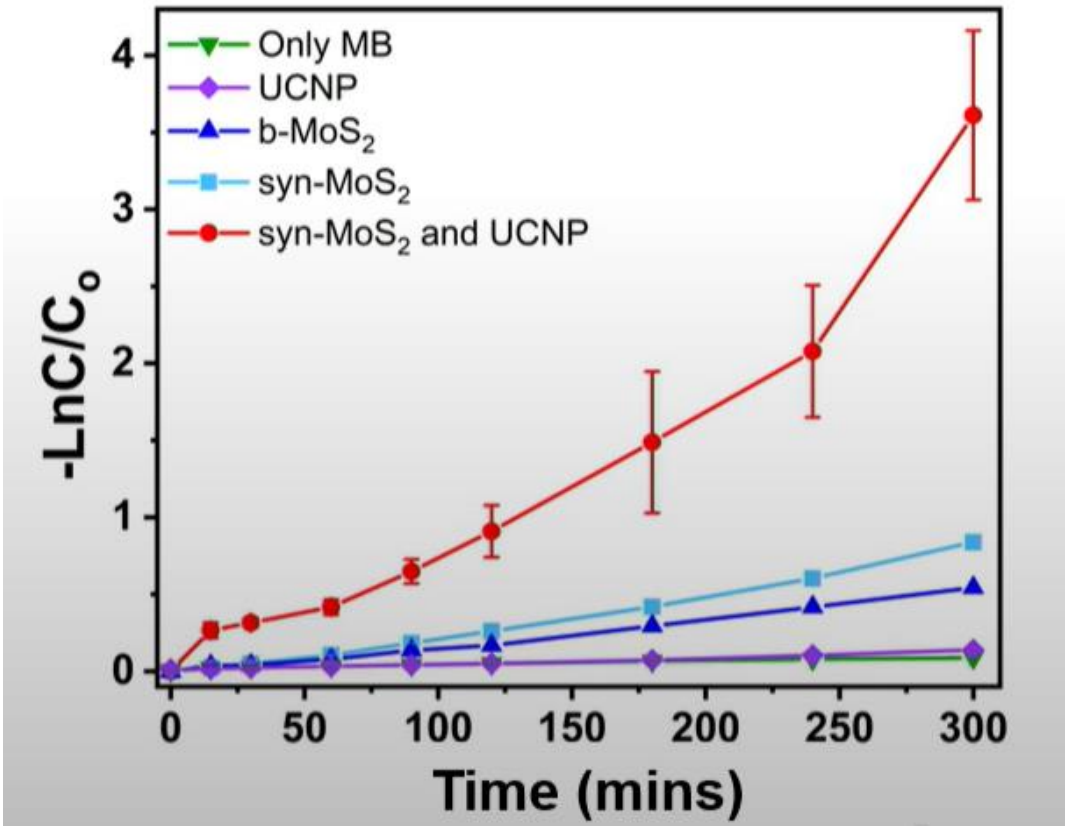
syn-MoS$_2$ and UCNP
NPTEL, IISc


-LnC/C$_o$
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So, we also calculate the percentage of dye adsorption some of materials high surface area materials has the ability to absorb the dye also. So, we can calculate using the same formula we could calculate the percentage of dye absorption or in case of photo catalyst we could calculate the percentage dye degradation efficiency of that particular material. So, after learning about our fourth application we would move towards kinetics. So, from the initial C by C naught curves with time. So, we calculated the degradation efficiency now there is something which is also called the kinetics of the reaction. So, our kinetics tells us how fast or how slow our reaction is proceeding. So, using the log of this formula using this formula ln C by C naught and plotting it with time we could also and then we fit it and we get the kinetics rate of reaction of our particular materials that we are using. So, in our case all the samples follow pseudo first order reaction and after fitting them we could find out the rate of the reaction and we could see for which case our rate of reaction is maximum. So, the kinetics rate of reaction could be determined using our UV visible spectroscopy. Now, moving from the environmental we will talk about one application which is called which is for the biomedical field.

So, for the biomedical field we have something which is called drug loading percentage or drug loading efficiency. So, supposedly let us take a example of ZnO again. So, we have ZnO material, this is ZnO particles, and we want to functionalize a particular drug on top of it. So, supposedly this part is a drug, and we want to load our nanomaterial with a particular drug.

So, this is widely used for drug delivery applications. So, we have certain nanomaterials because of its high surface area we functionalize them using various drugs and then we see that how much drug has been loaded on to our sample. To calculate this, we have to take two more samples. So, we have a sample in which we have the drug alone, then we have a sample in which we have the ZnO particles alone. So, I am writing as nanoparticles alone. So, this is our first sample, this is our second sample, and this would be our third sample.

So, this is our combination of both. So, how we could calculate the drug loading efficiency? So, first is the direct method we will directly take the UV visible spectroscopy of this, and we will calculate how much of the drug has been loaded onto the particles we will directly get. So, for this also you will have to plot the calibration curve like I told you earlier. So, the known concentration of drug you have to calculate and depending on that you can calculate how much drug has been loaded onto your particular material.

So, you could directly do it either. So, this would be our direct method. and there is something which is called indirect method also your direct method is useful, but in some cases like in zinc oxide the material also has its absorbance peak. So, if your material and

your drug that you load onto your particles are interfering with each other having their peaks relative peaks in the UV visible region. You go through something which is called indirect method and from this formula you could calculate the drug loading efficiency in which you have the initial drug loading concentration, which is represented by C naught, then you have the concentration of the supernatant. So, the supernatant would be the drug which is not being absorbed by the particles. So, you take the initial concentration of the drug, you put our particles, you incubate it for some time, then the drug has been loaded onto your particles, some of the drug has been loaded on to your particles and most of it would be unloaded on to the particles. So, the supernatant that you will have the unloaded drug which has not been loaded on to the particles. So, we take the concentration initial concentration C, we take the concentration of the supernatant and from this formula we could calculate the percentage drug loading efficiency of that particular material. So, talking about the environmental coming to the biomedical in some of the UV and the visible instrumentation there is a also some facility in which you can use a solid state mode and also in some cases you can use thin film modes. So, our thin film modes are usually useful when we want to see the quality of the thin film that we deposit for our electronic device fabrication.

So, we deposit various thin film, we want to confirm whether our film has been properly deposited onto the sample substrate or not for that we run it through the thin film mode of the UV or we also have a solid state. So, it is not available in all the instruments, but mostly it is available in the liquid form, but some of the UV and the visible also has the solid state and the thin film mode also. So, using the thin film mode we could actually calculate whether our thin film has been properly deposited onto our substrate or not and how is the quality of the film. So, we could also use it for device fabrication. So, after each step whenever we have a thin film deposition, we could confirm through the UV visible analysis that whether our film has been properly deposited or not.

So, that concludes us for the UV visible spectroscopy. Now, let us quickly recap what we studied. So, coming to the summary initially we talked about the basics of the EM waves we got a recap of the previous lecture. We talked about their application and how they can be used for the characterization and the IR spectroscopy that was previously studied. I talked about the very basics of that. Then, I talked about the UV visible spectroscopy basics of electronic transition. So, right from the atomic model we went to the molecular orbital theory, we talked in detail about electronic transition and how our material has the ability to absorb that particular wavelength and have electronic transition and then what is absorbance and what is band gap and everything was discussed.

Then we talked about basic principle of the UV visible spectroscopy, how that works and after that we talked about the mechanism of the UV visible spectroscopy, what is its instrumentation, how it can be used and how to study the UV visible analysis. Then we

talked about some of the practical applications in which we talked about in detail that we could use to confirm whether our material has been synthesized or not. We talked about some of the environmental applications, we talked about from the band gap calculation and the drug loading application was also explained to you and then the kinetics how you study the kinetics rate of reaction of that material. material that could also be studied. So, these all applications were studied was told you in detail and also how in the solid state or thin film mode you could also use it for the thin film analysis of your electronic devices that you fabricate.

So, talking about all these. I would like to conclude this lecture here. So, thank you very much for attending this lecture. I hope this was helpful and we will talk about the X-rays, how X-rays could be used for the characterization of the materials in our next lecture. Thank you. I hope this was helpful. Thank you.