Non-conventional Energy Resources

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Lecture – 19
Solar Energy: Solar photocatalysis

In the last several classes we have looked at various aspects associated with solar energy, and how we can capture the energy and utilize the energy. More specifically we looked at solar thermal and the solar photovoltaic as these are the two major processes that are used for doing this you know process of capturing solar energy, and really most of the technologies that you see commercially that are out there really fall on those in those two categories, that's what you will see you will see solar water heaters, you will also see solar based power generation systems, and you also have these solar volt photovoltaic based you know street lamps, household you know electricity from rooftop and so on.

So, largely it is these two; and so for these two we looked at in considerable detail the science aspects associated with, the technology aspects associated with it and how it is put together, what are some issues related to them, and how they work etcetera. So, all this we did in the last few classes, with in today's class we will look at a specific aspect of you know utilizing solar energy, which is referred to as solar photo catalysis and really with this topic we will sort of wind up our discussion on or you know our focus on solar energy in these last few classes, will sort off you know come together. In this class and fill wind up with that with this topic on the solar related aspects.

So, photo catalysis is the primary topic, it is different from the solar thermal and the solar you know electric that we looked at photovoltaic that we looked at and that's why it is interesting to look at.

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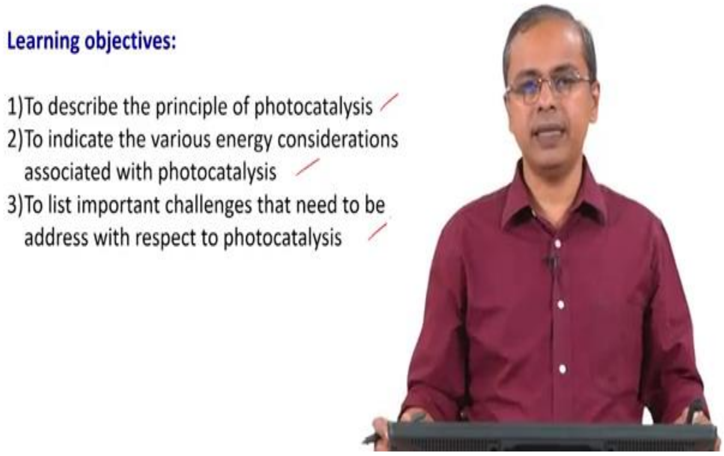

Learning objectives:

1)To describe the principle of photocatalysis

2)To indicate the various energy considerations associated with photocatalysis

3)To list important challenges that need to be address with respect to photocatalysis

Our learning objectives for this class are to describe the principle of photocatalysis and that is something that. We will look at we will look at various considerations energy considerations associated with the photocatalysis, how it is put together, what's the thought process behind it what's the science behind it and so to speak. So, to speak and also we look at as always it is important to understand, what are the challenges that one needs to address in the context of photocatalysis.

So, these are broadly the ideas that we will look at. Now photocatalysis is used for a variety different things, the idea is simply that you are using incident solar energy incident light. In fact, and then solar energy is the most you know accessible form of light that we have; to do to help catalyze a reaction. So, to help catalyze a reaction and in that process the you know some other reaction happens, maybe we have interested in the products of the reaction and therefore, we look at it. In the context of our discussion we will really look at primarily the use of solar energy to generate hydrogen. We have looked at through this course the idea that you know if you are using mostly carbon based fuel, then necessarily you are going to be generating carbon dioxide.

So, this is we are stuck in this situation, and if our understanding of the whole process is correct, then it is not a great idea to keep on generating carbon dioxide and putting it into our atmosphere. So, it helps if we can look at fuel systems or processes, that essentially avoid the introduction of carbon into the system into the atmosphere. So, the good solution that is provided quite often is the idea that you can convert water to hydrogen and then you can use hydrogen as a fuel. So, when you burn hydrogen you are essentially doing you know oxidizing hydrogen and you are generating back water. So, if you can set up a process by which you take water, supply energy in some form, break it up into hydrogen and oxygen and then later when you utilize it in some location you are simply recombining hydrogen and oxygen and getting back water.

If you keep doing this cycle then you are essentially clean I mean there is no problem at all and in fact, the product water is say if you do it properly, the product water is probably can even be made in such a way that it’s really clean, and available for drinking. So, it is a nice cycle to tie yourself into it’s very clean and it is a complete cycle you introduce hydrogen, you take out hydrogen back into water. From water you get out hydrogen and then put hydrogen back into in the state, where it is in you know it’s oxidized and you are sitting it is sitting as water. So, this cycle is kind of complete you are not you know suddenly increasing the percentage of hydrogen in the atmosphere that’s not what is happening, and there is no CO_2 involve this process if you know how to do it properly and cleanly.

And incidentally if you look at say for example, manned space, space mission and so on. This is actually a cycle that people would like to use, they would like to split hydrogen and oxygen, I mean split water to get hydrogen and oxygen and then use hydrogen as some kind of a fuel to power various aspects associated with the manned space program and then in the end you will the process of powering, you will again re get you know get back the water that we use and that water can be used for various purposes. So, this a nice cycle as I said to tie into. So, therefore, it is very interesting to do this. So, now, let’s begin by first looking at what is required to do this water splitting.

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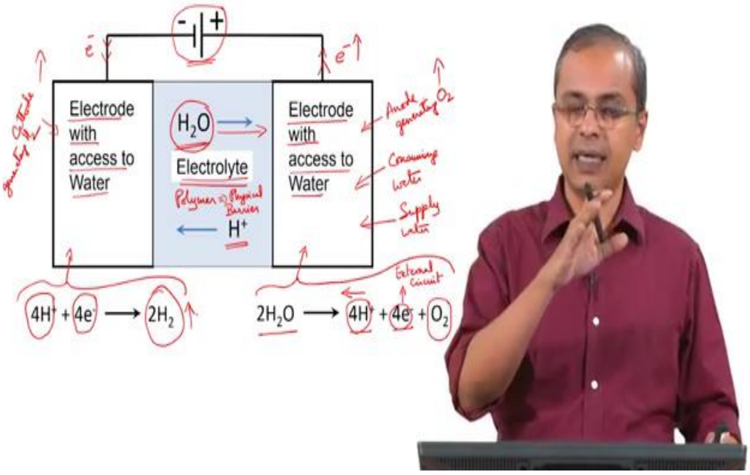

So, the simplest example of doing that would be what you see on your screen, which is simply an electrochemical cell. So, an electrochemical cell, you have here a battery and that is powering a process by which you are taking water and converting it to hydrogen and oxygen. So, we have an electrode, which has you know where you are pushing in the electrons, and you have an electrode from which you are pulling out the electrons okay. So, you are pulling out the electrons in one side, you are pushing in the electrons in the other side. Generally we say that if you are adding electrons to an to a species, then we describe that as a reduction process. And if you are pulling electrons away from the species you describe that as an oxidation process and in the electrochemical scheme of things the electrode at which the oxidation occurs from where you are pulling the electrons off into the external circuit is called the anode.

So, in this case this would be the anode, and the electrode where you are pushing electrons in and from the external circuit and therefore, enabling some species in that electrode to get reduced is is where the reduction is occurring, and the electrode where the reduction is occurring is referred to as the cathode. So, this is our cathode okay. So, we have anode cathode and in the middle we have the electrolyte. So, now, this electrolyte and all we are going to do is take water and split that to hydrogen and oxygen. So, it is actually a two step process, we can take water and you can generate 4 H plus ions, which is basically a proton because once you remove the electron it’s a proton and of course, you will correspondingly also release 4 electrons and you create oxygen ok.

So, this is the way it happens, these electrons go into the external circuit. So, this goes to the external circuit and this H plus is going across okay. So, that's what you see here. So, at the anode this reaction that I have shown you down here okay, this reaction is occurring here this whole reaction is occurring here. So, these electrons that you see here are the electrons that are being pushed into the external circuit there.

So, this e minus is going that to it, that is what is happening the same e minus is then pushed back into this circuit here in this part of the system, and then it arrives into this electrode which is the cathode and so, that is this 4 e minus here. So, I have just balanced it out. So, that it looks the same and the proton has also got to arrive there, that proton arrives through the electrolyte which is what I described here, this proton that you generated on the anode side, is now being pushed through the electrolyte and it arrives at the cathode.

So, at the cathode that same 4 H plus will now react with the 4 e minus and generate hydrogen. So, this is what we have as our overall reaction. So, so this reaction is occurring at the cathode, at this electrode. To do this we are using an external source of energy which is the battery that is sitting here and which is appropriately connected. So, that you are pushing electrons in one side pulling electrons off of the other side and therefore, it encourages the reduction reaction on one electrode it encourages the oxidation reaction on the other electrode. And generally what happens is if you want to do this, you give access enough access to for both the electrodes to water and based on the your electrolyte properties typically electrolyte may also desire or prefer to be wet.

So, you have to have water in the electrolyte. So, generally we provide water on both sides of the system, and in principle you are actually as you keep consuming water, you are consuming water on the anode side. So, water is getting consumed because it is getting split into hydrogen and oxygen, you can, if you supply water on the cathode as well, that water will just transport itself across, the way I have pointed out here right. So, you have a movement of water from your cathode to the anode, you have movement of protons from the anode to the cathode. So, all this is happening and of course, you can also have as I said you can keep supplying more and more water to the anode side. So, that it is not only dependent on this water that is coming here. So, it does not have to depend only on this water, you can directly supply water.

That’s what I say by may mean by saying electrode with access to water, the same is true here also electrode with access to water okay. So, you do this,, usually in a system like this, this electrolyte that I have put in the middle is some kind of a polymer, that is in a position to transport protons and it’s also in a position to transport water. So, it’s a polymer of that nature, and because it is a polymer it is a solid, it’s a solid polymer I mean where it is a solid polymer in this case which we select a solid polymer, solid polymer based electrolyte and therefore, it acts as a physical barrier. So, acts as a physical barrier between the anode, and the cathode between what is the anode and what is the cathode.

So, it acts as a physical barrier, which is a nice thing in this case because on your anode side we are generating O_2; that’s a gas and the gas is going to come out. Or if you have some outlet in your system in the physical cell that you build there’s a separate outlet in that outlet the oxygen will come on. On the cathode side you are generating hydrogen. So, hydrogen is going to come out here. So, this hydrogen gas is going to come out. So, you have hydrogen coming out on from one electrode you have oxygen coming out from the other electrode and because the electrolyte is a solid electrolyte and therefore, acts as a physical barrier you can separately collect the oxygen, you can separately collect the hydrogen and they will not mix and so, whatever hydrogen you generate you can safely collect and store away whatever oxygen you generate you can safely collect and store away and there is no wastage whatever electricity you use does all of this processes ok.

So, this is the way in which you can envision, how electrolysis of water can happen. Now you can generate this in this in the manner that I have shown you, using this power supply that we are using here some DC power source which could be a battery. You can use a battery there, you can even connect it to the mains and use some circuit which gets you DC source and that source you can use to do this activity, you can also connect a solar cell. So, in this case the solar cell will simply act as a source of energy, and from where the electricity is generated that electricity will enter into a cell of this nature, and once it enters the cell of this nature it will do electrolysis and generate your hydrogen and oxygen. When you use a solar cell in this process what you are actually doing is, you are doing a two step process.

You are first doing a process by which you are using solar energy to generate electricity, then you do a second step where independently the electricity comes into a separate system, where you are doing the electrolysis. So, it becomes a two step process generally speaking in all in any any form of engineering just because of the thermodynamics of you know involved with all of these processes, typically in any engineering process the more steps you in include the more your inefficiency is; because by nature none of these energy conversion processes or most of these energy conversion processes are not necessarily 100 percent efficient. So, you will invariably find some inefficiency in the process due to heat that is generated, due to movement of ions, lot of different things that are happening here that there is going to be some inefficiency if there is inefficiency. So, that those inefficiencies are multiplied.

So, if one you know process is 90 percent efficient, and another process is also 90percent efficient and both of these are in series then you basically have a process which is only 81 percent efficient right. So, 0.9 into 0.9 will get to 0.81. So, these kinds of processes will these kinds of issues will be there and therefore, it is not necessarily a great idea to have multi step processes. So, ideally you would like to have a situation where sunlight comes into a into a into a system, and in that system directly you are generating hydrogen, without having to do multiple steps where you have a separate process generating electricity, and separate process doing the electrolysis. So, that's something we would like to keep in mind ok.

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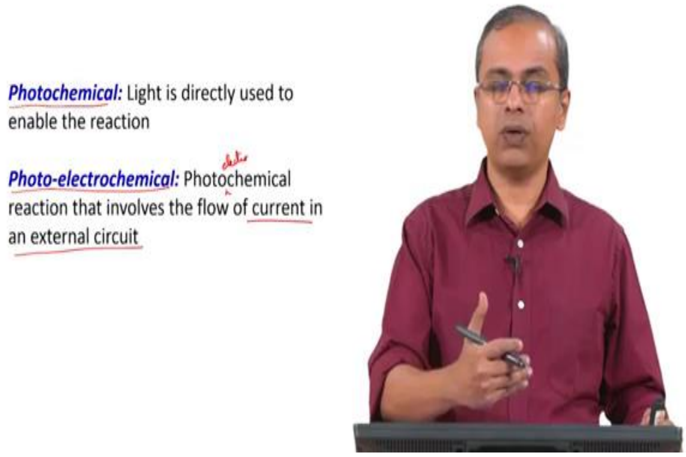

Photochemical: Light is directly used to enable the reaction

Photo-electrochemical: Photochemical reaction that involves the flow of current in an external circuit

So, in this context there are two terms that are of interest, one is this idea of something called photo chemical and the other is photo electrochemical. So, if you look at photo electrochemical. So, this is photo electrochemical. So, photo electrochemical reaction is one that involves the flow of current in an external circuit okay. So, this is not really electrolysis, but it is slightly different from what we just discussed, where you have the you know solar panel sitting outside.

You can have here a situation where the you know light falls on a material which generates these photoelectrons and then right there you do the reaction, but you still separate the container. So, that you have flow of current in the external circuit and you can also have something called photochemical, where light is directly used to do the reaction. So, we will spend most of our time looking at photochemical process in this class, and that's because that is of interest as something that a lot of people are working on and pursue it right.

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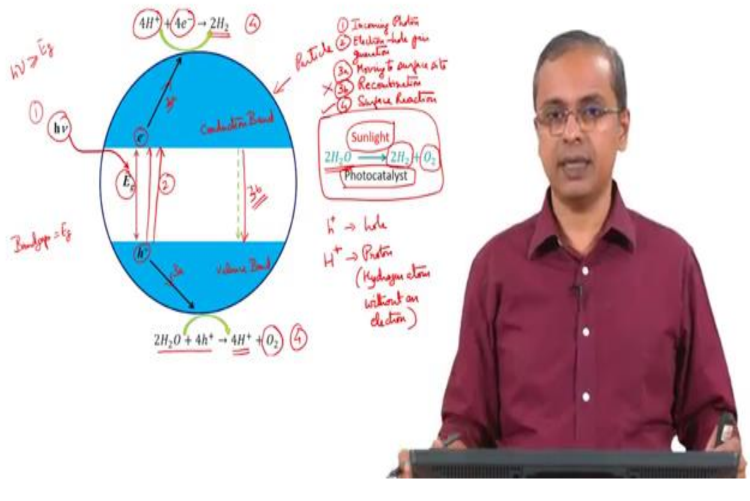

So, for a photochemical process basic idea is that you first of all have a particle. So, some kind of a particle is what we are you know using a schematic here, to indicate it is a particle. Now that particle is of some semiconducting material; some semiconducting material is there, which means there is a band gap. So, band gap equals Eg, and of course, as we know if if you have an incident radiation of with frequency nu, if h nu is greater than or equal to Eg, then you have a transition. You have the possibility of a transition which is what you see here.

So, you will have a transition of an electron that goes from the so valence band, to conduction band. So, you put in enough energy e greater than I mean h nu greater than or equal to the band gap, then you get this transfer of a you know electron from the valence band to the conduction band, and which leaves behind a hole here and so you now have an electron sitting in the conduction band, you have a hole sitting in the valence band.

Now, when this has access to water, when this has access to water, this H plus which is the you know hole and not to be confused with the proton, the H plus the that's why have you small h. So, small h is the hole. So, h plus hole capital H plus is a proton okay, hydrogen atom without electron. So, that capital H plus is a proton which is basically a hydrogen atom without it's electron right. So, now, this h plus is available this hole is available it's a basically a positive charge. So, if it reacts with the species and pulls off an electron, it can essentially do oxidation. So, that's what it does. So, it reacts with water and creates 4 protons plus oxygen ok.

So, it has now created 4 protons of the 4 holes reacted with water and created 4 protons and released the oxygen. So, the 2HO we gave you 4 H plus and O_2. So, this happens at one location, some location on that particle. Now the electron has been put into the conduction band it may go to some other location, that location it will if it finds protons in that location 4 H plus these electrons that you brought here will now react with that proton and get you hydrogen okay.

So, this process you have now taken you know a situation where at several locations on the particle, the holes are reacting with water generating protons and generating oxygen. This proton is moving around or is in a position to move on and if it happens to also see electrons coming there from the conduction band these protons react with those electrons and generate hydrogen. So, you can generate oxygen on at some sites and you can generate hydrogen at some sites.

So, this is the overall reaction, you have water and in the presence of sunlight and in the presence of this photo catalyst, you are generating hydrogen and you are generating oxygen okay. But the photo catalysis is important; if you just add sunlight this is not going to happen. The sunlight acts on the photo catalyst and does this transition, only because of this transition now you have an electron that is available at some location which can do the reduction, and a hole that is available at some other location which can do the oxidation. And since you are able to switch these two reactions I mean locate these two reactions and specific sites, you are able to get the hydrogen off the location where reduction is happening and you get oxygen at the location where the oxidation is happening okay. So, so this is how it is happening, now I must also point out that you know you had first step of this before this is the first step of this you know incoming radiation that came in and did this transition. So, you can consider this is step 2 and so, you created in step 2 you created these electron hole pairs right.

So, as step 2 was electron hole pair creation. So, in step 2 after that is done, the electron and holes actually have two options available to them. They can migrate to the surface which is what you are seeing here. So, after step 2 they could either migrate to the surface or alternately they can simply recombine which is what you see here. So, we can consider this as 2 a for example, and this is 2 b for example, two possible ways in which this can happen right. So, or we can 3 a and 3 b if you want to look at it that way. So, two you have done the you know transition from valence band to conduction band, and then a step 3 you can do something with those that electron hole pair.

So, one possibility is that it goes to the surface. So, that is 3 a, and the other possibility it is that it simply recombine. So, this is also 3 a. So, 3 a is that this electron hole pair moved to surface sites, where they can do the you know any reaction or 3 b is simply they recombine. So, this recombination 3 b is the recombination and that is a loss in the sense that you use the photon to create this electron hole pair, but you could not use that electron hole pair to do anything useful you lost the electron hole pair right. So, that 3 b is a loss and then the final thing that happens is 4 which is the reaction right. So, these are the various steps. So, if you want to put it down we have one incoming photon, 2 electron hole pair generation, 3 a moving to surface site, 3 b recombination and 4 surface reaction.

So, these are the various processes, clearly we want to do 4. So, we want to in the scheme of what I have just described here we want to avoid 3 b. So, this is something we want to avoid, 3 b is the recombination is something that we want to avoid 4 is what we want to enable. So, that is the general idea. So, this is what is happening in photocatalysis, this is photocatalysis. So, this particle would be present. So, essentially all you need is beaker in which you have water and you have this photocatalyst material is in powder form available within that beaker. Once that is there and then you put it out in sunlight you would start seeing bubbles coming out, the bubbles should be both hydrogen as well as oxygen okay because in this beaker both are being generated. So, this is what is happening.

So, that also causes a challenge because if you have hydrogen and oxygen present in the same beaker, they can react and again reform water. So, that is the reverse reaction is also possible here. So, that is also something that we don't want. We don't want recombination; we do not want a reverse reaction. So, this is something that we will keep in mind ok.

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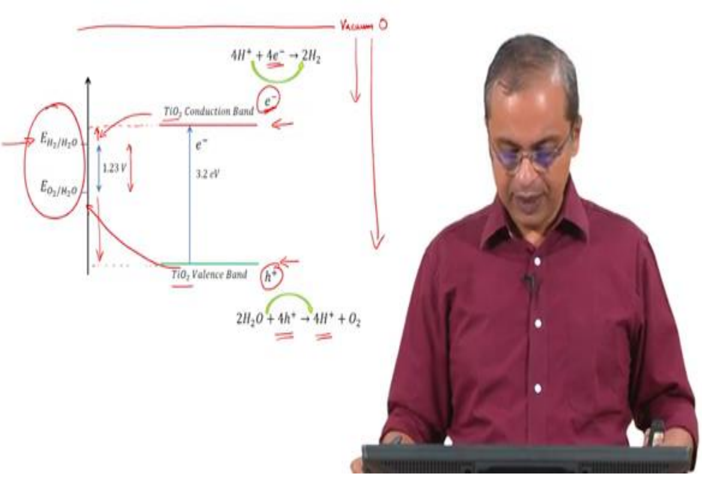

So, what are some considerations relative to this? So, now, if we see here we have if you go to the electrochemical series you will have here a potential for the hydrogen you know redox reaction, and that is usually set at zero volts, and with respect to that you have the oxygen reduction potential and so that, that will come to your 1.23 volts okay. So, this potential is difference in potential is what you have to provide to water to start splitting the water okay. Now you have using some photo catalysts right. So, you are generating an electron and you are generating a hole. Where should those electron and hole be in terms of energy for them to enable this reaction to happen?

So, the way that is matched is that whatever is the conduction band level, that should be higher than this okay and whatever is the valence band level should be here. Only if you have this situation the electrons from here that electrons that are sitting up in this conduction band, will go and do this reduction process and the here you will also have the oxidation and therefore, I mean the holes from here will be in a position to participate in the oxidation process okay. So, that is how the energy of this system is set up, and that is what you see here this hole reacts with the water, and generates the protons and that electron which is sitting here reacts with the protons and generates hydrogen.

So, that is how this relative energy levels are set up. So, you have to have a band gap which is higher than that that corresponds to this 1.23 volts, and you have to have it's not just the value that is important, the position of the band is also very important. Because only then you will have oxidation occurring at one location and reduction occurring at the other location, otherwise only one reaction will be favored, the other reaction will not be favored and since you have to have continuity the reaction will stop. Otherwise you little it will it will not proceed so, because you are not completing the process.

Now incidentally there is something that we have to pay attention to here when you look at the band energy levels. So so, for example, this energy level and this energy level here, these are defined relative to vacuum level. So so, there is some vacuum level sitting there which is set at 0. So, this is vacuum, this is set at 0 and relative to that you have all these energy levels. This on the other hand is a you know standard electrochemical series based set up, where arbitrarily this reaction has been set at zero volts, and relative to that you have all the other voltages. So, on the one side you have an absolute scale, on the other side you have a relative scale okay. So, we have to at least be alert to that.

So, they on the one side you have an absolute scale and the other side you have a relative to scale. So, then how do you match them up? So, sometime in the seventies people have done a lot of work on this. So, they have looked at what happens when a metal gets oxidized. So, oxidation of different systems they have looked at especially metallic systems getting oxidized, and then and looked at how you know oxidation occurs in different systems.

The oxidation of many solids is directly related to the location of their bands, because that is how again this is exactly what is happening what I have shown you on the picture here is exactly happening when you oxidize a metal also when you create a metal oxide things like that. So, by comparing those band energies they have been able to figure out how to line up those band energies relative to the electrochemical series, because that potential is required and that position is required for the process to occur.

So, by understanding that carefully, they have understood how to line these two up and that is how you know that the TiO_2 which is a material that I have mentioning here, titanium dioxide is usable in this condition. Incidentally the material that has been most used for doing this photo catalysis is titanium dioxide, that's why it is shown here as well the it is basically the I mean it is one of the earliest materials studied for this process, but there is more to it is also very stable material, and although they have looked at various other materials it's also very I mean it's not really toxic in any way, it is a relatively safe material and therefore, it is you know preferred over many of the other systems that have been studied. People are still it still has some drawbacks. So, they have not completely sorted out all the issues with titanium dioxide, but it is still the preferred material for use.

So, so that's how you know this process is happening and that is how the band structure of the material which is your photocatalyst relates to the kinds of potential is required for water electrolysis and this is how the process works okay. So, this is what we are looking at.

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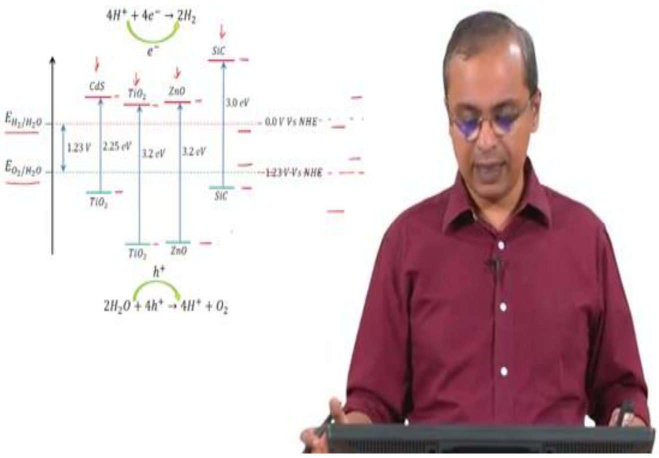

Now, just to you know convey this idea of this band position versus you know the water electrolysis process, I have just shown you here not just the titanium dioxide which is what we first looked at, but other materials you have zinc oxide, you have silicon carbide, and you have cadmium sulfide.

So, 3 different additional materials I am showing you, in all of these materials have enough window between enough band gap that and the position of their bands is correct, because all of them have their valence bands sitting below this value, and all of them have conduction bands sitting above this value. And therefore, they are able to support reduction processes the conduction bands are able to support reduction processes of the given that they have access to water, and the valence bands are able to support the oxidation processes given that they have access to water right.

So, this is the way in which it is set up, and the band gaps are also very important because they decide; what is the energy of the incoming photon that will be required to do the transition right. So, it is not a it’s not something that we can ignore. So, for example, I mean we if you have a band gap that is too small, that will that’s a material that will not work. If you have material which has this position for band gap that will also not work, if you have this position for band gap also will not work relative to these dotted lines okay.

So, the only ones that will work are the ones that you are seeing on your image. So, that’s the way you want to look at. But I mean even though you have no a choice of materials that are listed here, as I said you know other considerations are there such as you know toxicity and so on. So, cadmium is for example, not at all favorable from that perspective, but you should also understand that the if you have a very large band gap, then you are expecting very high energy photon to enable the transition and therefore, we need to compare this set of band gaps that you see here, to what is coming in your our solar radiation.

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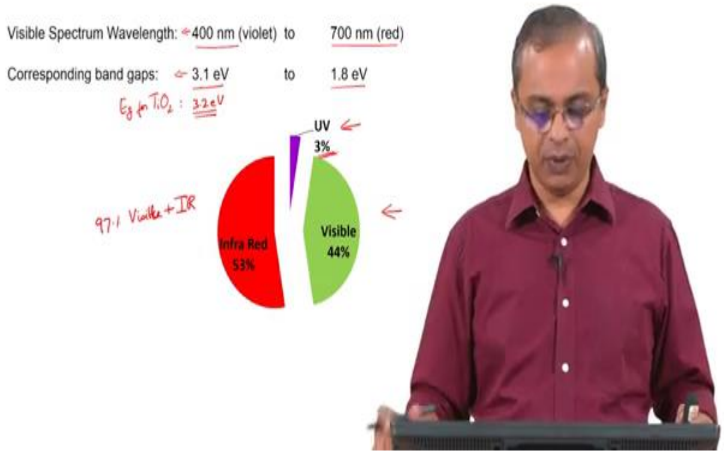

Visible Spectrum Wavelength: 400 nm (violet) to 700 nm (red)

Corresponding band gaps: 3.1 eV to 1.8 eV

Eg for TiO_2 : 3.2 eV

So, if you look at it the visible spectrum is has wavelengths from 400 nanometers to 700 nanometers, and this corresponds to band gaps of 3.1 electron volts to 1.8 electron volts. So, 1.8 would be your red end of the spectrum going up to 3.1 which is the violet end of the spectrum. So, if you go back here, you you find that titanium dioxide which is extensively used is 3.2, which is even more than 3.1 right. And so, these are all significantly large band gaps that you are seeing here. So, if you compare 3.2 which is as I said the titanium dioxide is the most commonly used material that is a value that is greater than this, 3.2 electron volt Eg for Ti right. So, Eg for Ti is 3.2 if you want I put it there TiO_2, 3.2 electron volts.

So, it means you have to have a photon of energy greater than 3.2 electron volts, to do the transition which means it is of energy level higher than this and wavelength the values lower than this, which basically means you are looking at not the visible spectrum. So, the visible spectrum cannot do a transition in the titanium dioxide sample okay. So, the visible spectrum cannot participate in photocatalysis. If you are using titanium dioxide as the catalyst, you cannot use infrared also because infrared is even lower energy than visible spectrum. You can you only use ultraviolet radiation that too with a small I mean not all of it, but little past 3.2 from 3.2 electron volts onwards. So, you can use ultraviolet part of the radiation. So, now, if you look at the spectrum, which is what you see here, you are looking at 97 percent is visible plus IR infrared; visible plus IR is 97 percent of the spectrum, only 3 percent is ultraviolet.

So, by using titanium dioxide even though it is the most popular photo catalysts and so a lot of people work with it, you are actually working only with 3 percent of the incoming radiation you are missing out 97 percent of the radiation and therefore, from a scientific perspective it is interesting to try and see if we can do things, to I know alter the situation right. So, this situation is not necessarily acceptable to us right.

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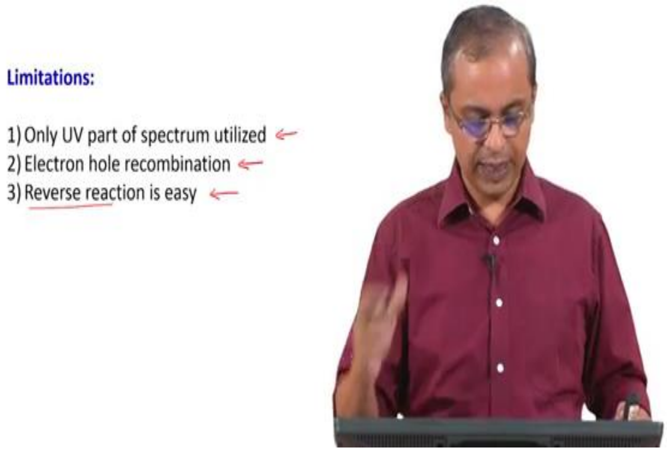

Limitations:

1) Only UV part of spectrum utilized ←
2) Electron hole recombination ←
3) Reverse reaction is easy ←

So, as I said here the limitations are only the ultraviolet part of the spectrum is utilized, we also said that you know that you can have some amount of electron hole recombination, because you have put you know electron in the conduction band well in the hole in the valence band, and if you just give it some time it will recombine. I mean it it’s just a, you know there is a probability associated with it if you the longer the time will give, it will recombine. And also given that hydrogen and oxygen are getting generated in the same chamber essentially, you have a great possibility that after doing all this you are still not able to use the hydrogen, because before you use the hydrogen it is already reacted back with water we are reacted back with oxygen and generated back water.

So, that’s the reverse reaction. So, you have 3 challenges there, you have to deal with these challenges to know more effectively utilize this idea of photocatalysis.

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Approaches:

1) Bandgap tuning
2) Adding sacrificial agent, reduce particle size
3) Presence of co-catalyst

So, there are some approaches. So, the approaches are you have to do some possible band gap tuning. So, there are ways in which you can change the band gap or at least provide different kind of band gaps for the reaction to occur, which will then help you create a situation where you are not restricted only to the ultraviolet part of the spectrum that you can actually use the rest of the spectrum as well.

We could also look at adding something called a sacrificial agent or reducing the particle size, both of these actually help prevent the recombination process. So, for example, this particle size reduction is an interesting way to go because, when you reduce the particle size there is less distance for the electron or hole to travel to reach the surface site.

And the lower the distance that is there for it to reach the surface site, you are reducing the chance that it will participate in any other reaction that it will actually recombine itself, it will actually reach the surface and do the reaction that you want. So, that’s one thing that you can do sacrificial agents are another way in which you can you know prevent the electron hole from recombining, we look at look at it and of course, co catalysts can be used to you know which slow down the reverse reaction ok.

So, that is something. So, I will particularly more actively look at the band gap tuning and the use of the sacrificial agent.

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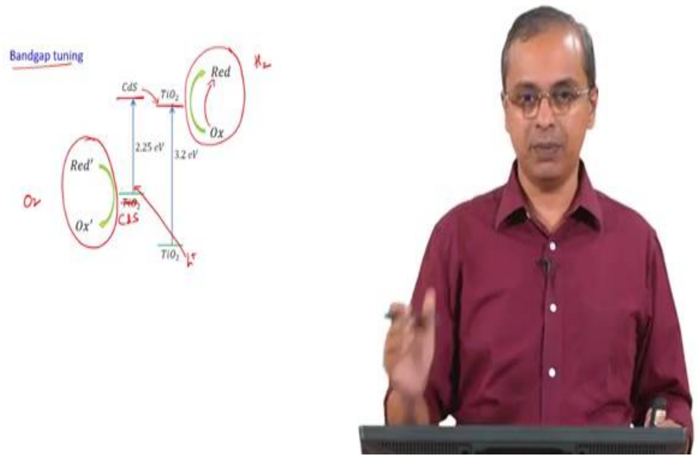

So, the band gap tuning can be done something like this. So, this is band gap tuning. So, let us say you have CdS in addition to TiO_2. So, now, this is a little bit tricky because there are a number of things that we have to consider, we have to consider what is the kind of contact between them, how do those band gaps line up because typically Fermi energy will be used to figure out, how they line up.

So, those there are issues associated with this which we have to look at little bit more carefully, but assuming we have looked at all that and this is the this is the situation we have, then when you do the transition, when you do the transition, from you know TiO_2 and you get. So, this is CdS here, you do the transition then basically the electron will stay the conduction band level of TiO_2 is lower than the conduction band level of the CdS.

So, the electron continues to stay on the TiO_2, and then helps do the; this reduction process. So, some species it takes and then does the reduction process. So, you get hydrogen here right. The holes that you generate the hole that you generate here are actually in a position to move up here, and they become more stable in the CdS setting and therefore, they are actually able to do the reverse process.

So, they are in generating oxygen. So, the h plus moves off to the CdS, the e minus remains on titanium dioxide, and in that process and even if you generate any electron hole pairs on the CdS, that will also do the same thing it will the electron will come off here the holes will remain here.

So, the holes will preferentially collect on the cadmium sulphide, electrons will preferentially collect on the titanium dioxide. It is sort of like a p-n junction kind of it’s although you are not really looking at I mean not necessarily looking at you know it is at least a junction between two materials, and then you may not have been doped it in anyway, but you are creating a situation where electrons will preferentially stay on one the material, the holes will preferentially stay on the other material. And therefore, you generate oxygen at slightly different location you generate a hydrogen at a slightly different location.

And more specifically the electron holes have a less of a tendency to now recombine, because you have not given them an opportunity to stabilize themselves later at different locations. So, this is called band gap tuning, and more specifically it also helps you create a situation where you access a little bit more of the visible spectrum, because you also now have the band gap associated with CdS right, which is now smaller than the band gap associated with the titanium dioxide right. So, therefore, photons of even lower energy can participate in this process. So, this is called band gap tuning.

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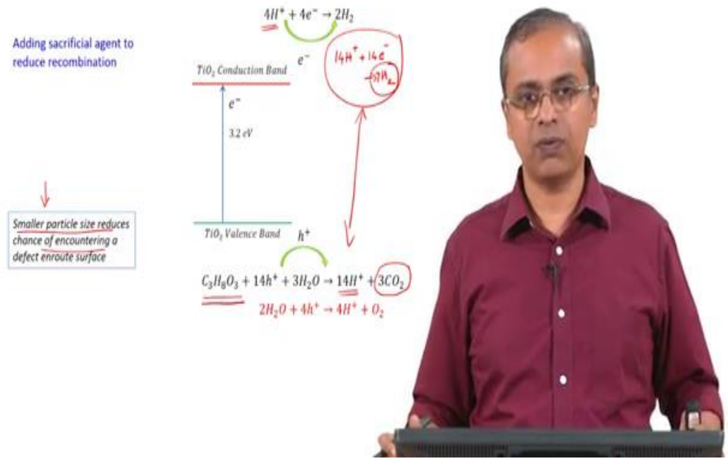

Adding sacrificial agent to reduce recombination

Smaller particle size reduces chance of encountering a defect enroute surface

$4H^+ + 4e^- \rightarrow 2H_2$

$14H^+ + 14e^- \rightarrow 7H_2$

$C_3H_8O_3 + 14h^+ + 3H_2O \rightarrow 14H^+ + 3CO_2$

$2H_2O + 4h^+ \rightarrow 4H^+ + O_2$

Now, having created the electron hole pair, we if we we want to first of all again stabilize electron hole pair, we want to not have a recombination process, we also want to you know prevent the reverse reaction. So, as I said you know making the particle size smaller, reduces the chances of either of these electrons or holes encountering a defect in route and therefore, they don't recombined they sustainably reach the surface and enable the reaction.

But what do we mean by a sacrificial agent. So, for example, if you had glycerol, then what happens is after you have generated the electron and hole pair, the glycerol is what preferentially gets oxidized. So, glycerol gets preferentially oxidized generating all of these protons and generate CO_2 okay. So, oxygen is not sitting freely now.

Previously you had oxygen being generated and oxygen was available there that oxygen can re react with the hydrogen that you generated, and then essentially you know do the reverse reaction of what you had originally set out to do. Therefore, availability of free oxygen in the same location as hydrogen is not at all a preferred situation. In fact, it's a safety hazard you do not want to do that. So, by having another agent there will some kind of an alcohol you can create a situation where the holes that you generate will preferentially react with thus that alcohol oxidized alcohol generate CO_2 and the protons?

So, the same protons can additionally now go back here, in addition to the protons that are coming I mean. So, you get a lot of protons in the process and those protons can react with the electrons that are generated, and generate the H_2. So, in this case for example, if you have 14 hydrogen. So, you will have 14 protons here, and that will react with the 14 electrons and you will get 7 H_2. So, 14 protons and 14 electrons will react and get you your 7 H_2, and that way this is you know balanced with respect to the reaction that you see below here. So, that is how you can use and this agent that you are using this glycerol that you are using is what is being referred to as a sacrificial agent, and it is something that we do in an experimental setup we do it, but actually this opens up possibilities which are very interesting.

So, in the realm of photocatalysis people actually look at photocatalysis for multiple purposes. So, we have spoken about it from the perspective of hydrogen generation right. So, that is the perspective in which we have spoken about it. We can also look at photocatalysis as a means of cleaning impurities that may be present in water okay, and that process would be essentially similar to what I have just described, the process is exactly similar except that your impurity would be to take the place of this glycerol take the place mean. So, you have water with impurity and you put photocatalysts catalyst in it, and you expose it to sunlight.

When you do that you have this electron hole pair being generated, the electron goes ahead and creates your hydrogen which is what you see here. So, your hydrogen gets generated; the hole actually goes and oxidizes some species in the water present in the water that species could be the impurity that you are trying to get rid of. So, it cleans up the impurities destroys, the impurity and converts them to carbon dioxide etcetera and generates more protons for you to convert to hydrogen.

So, this is actually a nice way of combining two activities; you can do water purification you can also do hydrogen generation. And then the hydrogen generation the generated hydrogen you can use for running some you know activity that requires energy and when once that is completed, that hydrogen will again end up as water and so, you get back clean water right.

So, this is a nice combination of activities that can be done, if you look at the possibility that your water might contain some contaminant, which you are sort of you know doing a dual duty with this activity. So, this is one possibility. So, as you can see there are some challenges associated with the use of photo catalyst, and at least I have described you two two different ways in which you can handle those challenges. So, you can use this sacrificial agent, you can also do band gap tuning.

A band gap tuning can also be done in different ways which is something we have not actively looked at through this course, basically again if you take a semiconductor which has a small band gap and then you make nano sized particles out of it, it turns out that the the you know the physics of it is such that the band gap begins to increase right.

So, therefore, you are actually accomplishing two things, you are also getting the small particle size plus you are also getting a larger band gap of a say of a system. So, you can actually have as I have mentioned once before you can actually have a range of band gaps with the same starting material. So, therefore, you can have a range of band gaps which go through the entire visible spectrum.

So, you can have photo catalysts with a wide range of sizes present inside the of the same material, present inside water and then it will take care of taking the entire sunlight that comes in the spectrum of the sunlight that comes in and a vast majority of the spectrum will now get utilized for generating your hydrogen and oxygen. And then if you have some others you know you know sacrificial agent there that will take care of holding off the oxygen and so, you only get the hydrogen and some you know relatively stable species like carbon dioxide and so, that hydrogen you can then tap independently.

So, this is a set of things that we can do and a lot of possibilities are there, extensive research goes on photocatalyst and it is something that you can definitely look at in the literature.

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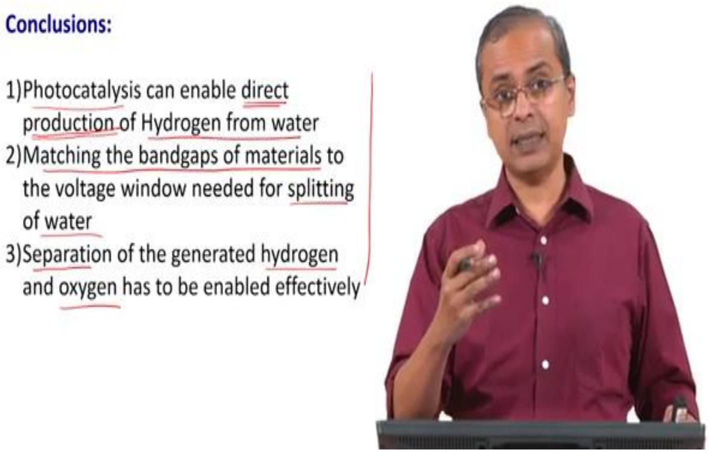

Conclusions:

1)Photocatalysis can enable direct production of Hydrogen from water
2)Matching the bandgaps of materials to the voltage window needed for splitting of water
3)Separation of the generated hydrogen and oxygen has to be enabled effectively

So, to conclude photocatalysis can enable direct production of hydrogen from water, and that is the important thing here. We started off by looking at electrolysis as a way of generating hydrogen and oxygen, and there are also some positives are there because hydrogen comes in a separate chamber oxygen comes in a separate chamber and therefore, it is convenient to handle, but I told you that that’ a two step process and therefore, there is inefficiency associated with it.

So, when you can do a direct process direct production, that is generally more preferred. So, this direct production of hydrogen from water is preferred and therefore, photocatalysis is a preferred route to utilize, and it is also kind of static. You know you just put the catalyst you put the water you show it in sunlight that’s all you have to do and then you have you know one tube, which is pulling off the hydrogen that’s really all that you have to do, you do not have to you know come and check for battery this is that what not once the water runs out you add more water it keeps on generating hydrogen. And by definition because it is a catalyst, the catalyst is not consumed in any way the catalyst stays there. It is only helping the reaction by enabling this electron hole pair generation by taking in the photon enabling the electron hole pair generation.

If you set it up correctly the catalyst will not react and only then it is considered as a catalyst, it will continue to be there. So, you can keep on sending in water you can keep on getting hydrogen and oxygen out. If you just set it set it up correctly and leave it in the sunlight. So, therefore, that’s a great positive you know all the time we are looking at ways of adding more energy to the system to get our job done here, you don’t have to do that you will get your job done.

We also discussed the fact that matching the band gap of the materials to the voltage window needed for splitting of water is important. We have to understand what is that band gap, we have to understand those band positions and you have to understand where is this water you know splitting voltage window that is present. And only when you understand those do you will you are be in a position to you know properly do this process and actually generate the hydrogen in an effective manner.

Otherwise you will think it’s supposed to happen, but it is not going to happen. So, there is some you know fair bit of you know knowledge that you have, to have to figure out which materials will work for this splitting, and that’s not simply based on band gap it is also required that you match the window correctly window of this of the band gap with the window for the water electrolysis process. And as I said one major challenge always remains about the separation of the generated hydrogen and oxygen and of course, if you want to use the oxygen itself, then it’s ideal to do it in such a way that you can tap the oxygen independently and tap the hydrogen independently.

So, that’s not easy process you have to think of some nice way of doing it. More likely that you if you can combine it with a process, where you are also doing some cleaning of some impurity in the water stream, then it works out much more conveniently because you are essentially doing two activities at the same time, and you are also not having this oxygen present there in as oxygen molecule which might then end up doing the reverse reaction.

So, this separation can be done in multiple ways is what the point we have to remember. So, these are our major conclusions for this class, and as I said this is a important research area, lot of people work in this research area for photocatalysis; because as I said this is also this is a lot of emphasis in there in this area for the hydrogen production part, but there is also a lot of emphasis in this area independent of hydrogen production, but focused on you know removal of impurities. So, for both those reasons this is a very important area of research.

And from the perspective of this course, from the perspective of all the discussion that we have done on solar energy, this is one additional way in which you can utilize the solar energy and with this discussion we will sort of conclude our series of lectures associated with the solar energy. How it is captured, how it is utilized, what are material aspects associated with it, what are scientific aspects associated with it and what are technological aspects associated with it. So, that’s with that we will wrap up our discussion the solar energy usage, we will look at additional technologies and different ways in which we can use renewable energy in the classes going forward.

Thank you.

KEYWORDS:

Solar Photo catalysis; Splitting Water; Electrochemical Cell; Oxidation; Reduction; Electrolyte; Solid Polymer Electrolyte; Electrolysis; Photochemical; Photoelectrochemical; Lining up band energies relative to the electrochemical series; Titanium Dioxide; Zinc Oxide; Silicon Carbide; Cadmium Sulfide; Ultraviolet; Infrared; Visible; Tuning Bandgap; Preventing Recombination; Limitations of Photocatalysis; Sacrificial Agent; Particle Size Reduction; Hydrogen Production; Water treatment

LECTURE:

The advantages of Hydrogen production and water splitting by Photocatalysis over electrolysis is discussed. Ways to tackle electron-hole recombination and some of the disadvantages of Photocatalysts are listed and discussed. Those methods include band tuning, particle size reduction and usage of sacrificial agent.