Nano structured Materials-Synthesis, Properties, Self Assembly and Applications

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Module - 4
Lecture - 30
Photocatalysis – II

Welcome back to this course on Nano structure Materials, Synthesis, Properties, Self Assembly and Applications. So, we are in the Module 4 and today is the second lecture of module 4 and it is also the second lecture on photo catalysis, so in the previous lecture we discussed the preliminaries and the basics of photo catalysis, that is you are catalyzing a reaction in the presence of light. And a catalyst is being used and a catalyst the definition of a catalyst is one, which is participating in a reaction and lowering the activation energy of the reaction and hence the ((Refer Time: 01:16)) is also regenerated at the end of the reaction.

Now, this is a definition for a general catalyst, a photo catalyst has these properties in the presence of light. So, it works in the presence of light and light can be of different frequencies and the frequencies of light, which are of interest is mainly in the visible and in the ultraviolet. Because that is the light or the, which we want to use from the solar radiation, and hence the region of the electromagnetic spectrum that is of interest in photo catalysis is the visible region and the ultraviolet region.

So, continuing our lecture on photo catalysis, today we will be discussing specially the photo catalysis or splitting of water in the presence of light, how materials can catalyze this splitting of water to give hydrogen and oxygen, which is the photo catalytic process in the presence of sunlight.

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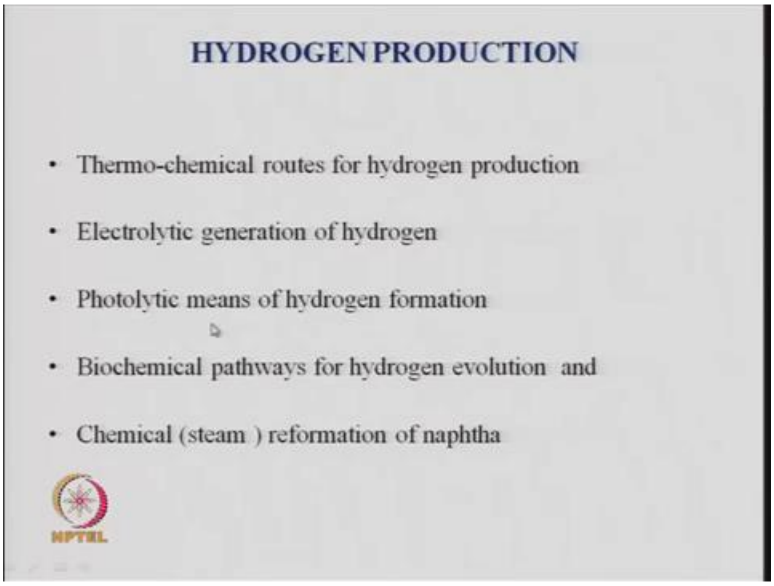

HYDROGEN PRODUCTION

- Thermo-chemical routes for hydrogen production
- Electrolytic generation of hydrogen
- Photolytic means of hydrogen formation
- Biochemical pathways for hydrogen evolution and
- Chemical (steam) reformation of naphtha

Now, as you know the fuel is a real problem for the future, you have a coal based fuel, you have natural gas, you have hydroelectricity from different sources, you can generate power. But, one of the future sources of power is considered to be hydrogen and people want to know how to produce hydrogen for different purposes, for local use and for use as a fuel for large industries, etcetera. So, among the various methods for hydrogen production, thermo chemical routes are there electrolytic routes are there, photolytic routes of hydrogen formation are there.

Then there are biochemical pathways and also chemical reformation of naphtha, which is obtained naturally. So, you can have several methods by which you can produce hydrogen, the process which we are interested in this part of our course is the electrolytic generation of hydrogen or the photolytic generation of hydrogen. So, this is a photo catalytic process, this is photo electro chemical process by which you can generate hydrogen.

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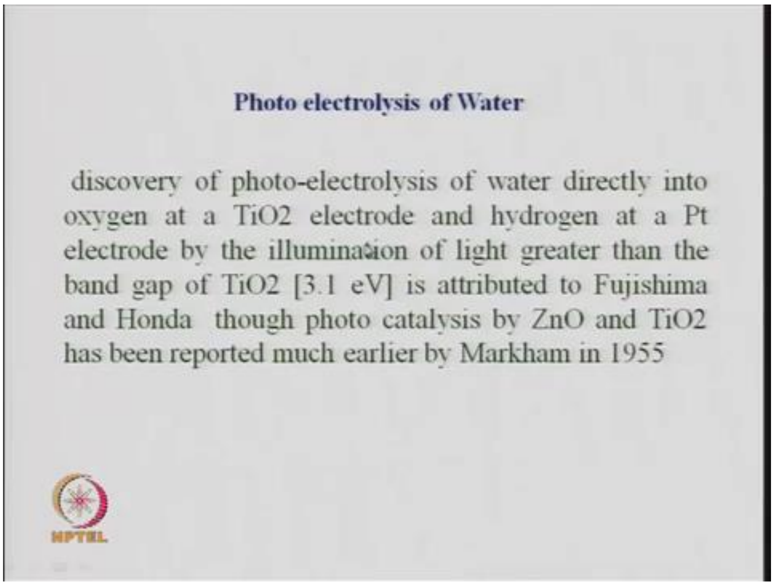

Photo electrolysis of Water

discovery of photo-electrolysis of water directly into oxygen at a TiO2 electrode and hydrogen at a Pt electrode by the illumination of light greater than the band gap of TiO2 [3.1 eV] is attributed to Fujishima and Honda though photo catalysis by ZnO and TiO2 has been reported much earlier by Markham in 1955

So, what is the photo electrolysis of water, now the discovery of photo electrolysis of water directly giving oxygen at a titanium dioxide electrode and hydrogen at a platinum electrode was of tremendous, interest and is a major breakthrough in science. And this was attributed to Fujishima and Honda and they showed this reaction, some time it is reported in the paper chemical reviews in 1972. And so it is a long time that people have been working on titanium dioxide as the material at the electrode, where oxygen is generated.

And you have another electrode, which is platinum where hydrogen is generated and these two electrodes are in aqueous medium. So, from water you are generating a oxygen and hydrogen, so this is basically water splitting and you are doing water splitting in a electro chemical cell. So, this is photo electro chemical splitting of water or we can call it photo electrolysis of water and Fujishima and Honda's work is a major breakthrough, using titanium dioxide as one of the photo catalyst.

And titanium dioxide has a band gap of around 3.1 electron volt and this semiconductor and as we will see that the semiconductor band gap for photo catalyst is very important for water splitting and what kind of band gaps are important that we will study in the near future. Just photo catalysis that is not splitting of water, but catalysis of certain reaction in the presence of light by titanium dioxide; however, has been reported much earlier than 1972 and it was reported 1955 by Markham.

So, photo catalysis was studied much earlier, although photo electrochemical synthesis of oxygen and hydrogen from water, which is water splitting reaction was first shown by Fujishima and Honda and is a remarkable breakthrough in science.

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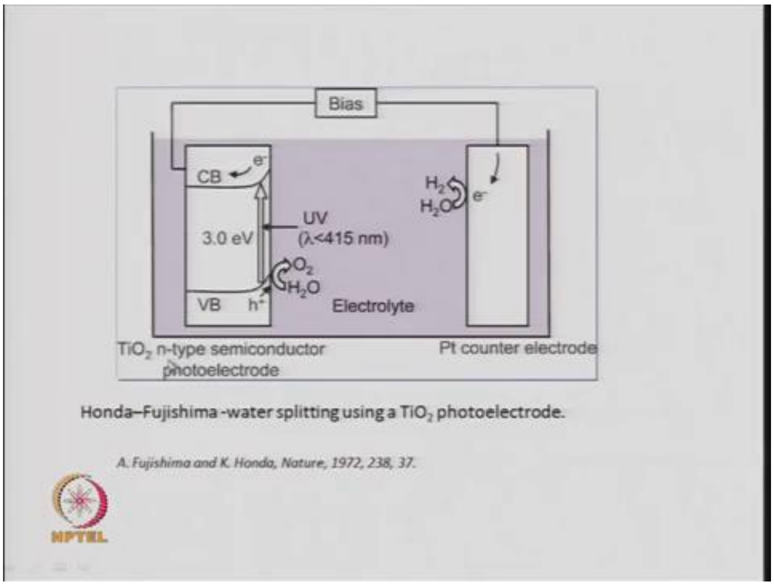

Honda–Fujishima -water splitting using a TiO_2 photoelectrode.

A. Fujishima and K. Honda, Nature, 1972, 238, 37.

So, the electrode of Fujishima and Honda, so this is the work that I was referring to it is published in nature in 1972 and you have this electro chemical cell. So, what is there in an electro chemical cell, you normally have 2 electrodes, so here also you have 2 electrodes, you have this cathode where you have this electrons, which are going to the external circuit. And this cathode is of a material, which is a titanium dioxide with the band gap of around 3, 3.1 electron volts.

So, this is the valence band of titanium dioxide, this is the conduction band of titanium dioxide and this is an n type semiconductor. And this is the photo electrode, what you mean by a photo electrode is when you want to do electrochemical reaction in the presence of light, then you have electrodes on which light has to shine. So that electrode that particular electrode, where out of the two electrodes you have one electrode where you shine light and that is called the photo electrode.

So, the photo electrode here is titanium dioxide is a n type semiconductor material and as shown this is the band gap and the other electrode is the platinum electrode. So, in this electrode when you shine light, which is the light should have a wavelength less than 415 nanometers. Because, than only it will have energy more than 3, 3.1 electron volts and if this light has energy more than the band gap, then only it can produce electros and holes.

That means, electron can be transferred from the valence band to the conduction band only when this light has energy, which is more than the band gap, which is around 3, 3.1 electron volts. And for that the light has to have a wavelength, which is lambda less than 415 nanometers, so that is in the ultra violate radiation it is in the U V region of the electromagnetic spectrum. And so when this light falls on this electrode, which is having titanium dioxide, electrons are produced in the conduction band and holes remain because, whenever electron goes away you generate a hole in that band.

So, an electron comes here and a hole is generated here, together this electron and hole is called an exciton. And then this electron than is goes out of into the external circuit and you generate this hole, which is generated reacts with the water or the aqueous solution, which is the electrolyte. And the reaction of this hole with this water will generate oxygen, so at this electrode, which is the cathode oxygen is generated, oxygen gas comes out and electrons are pushed in the external circuit on the anode, which is the platinum counter electrode, electrons come here.

And these electrons act on water, which is the aqueous solution and then hydrogen is generated. So, you are oxidizing here, you are reducing here the material and this hole is oxidizing water to oxygen and here you are reducing the protons from the aqueous solution into hydrogen. So, the hydrogen is generated in the anode and the oxygen is generated in the cathode, so basically from one water molecule plus one water molecule. So, two water molecules are getting used in this reaction and one mole of oxygen and one mole of hydrogen is being produced.

So, the overall reaction you have two moles of water giving you one mole of hydrogen and one mole of oxygen. So, this way you have to balance this equation of course, when you write 2 H 2 O giving you H 2 plus O 2, so you have to balance that equation and you will have two moles of H 2 in this process. Now, if you, so this is a typical electro chemical cell, which was used by Fujishima and Honda to show that titanium dioxide is an semiconductor, which can act as a photo catalyst and can split water and this semiconductor is used as a photo electrode. Normally, the semiconductor is coated on another metal, which acts as a foil behind it to give it is mechanical strength and conductivity. But, the actual reaction of light is with the semiconductor to generate the electrons and the holes, so that is the photocathode.

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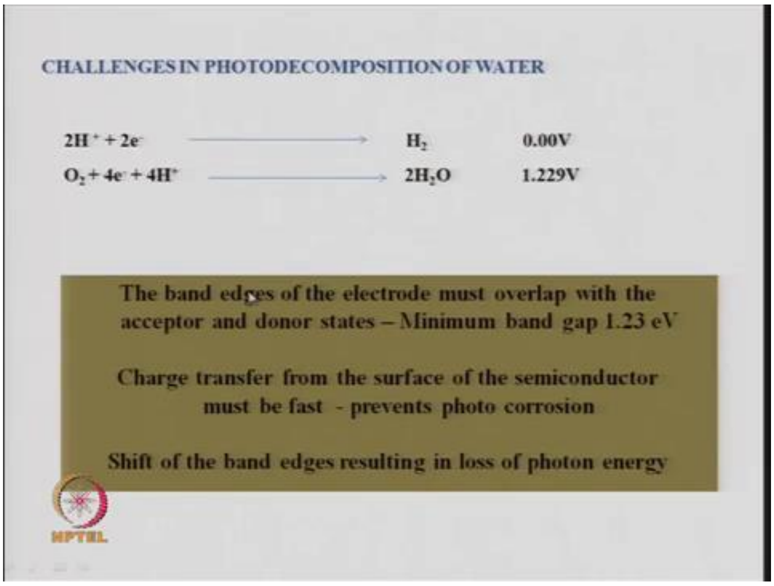

CHALLENGES IN PHOTODECOMPOSITION OF WATER

$2H^+ + 2e^- \longrightarrow H_2$ 0.00V

$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O$ 1.229V

The band edges of the electrode must overlap with the acceptor and donor states – Minimum band gap 1.23 eV

Charge transfer from the surface of the semiconductor must be fast - prevents photo corrosion

Shift of the band edges resulting in loss of photon energy

Now, what is the challenges in this decomposition of water, so as I said that the protons H plus ions react and at the anode with the electrons, which are coming from the external circuit and produce hydrogen at the anode. And on the other electrode you have got oxygen and this oxygen plus will take 4 electrons plus protons to give water, so in the other electrode actually it is this reaction, the reverse reaction H 2 O giving you oxygen the reverse way and the difference of the potential required for this because, this is a standard hydrogen potential.

So, that is at kept at 0 volts and this is the potential you require for this reaction, since you want the reverse reaction, so this will be negative. But, anyway the energy difference that you require is around 1.23 volts, so the minimum band gap because, so much energy is required for sum of these two reactions requires 1.23 volts. Hence, the band gap should be of the semiconductor, should be at least 1.23 electron volts, so ((Refer Time: 13:15)) as T i O 2 has a band gap of around 3 electron volts.

So, that takes care of the 1.23 electron volts, which is minimum for water splitting, so this 1.23 electron volt which you get by subtracting this from this. You subtract the cathode minus anode and this is you will get the difference is 1.23 electron volt, and this the minimum energy and this minimum energy means, when you have a photo generated electrons and holes that is when light shines on the photo cathode, electrons and holes will be generated, then the band gap between them should be at least 1.23 electron volts.

The other point is, so this is the first key point that the band gap should be minimum 1.23 electron volt for water splitting, the second point is the charge must transfer from the surface of the semiconductor very quickly. So, the charge means you have got electrons and holes in the semiconductor and this electron and hole are required at separate parts of the material for reaction and they must not recombine; otherwise you do not use the electron and the hole. So, charge transfer must be fast to prevent what is called photo corrosion, an shift of the band edges result in loss of photon energy, so the band edge shifting a can lead to loss in photon energy.

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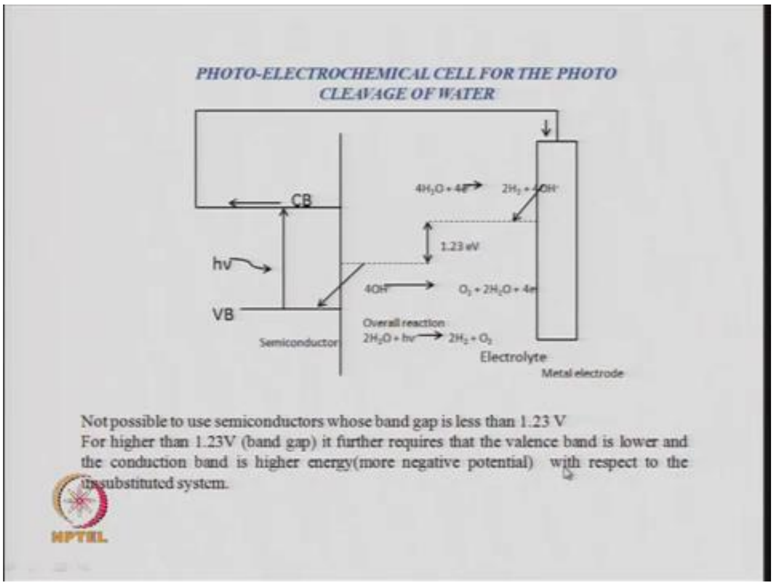

PHOTO-ELECTROCHEMICAL CELL FOR THE PHOTO CLEAVAGE OF WATER

Not possible to use semiconductors whose band gap is less than 1.23 V
For higher than 1.23V (band gap) it further requires that the valence band is lower and the conduction band is higher energy(more negative potential) with respect to the unsubstituted system.

So, these are some of the points which are important for the photo electrochemical splitting of water, this is the same reaction shown in a different way. Where this is a semiconductor and you shine light, this is a valence band, this is a conduction band and this is the other electrode, which is normally the metal electrode, is the semiconductor like, titanium dioxide or any semiconductor, which has got appropriate band gap; that means, more than 1.23 electron volt.

And also the band edges that is the conduction band edge and the valence band edge should be in such a manner that electron can be transferred to the conduction band of the H 2 the water and H plus couple. So, this for this reaction the upper band or the conduction band is here and the valence band can be thought of as here and so the difference is what we discussed earlier 1.23 electron volt. Now, this conduction band of the semiconductor is higher than the conduction band of the water couple.

And, so electrons can be transferred here and the holes have are the valence band, where the holes are present in the semiconductor are lower than the band edge of the valence band of the water hydrogen couple and hence holes can be transferred here. So, we say that electrons can be transferred from the conduction band of T i O 2 to the conduction band of the hydrogen and holes can be transferred in this way. And so the overall reaction written here in aqueous medium is basically 2 water molecule give you 2 moles of hydrogen and oxygen.

So, this is the water splitting reaction in the presence of light and as we said it is not possible to use semiconductors, whose band gap is less than 1.23 electron volt. For higher than 1.23 electron volt all semiconductors which have higher than 1.23 volts there are additional points which one must consider. And that additional point is that the valence band is lower, than the valence band of the couple and the conduction band of the semiconductor is much higher than, which means more negative potential as you are going up you are more negative potential and it should be much more negative potential, than the conduction band of the couple which is the un substituted system.

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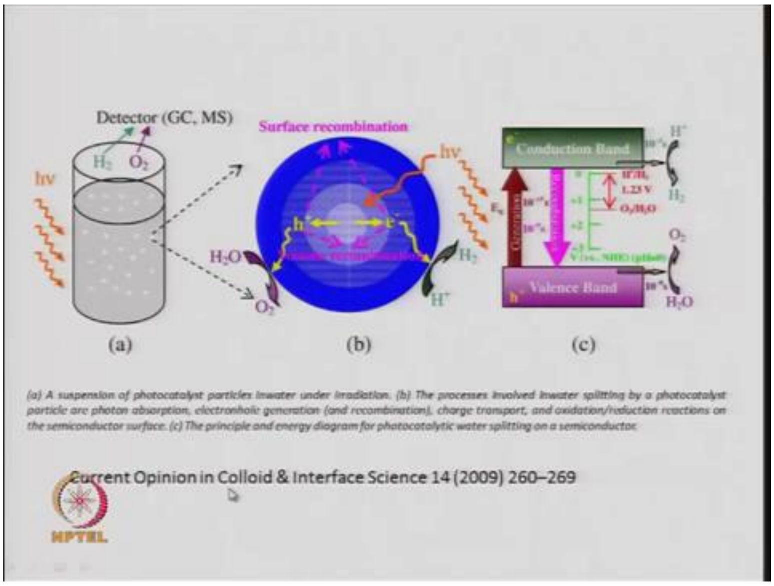

(a) A suspension of photocatalyst particles inwater under irradiation. (b) The processes involved inwater splitting by a photocatalyst particle are photon absorption, electronhole generation (and recombination), charge transport, and oxidation/reduction reactions on the semiconductor surface. (c) The principle and energy diagram for photocatalytic water splitting on a semiconductor.

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Now, how to understand this process or how to do an experiment to find out hydrogen and oxygen are being generated. So, you can use a the catalyst which is titania and you irradiate with light, so you shine light of a particular frequency, which is a h nu and h nu is can be in the region of a the ultra violet or the visible. And hydrogen and oxygen are detected through a gas chromatograph or through mass spectrometry and this is the process what is happening, which discussed that electrons and holes are produced when light falls on the semiconductor particle.

And the electron moves towards a direction, where it can reduce the protons to hydrogen and the holes have to migrate to the surface, where it can oxidize H 2 O 2 oxygen. So, the electrons produce the hydrogen and the holes produce the oxygen and this is the water splitting reaction. And this band diagram we already discussed, where the valence band is here and the conduction band is here and the H plus H 2 and O 2 H 2 a couple is shown here, as 1.23 electron volt.

And, so you need higher energy than that and this is on a scale taken with normal hydrogen electrode. And all the holes will be in the valence band, which then react with water to give you oxygen and all the electrons can be pushed to the conduction band and they react with H plus 2 give hydrogen. And the rate at which electrons can react, you know this migration is around 10 minus 3 seconds, so it is in milliseconds where as holes it takes much small time that is 10 to the power minus 8 seconds. So, there is a difference in the electron and hole transport and these points are important while planning or designing new photo catalytic systems.

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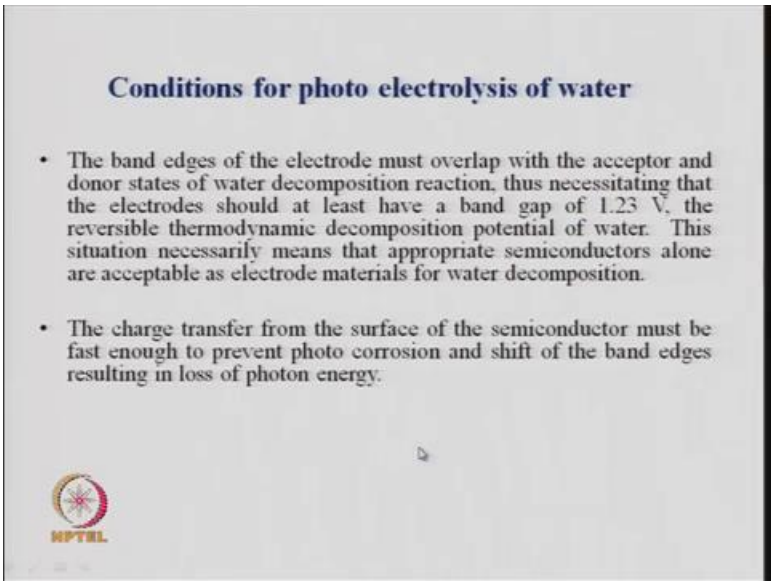

Conditions for photo electrolysis of water

- The band edges of the electrode must overlap with the acceptor and donor states of water decomposition reaction, thus necessitating that the electrodes should at least have a band gap of 1.23 V, the reversible thermodynamic decomposition potential of water. This situation necessarily means that appropriate semiconductors alone are acceptable as electrode materials for water decomposition.
- The charge transfer from the surface of the semiconductor must be fast enough to prevent photo corrosion and shift of the band edges resulting in loss of photon energy.

Now, the conditions for photo electro catalysis or photo electrolysis are that the bandages of the electrode must overlap with the accepted and donor states of water the composition reaction, which we already discussed. And thus the electrode should have at least a band gap of 1.23 volt, which is the reversible thermodynamic decomposition potential of water, this also we discussed earlier. And hence all semiconductors need not be able to split water, unless they have this condition.

The other important condition is the charge transfer from the surface of the semiconductor must be very fast to prevent recombination of the electrons and holes and to prevent photo corrosion. So, photo corrosion will lead to shift of the band edges and result in loss of photon energy, so these are some of the conditions for having efficient splitting of water through photo electrochemical process.

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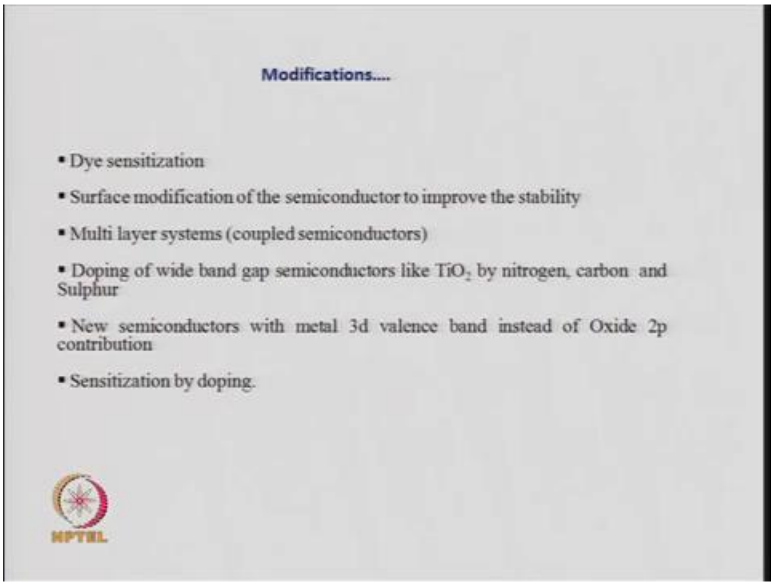

Modifications....

- Dye sensitization
- Surface modification of the semiconductor to improve the stability
- Multi layer systems (coupled semiconductors)
- Doping of wide band gap semiconductors like TiO_2 by nitrogen, carbon and Sulphur
- New semiconductors with metal 3d valence band instead of Oxide 2p contribution
- Sensitization by doping.

Now, what one can do is to get better and better photo catalyst is to modify for example, the surface or use sensitizers, you can do several things. So, what these modifications one can do to improve the efficiency of the photo catalyst, so one of the methods is dye sensitization. So, dye can be normally organic dye, so these are organic molecules, which can help in electron transfer, so that is used in certain cases, where you can sensitize a semiconductor using dye, which is basically an organic molecule.

Then you can do surface modification of the semiconductor to improve it is stability, you can combine two semiconductors. So, the for multi layered systems, then you can dope wide band gap semiconductors like T i O 2 by nitrogen, carbon and sulphur, so you will have states within the band gaps. And those states can then act as, which can be at lower level, than the conduction band of the semiconductor and can be useful in transfer of electrons.

So, doping it can also help in the holes presence of holes, so depending of what kind of dopant, you use you can change the nature of the electron hole stability in wide band gap semiconductors by doping with atoms like nitrogen, carbon and sulphur. Now, several semiconductors with metal 3 d valence band can be used, instead of oxygen 2 p contribution, you can use sulphur for example, So, you will have a sulfide band which is overlapping with the metal band, so there can be other than metal oxides as semiconductors.

And of course, depends whether you want they should have band gap more than 1.23 normally the band gap will decrease when you change an oxide to a sulfide, you can also sensitize the photo catalyst by doping. So, several modifications one can do and some of these lead to enhancement of very high enhancement in the photo catalytic efficiency of splitting of water.

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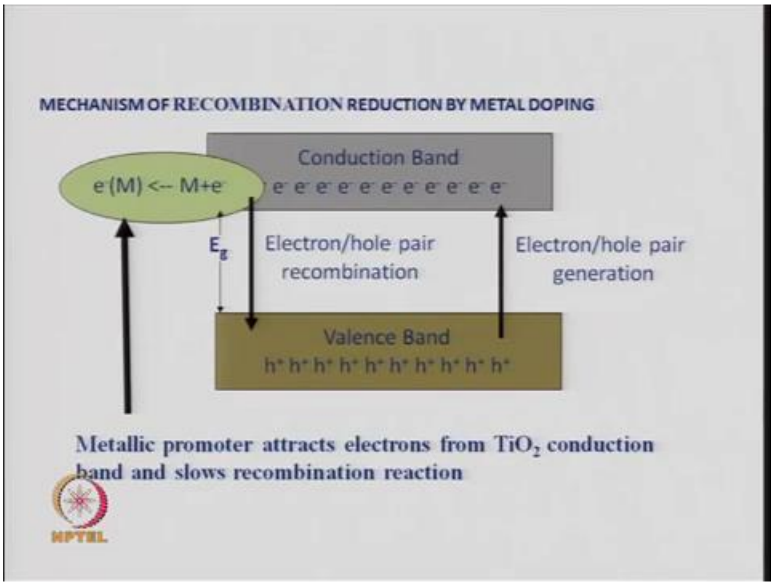

MECHANISM OF RECOMBINATION REDUCTION BY METAL DOPING

Metallic promoter attracts electrons from TiO_2 conduction band and slows recombination reaction

So, the mechanism of the recombination reduction by metal doping, so you are trying to dope metals. So, what happens, the metallic promoter attracts electrons from T i O 2 conduction band, so now, in typical experiment you generate electrons in the conduction band and holes in the valence band, when you shine light. So, you have electron hole pair generation, and these electron hole pairs are called excitons and the opposite process of electron combining with holes is the electron hole pair recombination.

And this process is avoidable, this is not good for the photo catalyst, so you want to avoid this electron hole pair recombination. Now, when you have a metal as a promoter; that means, if you add dope metals, these metal a bands can attract electrons from the titanium dioxide conduction band. So, these electrons can be taken up by the metal and the metal can maintain these electron, so we are removing these electrons from the site, where from it can recombine with the holes. And that this process of recombination can be slowed down when you dope metals because, the metal are acting as electron traps.

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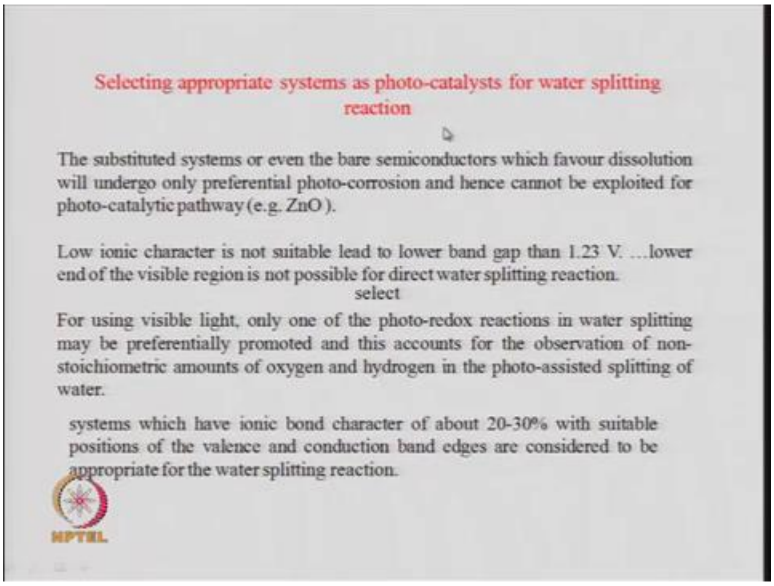

Selecting appropriate systems as photo-catalysts for water splitting reaction

The substituted systems or even the bare semiconductors which favour dissolution will undergo only preferential photo-corrosion and hence cannot be exploited for photo-catalytic pathway (e.g. ZnO).

Low ionic character is not suitable lead to lower band gap than 1.23 V. …lower end of the visible region is not possible for direct water splitting reaction.

select

For using visible light, only one of the photo-redox reactions in water splitting may be preferentially promoted and this accounts for the observation of non-stoichiometric amounts of oxygen and hydrogen in the photo-assisted splitting of water.

systems which have ionic bond character of about 20-30% with suitable positions of the valence and conduction band edges are considered to be appropriate for the water splitting reaction.

So, selecting appropriate systems as photo catalyst for water splitting reaction, how do you go about that, you can chose substituted systems like, as we just showed metal doped systems or even bare semiconductors, which favor dissolution they may undergo preferential photo corrosion. And hence cannot be exploited for photo catalytic pathway now if, so what we said is that, if you can add metals ((Refer Time: 26:45)) which can take up electrons, then the recombination process can be slowed down.

And this is helping the cause of photo electro chemical splitting of water; however if you have systems, which favour dissolution. Then only preferential photo corrosion will occur and cannot be exploited for the photo chemical splitting of water and this is an example of zinc oxide, where it cannot been used as for photo electro chemical splitting of water due to it is preferential photo corrosion. Now, low ionic character we discussed about ionic character of bonds in the previous lecture, where suppose you have a metal oxide, then the metal oxygen bond can be ionic or covalent or partially ionic.

And if it is partially ionic what is the polarity of the bond can be calculated from the difference of the electro negativity of the metal and oxygen. So, ionic character can be calculated and higher the ionic character, the higher is the band gap and if low ionic character is there, then the band gap will be very low and then you will not be able to use that for splitting of water because, lower than 1.23 volts will now allow you to split water.

So, hence if you want to use more than 1.23 volts, than the lower end of the visible region is not possible. So, you will have to use the higher end of the visible region, towards the ultra violet to have materials which have higher band gap than 1.23 volts. So, low ionic character which will give you low band gaps, than 1.23 volts will not be suitable for direct water splitting reaction, now if you want to use visible light then only one of the photo redox reactions in water splitting may be preferential promoted.

That means, either the reaction at the cathode or the reaction at the anode, may be promoted depending on where is your conduction band edge and where is your valence band edge. But, what you need for typical photo chemical splitting of water is both the reaction should be promoted, the reaction at the cathode, which is generation of oxygen and the reaction at the anode, which is generation of hydrogen both have to be equivalently efficient, then only you will have a good photo chemical splitting of water.

So, many catalyst may not do both of them and then it can only be used to do one part of the reaction. And that is what is mentioned here, that sometimes using visible light when you do not have energy more than 1.23 volts, you can still do some photo reaction photo catalytic reaction. But, here you may not have equivalent amount of oxygen and hydrogen a because, one of the processes is preferred more, so you may have a more of oxygen and much less of hydrogen being produced or much more hydrogen and much less oxygen.

So, it is not typical a photochemical splitting of water, now systems which have ionic bond character of around 20 to 30 percent with appropriate or the right kind of position of the violence bandage and the conduction bandage, it should be appropriate placed with respect to the levels which are of for the water and oxygen couple. And so if you have around 20 to 30 percent bond character, then it is possible to have water splitting reaction, when appropriately the conduction and the violence bandages are placed with you are a water, oxygen and water hydrogen couples.

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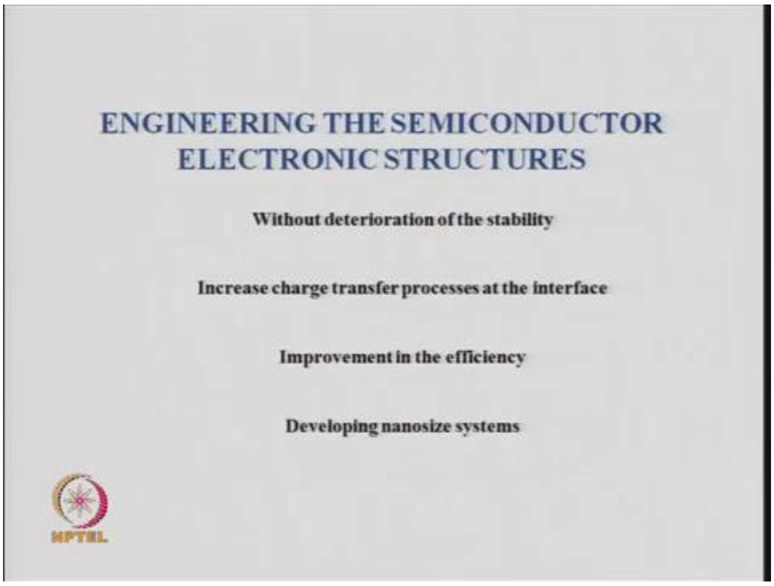

ENGINEERING THE SEMICONDUCTOR ELECTRONIC STRUCTURES

Without deterioration of the stability

Increase charge transfer processes at the interface

Improvement in the efficiency

Developing nanosize systems

Now, how do you engineer the semiconductor electronic structure, so you are using semiconductors as the photo catalyst. Now, how do you engineer them you have to take into an account certain points a like, one of the point of stability because, you want photo catalyst to be used and reused several cycles, several times. So, it should work without deterioration of the stability, so that is one of the important points, then how to increase charge transfer processes at the interface.

Let us at the interface where the semiconductor is meeting your junction, which is water how to improve the efficiency of this photo generation or charge transfer across the photo catalyst and developing nano size systems. So, how to develop nano structured material, which may help the efficiency of the photochemical splitting of water.

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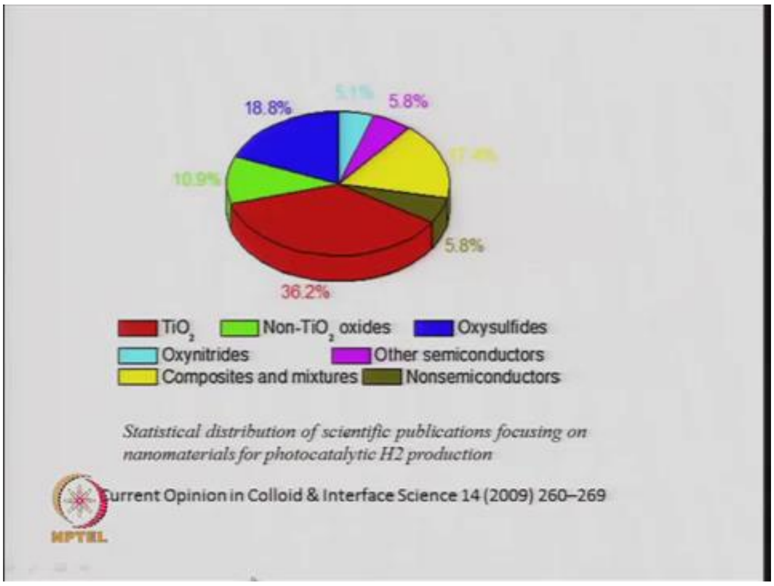

Statistical distribution of scientific publications focusing on nanomaterials for photocatalytic H2 production

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So, if you look at this pie chart, it shows different kinds of materials and on which work is being carried out and investigations have been carried out and people are studying them for photo catalytic hydrogen production. So, the amount of work that people are doing based on titanium dioxide is immense, so the whole world is working on titanium dioxide, large amount actually nearly 36 percent of the world on photo catalysis is based only on one material one only on one semiconductor and that is titanium dioxide and that is the brown colored part and that is 36.2 percent.

Whereas, other materials have also been used as a photo catalyst other semiconductors like oxysulfides, which is around 19 percent oxynitrides much less 5 percent then non titania based oxides. So, there can be other oxides, which have been use for a as a photo catalyst, a tantalum pentoxide, niobium pentoxide, many other materials and they have a share of around 11 percent. So, people have used a non semiconductors also like insulators or metals, but the amount of literature on that is much less.

So, from this pie chart one thing is clear that one compound, which is titanium dioxide is having more a importance nearly more than one third of the work done among all 100's and 1000's of compound which have been tried go be seen as a photo catalyst for splitting of water. So, titanium dioxide holds a great promise in the market and it is for two reasons because, it has a reasonable good efficiency is easily available and is also economical and nontoxic. So, for all those reasons titanium dioxide is a very important material for photo chemical splitting of water.

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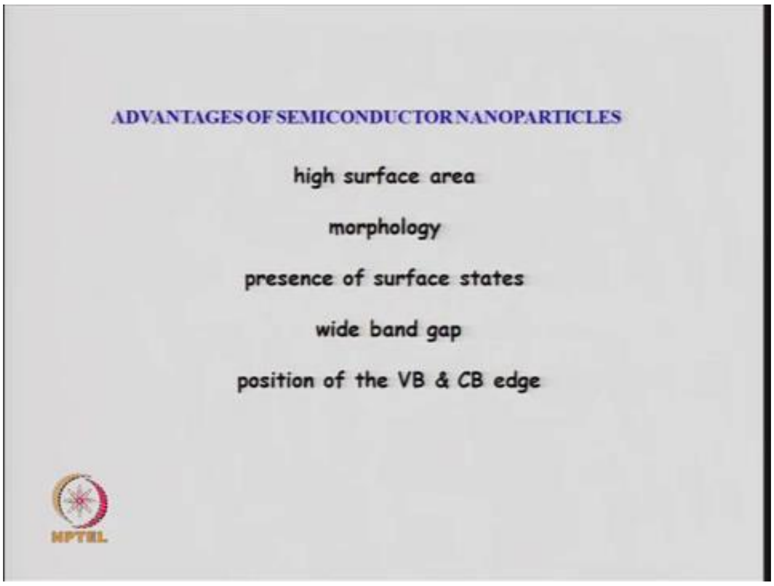

ADVANTAGES OF SEMICONDUCTOR NANOPARTICLES

high surface area

morphology

presence of surface states

wide band gap

position of the VB & CB edge

Now, the advantages of semiconductor nano particle; that means if you use nano particle instead of bulk particles. So, what is a difference we are going to use a simple semiconductor, but now you want to use a semiconductor whose particles size or grain size is much smaller than bulk semiconductors. So, the particle size is can be 30, 40, 50 nanometers and so what is the advantage that you gain in the photo catalysis splitting of water, using these semiconductors nano particles.

One you will have high surface area and for any catalytic reaction surface area is very important because, the more the larger the surface area you have more catalytic sites and so the reaction is much faster. Second is the morphology in nano structures you can tune the morphology, you can makes spears, you can make wires, you can make plates and so the morphology will affect the efficiency of the photo catalysis of water.

So, if it has high surface area; obviously you will have lot of surface states and this will give rise to efficiency of this photo catalyst. Then you can have wide band gap semiconductors, because as you know when you change the size of a particles from a bulk particle if you make it into an nano particle, then the band gap increases and the band gap is increasing means you are making something a wide band. So, from a narrow band you are changing it to a wide band, when you are making the size of the particles small.

The same semiconductor can have different band gaps depending on the size of the particles, say if you have a one micron size particle or if you have 40, 50 nanometers size particle of T i O 2 they will have different band gaps. And the band gap is larger for the smaller particle, so you can make wide band gap of a small a narrow band gap materials. Then the position of the valence band and the conduction band edges will also change as you change the size of the particles, so because of all of these properties it is advantages to use semiconductors nano particles for photochemical water splitting reactions.

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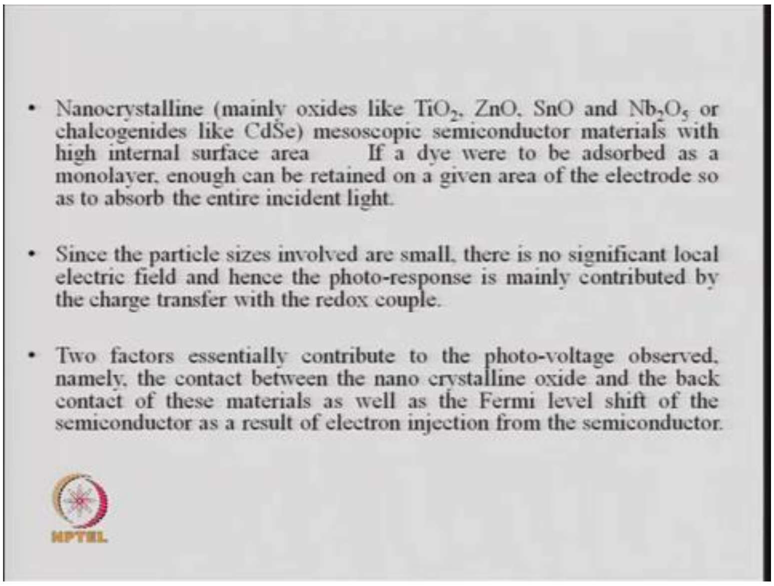

- Nanocrystalline (mainly oxides like TiO_2, ZnO, SnO and Nb_2O_5 or chalcogenides like CdSe) mesoscopic semiconductor materials with high internal surface area If a dye were to be adsorbed as a monolayer, enough can be retained on a given area of the electrode so as to absorb the entire incident light.
- Since the particle sizes involved are small, there is no significant local electric field and hence the photo-response is mainly contributed by the charge transfer with the redox couple.
- Two factors essentially contribute to the photo-voltage observed, namely, the contact between the nano crystalline oxide and the back contact of these materials as well as the Fermi level shift of the semiconductor as a result of electron injection from the semiconductor.

So, nano crystalline materials are typically titanium dioxide we discussed a lot other materials, which are very popular are zinc oxide, tin dioxide it should be S n O 2 and niobium pentoxide or chalcogenides like, cadmium selenides, etcetera with high internal surface area can be used with a dye. So, if you absorbed a dye is a organic compound as a monolayer, then the entire lot can be retained on a given area of the electrode, so as to absorb the entire incident light.

So, if you have nano crystalline material, then the dye will can be absorbed in a such a way that you can absorb the entire incident light. Also, since the particle size is small there is no significant local electric field due to the particle and hence the photo response; that means, the response of the material when you apply the a light. So, when photons fall on that material, the response will be mainly due to charge transfer with the redox couple and there will be no effect of the particles own or local electric field because the size of the particle is very small.

So, the photo response will then mainly be contributed by the charge transfer with the redox couple. A two essential factors which contribute to the voltage developed, because when you shine light on a semiconductor you will have a voltage, which is develop and there are two important factors, one is that the contact between the nano crystalline oxide and the back contact. That is you have to attach a wire to a connect the voltage that is though which the current will flow.

So, this contact it is called the back contact, which is having an interface with your semiconductor. So, this back an contact of the material as well as the Fermi level shift of the semiconductor as a result of electron injection, so when you have electrons from the semiconductor, which will go into the contact to a participate in the electro external circuit. Then there is a Fermi level shift and these two factors are important, how this shift in the Fermi level of the semiconductor affects the overall photo chemical efficiency that is one important thing. The other thing is the a interface between the back contact and the nano crystalline material, which is may be an oxide or a sulfide that also is very important.

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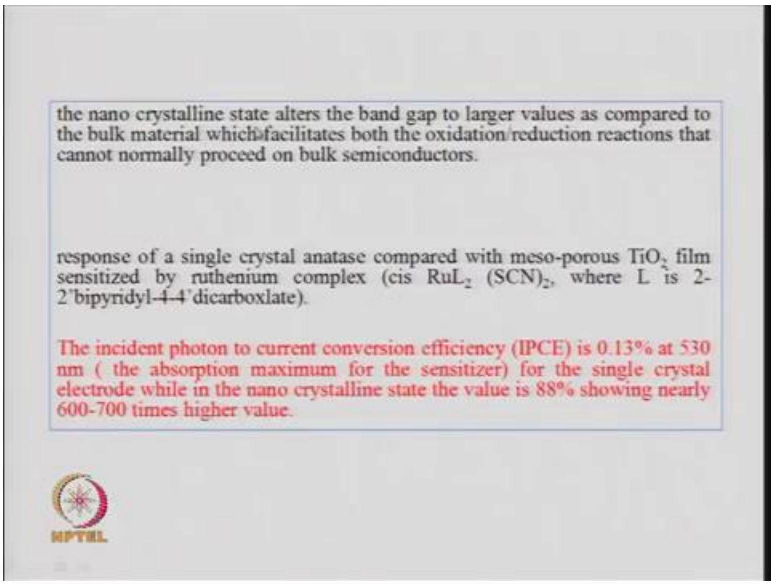

the nano crystalline state alters the band gap to larger values as compared to the bulk material which facilitates both the oxidation/reduction reactions that cannot normally proceed on bulk semiconductors.

response of a single crystal anatase compared with meso-porous TiO_2 film sensitized by ruthenium complex (cis RuL_2 $(SCN)_2$, where L is 2-2'bipyridyl-4-4'dicarboxlate).

The incident photon to current conversion efficiency (IPCE) is 0.13% at 530 nm (the absorption maximum for the sensitizer) for the single crystal electrode while in the nano crystalline state the value is 88% showing nearly 600-700 times higher value.

The as we said nano crystalline state will increase your band gap, so increase at the band gap compared to the bulk material. And this increase in band gap will facilitate both oxidation and reduction reactions, which may not be possible on bulk semiconductors. Say, if you have semiconductors which have micron sized particles, those are called bulk semiconductors and so when you have that bulk semiconductor will have some band gap and when you are making the nano particles of that bulk semiconductor, then it will have much larger band gap.

And which may promote the oxidation reduction reactions it may be because, the bulk band gap was much small. And now it the band gap which has increased is a appropriate for doing such oxidation reduction reactions, now if you a look into a particular example of say single crystal anatase, anatase is one of the forms of titanium dioxide. And this is the form which is used a lot for photo catalysis and if you look at the response of the a single crystal, so take one single crystal not a polycrystalline material.

And then compare it with a film of titanium dioxide, so one is a single crystal, the other is a porous a T i O 2 film. And it is sensitized by a dye, now this dye is a organo metallic compound it has a metal, which is a ruthenium and with some legends and there are two legends which is a bipyridyl a dicarboxlate ligand and there are two thiocyanate legends. So, this thiocyanate is a monodentate ligand and this bipyridyl is a bidentat legend. So, ruthenium is L 2 SCN 2 is like an octahedral molecule and it behaves like a dye and this is a common dye which is used.

Now, when you use this dye with the crystal single crystal or you use this dye with a meso porous film and calculate or measure the current conversion efficiency. So, there is a term which is called a IPCE, which is the incident photon to current conversion efficiency IPCE. And this value should be high, now this value is 0.13 percent at a particular wavelength, which is 530 nanometers, which is the wavelength which this dye absorbs, so the this dye is actually like a sensitizer.

So, the single crystal anatase and the meso porous T i O 2 film is doped with this dye, this ruthenium complex. This dye absorbs this radiation at 530 nanometers and a helps in the oxidation reduction reactions of the semiconductor using the semiconductor. So, without when you do not have a single crystal, when you have the meso porous film, which has very large surface area then the IPCE that is the efficiency photon light to current transfer efficiency increases drastically 0.13 was the efficiency of the single crystal and it became 88 percent when you take the meso porous film.

So, that is an increase of nearly 600 to 700 times and what has been changed, the only thing have changed is instead of using a single crystal, you are now using a meso porous titania film. The dye is the same, the incident light is the same, it is 530 nanometers, but the efficiency has increased to 88 percent from 0.13 percent, so this dramatic increase in the efficiency can be connected to the surface area of the meso porous titania film.

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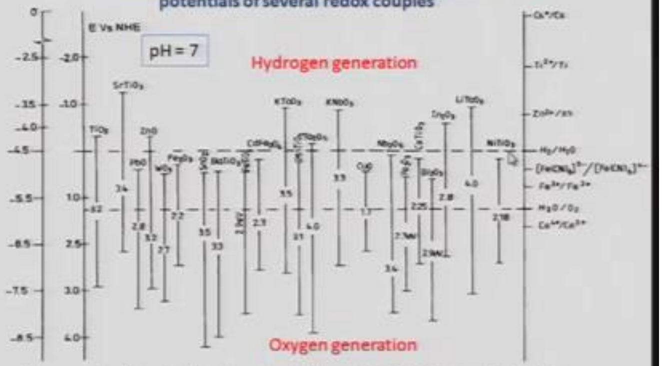
Positions of bands of semiconductors relative to the standard potentials of several redox couples



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Now, based on these energy levels which is the position of the band of different kind of semiconductors, a you can find out which semiconductor will be useful for hydrogen generation and a which semiconductor will be useful for oxygen generation. Now, this is the scale is given with respect to normal hydrogen electrode and with normal hydrogen electrode. You see that if you have a band edge, which is higher than the band edge of the other material, then it says that this will be better for hydrogen generation, but will be poorer for oxygen generation because, the valence band is higher than this.

So, if the valence band is lower that would help in oxygen generation, if the conduction band is higher it would help in hydrogen generation. So, this is given in the scale such that the water oxygen energy level is shown here and all these semiconductors these are oxides, you can find out from this plot, which one you will use to choose a material for semiconductor catalyst for hydrogen generation or for oxygen generation.

And, so as I said the lower the conduction band better it is for a oxygen generation catalyst, higher the lower the valence band better is the oxygen generation, higher the conduction band better is the hydrogen generation. And these are with respect to all these standard couples, which are values known in the literature and this is the scale with respect to the normal hydrogen electrode, so this is a very useful guide when you want to choose a photo catalyst.

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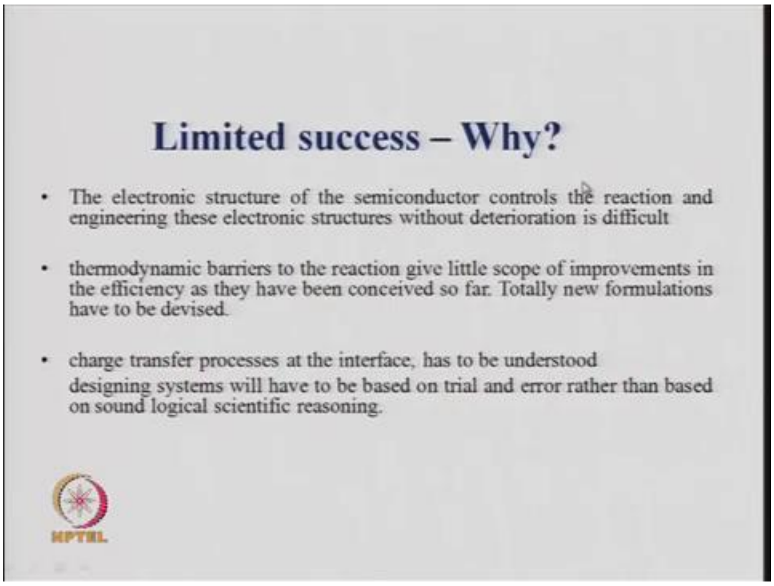

Limited success – Why?

- The electronic structure of the semiconductor controls the reaction and engineering these electronic structures without deterioration is difficult
- thermodynamic barriers to the reaction give little scope of improvements in the efficiency as they have been conceived so far. Totally new formulations have to be devised.
- charge transfer processes at the interface, has to be understood
  designing systems will have to be based on trial and error rather than based on sound logical scientific reasoning.

Now, the subject of water splitting or photo electrochemical splitting of water, which is one of the greatest challenges a man has. Because, if you are able to split water a we have immense source of water on earth even on other planets, then it will be very easy for us to generate hydrogen and oxygen. And if it is very easy to generate hydrogen and oxygen we will have vast source of hydrogen, vast source of hydrogen means, vast source of energy because, hydrogen can be used as a fuel.

So, tremendous amount of research and development is being tried in water splitting reactions, but we have had limited success, so far a globally in trying to get efficient water splitting reactions and why is that. So, one of the reason is that, the electronic structure of the semiconductor controls the reaction and to modify the electronic structure without spoiling the semiconductor, without deterioration of the semiconductor is difficult.

So, to improve the efficiency, you want to modify the electronic structure of the semiconductor, but while doing that you destroy it is stability or some other parameter. That is one of the reasons, then there are thermo dynamic barriers to the reaction, like you have to have 1.23 volts to have water splitting, that gives little scope of improvement because, most of the materials which can give you, which have band gap of 1.23 volts I have more or less been tried.

So, totally new formulation have to be devised, all the known binaries etcetera people have tried. So, you have to find very new complex metal oxides may be or complex metal chalcogenides, which have band gap more than 1.23 volts, but have not been experimentally tried or whose valence edge and conduction band edges have not yet been properly estimated they can be tried. So, you have to think totally in a new way and totally new compounds and formulations have to be devised.

The third point why we have limited success is the charge transfer processes at the interfaced has to be understood. Because, if you want to design systems based on logic, then you have to understand the interface; otherwise most of the time you will be doing trial and error and trial and error always takes long time. And charge transfer process has to be understood very well because, that is what will prevent recombination of the electrons and holes. And to improve the efficiency, you have to stop the recombination of the electrons and holes, so understanding the interface is very important for charge transfer processes.

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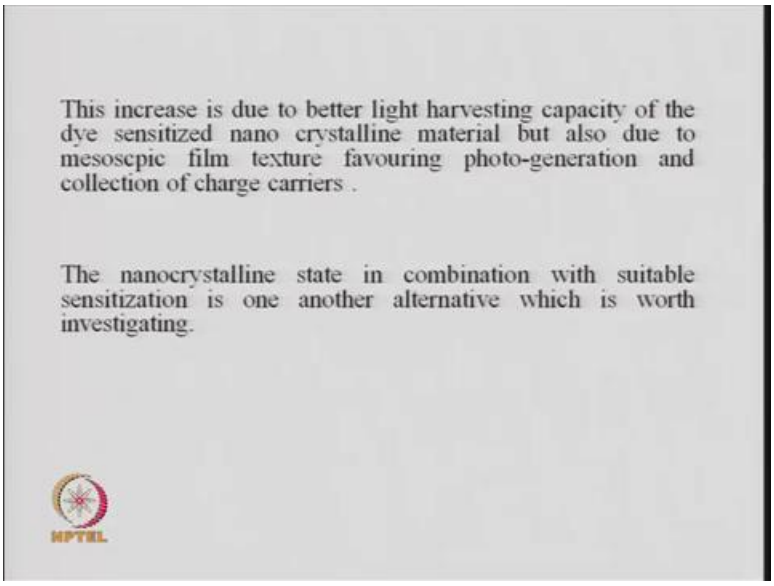

This increase is due to better light harvesting capacity of the dye sensitized nano crystalline material but also due to mesoscpic film texture favouring photo-generation and collection of charge carriers .

The nanocrystalline state in combination with suitable sensitization is one another alternative which is worth investigating.

Then the increase is due to better light harvesting capacity of the dye sensitized nano crystalline material. In dye sensitized cells we where we have added a dye the increase in the efficiency of the photo electrochemical splitting of water can be due to or is due to better light harvesting capacity. That means, the dye is actually trying to act as a antenna and picks up this radiation much more efficiently and that transforms the efficiency of the hydrogen and oxygen generation.

So, that is one thing, but it is also due to the case we discussed of the film, it is also due to mesoscopic film texture, which favours photo generation and collection of charge carriers. The other thing is the nano crystalline sate in combination with sensitization, together can be worthwhile alternative, so not only decreasing the size of the particle, but also using a photo sensitizer, together they can lead to a highly efficient system. The efficiency that we have reach needs to be increase further and challenges are lying a head.

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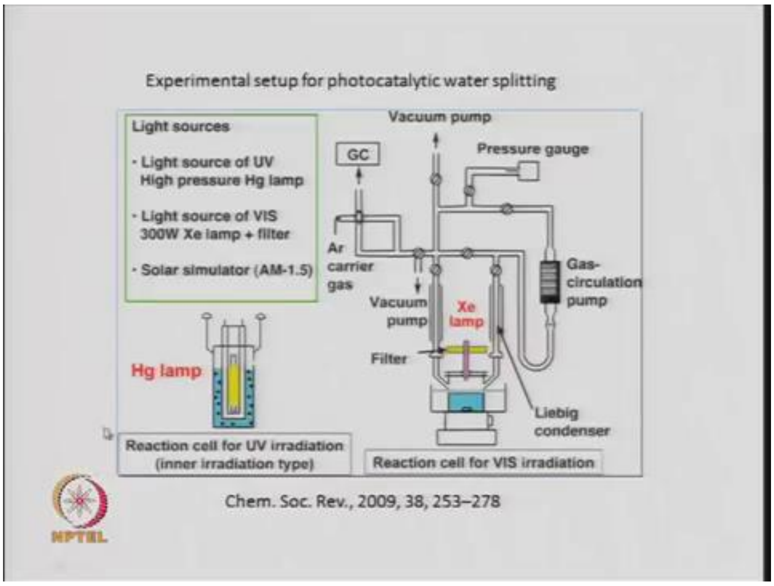

Experimental setup for photocatalytic water splitting

Light sources

- Light source of UV High pressure Hg lamp
- Light source of VIS 300W Xe lamp + filter
- Solar simulator (AM-1.5)

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This is an experimental set up for photo catalytic water splitting and you see the core are heart of the setup is the lamp. So, it can be a xenon lamp or a mercury lamp, an mercury lamp is basically used for ultraviolent radiation, it produces ultraviolent radiation. So, you put the mercury lamp, connect it to the mains and when the lamp glows ultraviolent race come out. And you have the solution with the nano particles or the semiconductor particles here, and their hydrogen and oxygen will be generated at the two electrodes.

So, this is one of the lamps and these you can also do similar thing with xenon lamp and this has this GC is attached for analyzing the gases which come out. So, both the xenon lamp and the mercury lamp can be use the xenon lamp gives or feasible radiation, so if you have catalyst is visible light active, then you use a xenon lamp if you are looking for UV radiation a then mercury lamp is fine. So, you can always use a higher energy lamp like a mercury lamp, but a two see whether a only visible region is active, than you need a xenon lamp to produce.

Because, UV radiation will also promote create electrons and holes in a system, where the band gap is in the visible. But, visible radiation will not promote electrons or and generate holes if the band gap is in the UV region, so visible light will show you certainly that the band gap is in the visible region.

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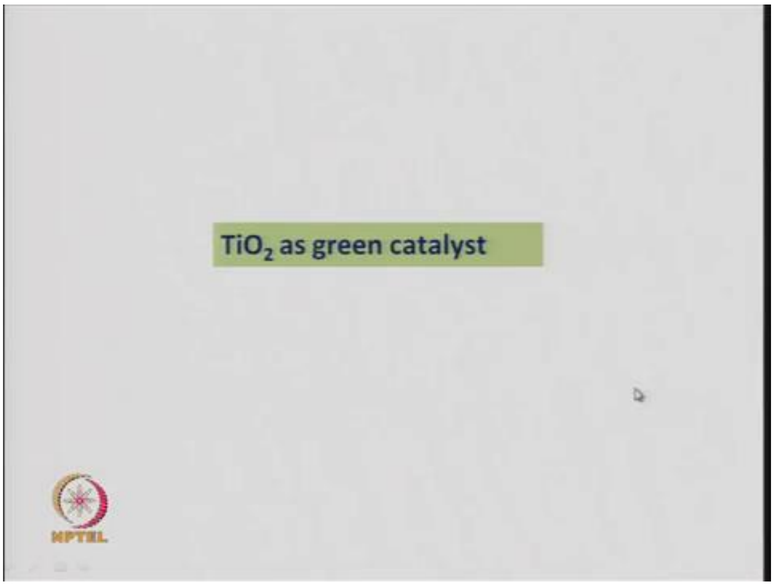

TiO$_2$ as green catalyst

So, why titanium dioxide has been used a lot and we discussed and that is because, titanium dioxide is a green catalyst it is nontoxic.

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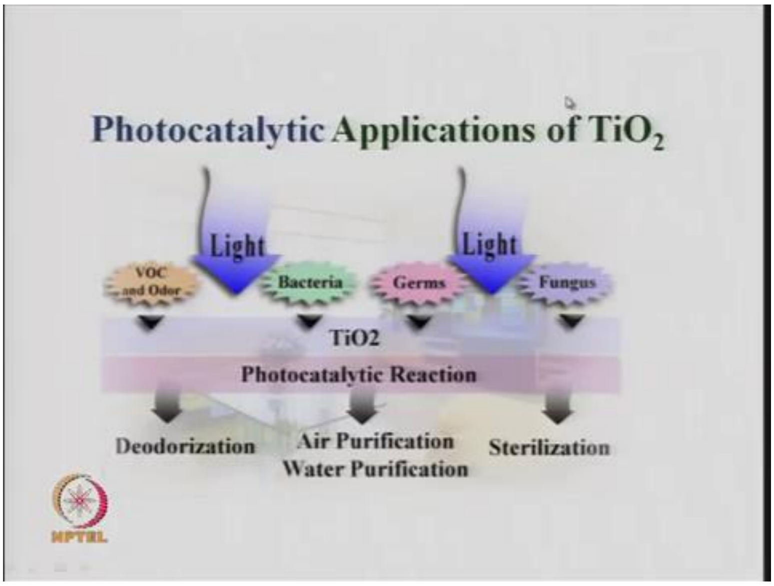

Photocatalytic Applications of TiO$_2$

So, photo catalytic applications of titanium dioxide, so in the presence of light titanium dioxide has been used to deodorize, your surfaces or any walls etcetera, by the removing a volatile organic compounds. The odor is basically caused by organic compounds, which are volatile, which are in the atmosphere and so they those organic compound, which are volatile are broken down by the photo catalytic reaction by T i O 2, which in the presence of light acts as a photo catalyst.

You can also purify air because, you can kill bacteria and germs in the presence of light and T i O 2 again acts as a photo catalyst. So, they are lots of these photo catalytic applications for deodorization, removal of odor, a air purification, water purification and sterilization in all these reactions there are tremendous applications of T i O 2 of course, T i O 2 is a UV light photo catalyst.

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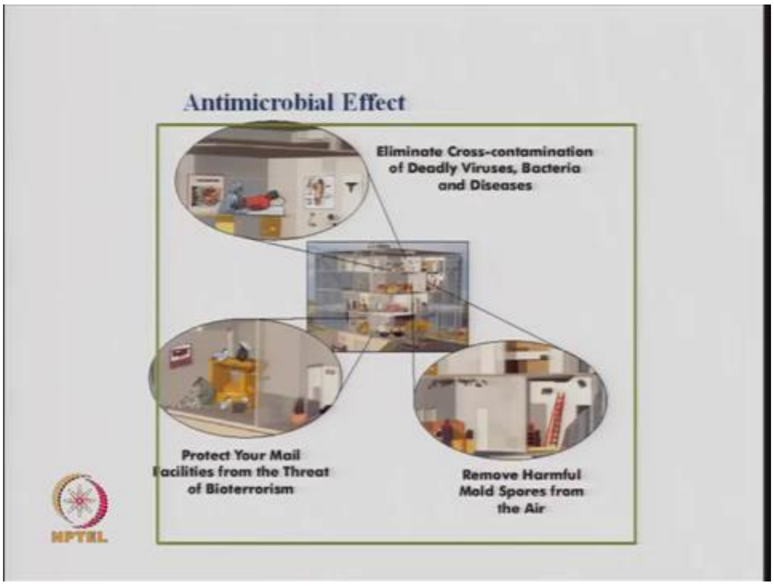

Antimicrobial Effect

Eliminate Cross-contamination of Deadly Viruses, Bacteria and Diseases

Protect Your Mail Facilities from the Threat of Bioterrorism

Remove Harmful Mold Spores from the Air

Now, you can have antimicrobial effect to remove viruses bacteria and diseases, so you can use T i O 2 for all these antimicrobial coatings. So, all these examples of coating on the walls, in hospitals and in offices or factories, removes a molds, spores from the air or removes viruses, bacteria, etcetera. So, it shows an antimicrobial air effect because of the a photo catalytic properties of titania.

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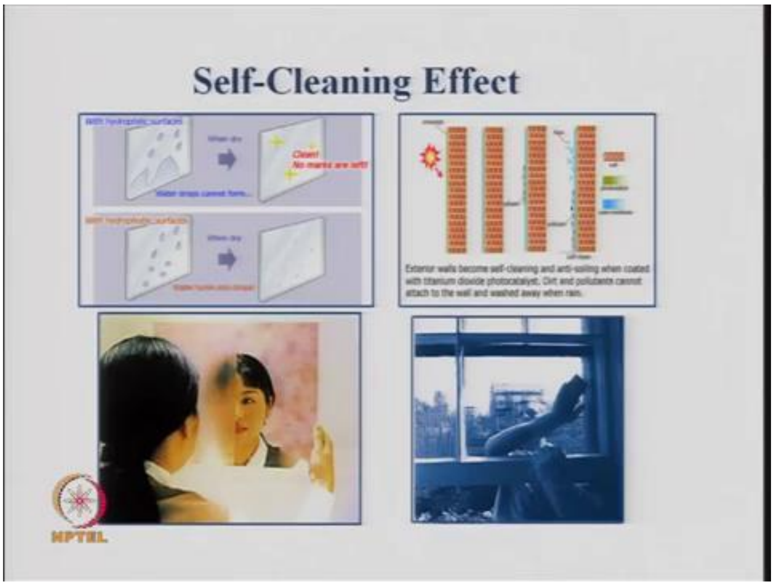

Self-Cleaning Effect

Exterior walls become self-cleaning and anti-soiling when coated with titanium dioxide photocatalyst. Dirt and pollutants cannot attach to the wall and washed away when rain.

Now, titania also shows self cleaning effect, so these are examples, you see this is a mirror and a this part of the mirror is coated with titania and the moisture on this part of the mirror does not allow you to see clearly. But, no moisture settle on this due to the a self cleaning effect of titania, which is also the hydrophobic effect of titania. Similarly, walls have been painted in several places, with the photo catalyst and the they are self cleaning in the presence of sun light the T i O 2 becomes active and it removes dirt and pollutants attach to the wall.

And washes them away after when it rains, this all those things which are attached to the wall will be washed away. So, it is self cleaning in the presence of light, the catalysis occurs and when you wash it with water or it rains, the walls become clean, so hence these are called self cleaning, effects and have been uses on doors, door handles, windows and buildings, etcetera.

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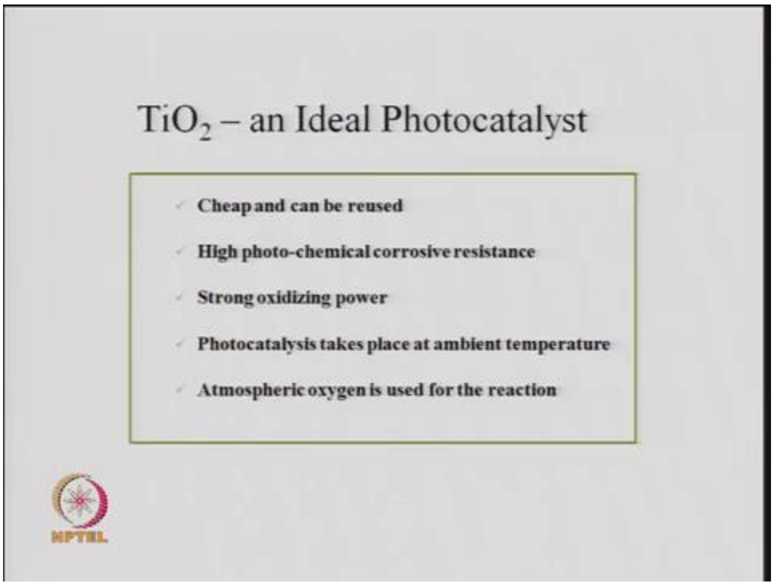

TiO_2 – an Ideal Photocatalyst

- ✓ **Cheap and can be reused**
- ✓ **High photo-chemical corrosive resistance**
- ✓ **Strong oxidizing power**
- ✓ **Photocatalysis takes place at ambient temperature**
- ✓ **Atmospheric oxygen is used for the reaction**

So, T i O 2 is an ideal photo catalyst and that is why 36 percent of the research of the world, as shown in the pie chart is done on T i O 2. It is cheap, it has high photochemical corrosiveness, a strong oxidizing power and photo catalysis takes place at ambient temperature and atmospheric oxygen is used for the reaction.

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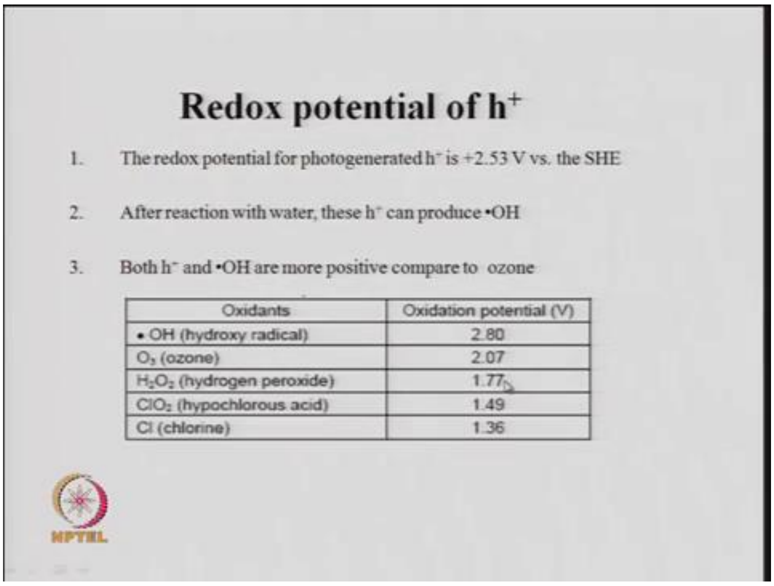

Redox potential of h^+

1. The redox potential for photogenerated h^+ is +2.53 V vs. the SHE
2. After reaction with water, these h^+ can produce •OH
3. Both h^+ and •OH are more positive compare to ozone

Oxidants	Oxidation potential (V)
• OH (hydroxy radical)	2.80
O_3 (ozone)	2.07
H_2O_2 (hydrogen peroxide)	1.77
ClO_2 (hypochlorous acid)	1.49
Cl (chlorine)	1.36

The redox potential for photo generated hole is a around 2.53 volts versus the standard hydrogen electrode. And after reaction with water, the holes will produce hydroxyl radicals, both holes and hydroxyl radicals are more positive compared to ozone. So, if you see these oxidation potential, you see the hydroxyl radical is much stronger than ozone as a oxidizing agent and much stronger than hydrogen peroxide. So, hydroxyl radical which is produce by the holes in a photo catalytic process is a powerful oxidizing agent, as seen by the oxidation potential and hence it will oxidize water into oxygen.

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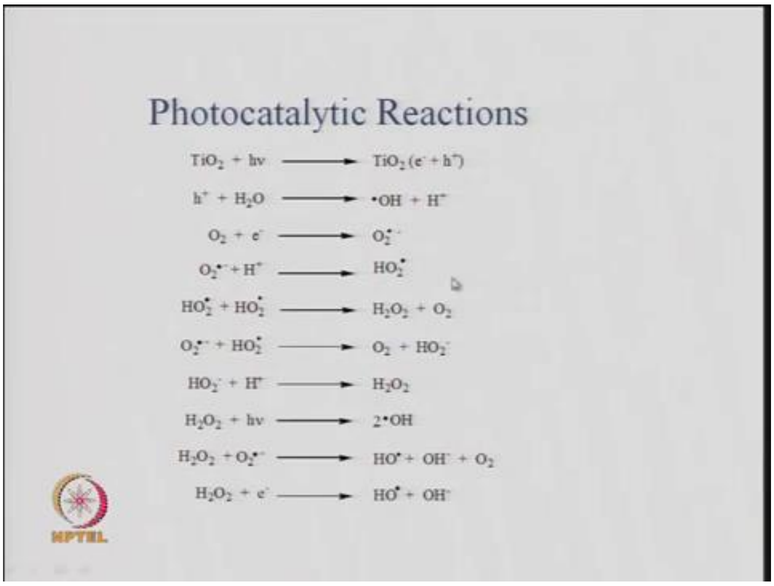

Photocatalytic Reactions

$$TiO_2 + h\nu \longrightarrow TiO_2(e^- + h^+)$$
$$h^+ + H_2O \longrightarrow {}^{\bullet}OH + H^+$$
$$O_2 + e^- \longrightarrow O_2^{\bullet -}$$
$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$$
$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$$
$$O_2^{\bullet -} + HO_2^{\bullet} \longrightarrow O_2 + HO_2^-$$
$$HO_2^- + H^+ \longrightarrow H_2O_2$$
$$H_2O_2 + h\nu \longrightarrow 2\,{}^{\bullet}OH$$
$$H_2O_2 + O_2^{\bullet -} \longrightarrow HO^{\bullet} + OH^- + O_2$$
$$H_2O_2 + e^- \longrightarrow HO^{\bullet} + OH^-$$

So, several photo chemical photo catalytic reactions are possible and in the presence of light, you generate electron and hole. The hole reacts with a water to produce hydroxyl radicals, the electron reaction oxygen to produce this dye oxygen radical anion, this radical anion reacts with protons to produce this a radical. So, several of these reactions can happen in the presence of a light and the photo catalyst titanium dioxide.

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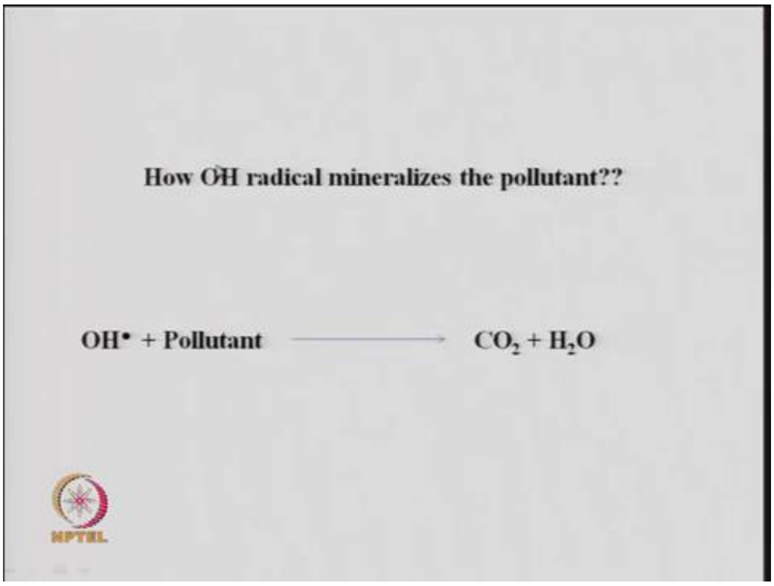

How OH radical mineralizes the pollutant??

$OH^{\bullet}$ + Pollutant $\longrightarrow$ $CO_2 + H_2O$

Now, how does O H radical mineralize the pollutant, the O H radical reacts with organic compounds, which is the pollutant and produces carbon dioxide in water, that is how it cleans the rivers which are full of pollutants by using titanium dioxide, etcetera.

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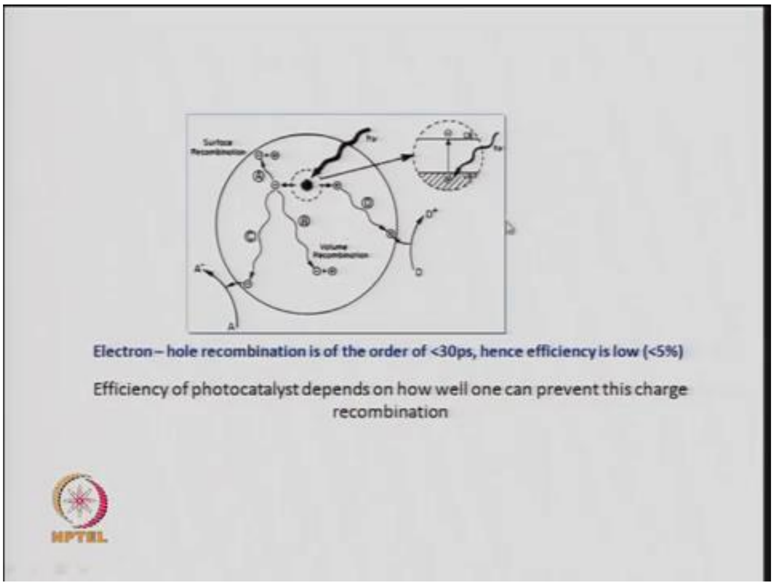

Electron – hole recombination is of the order of <30ps, hence efficiency is low (<5%)

Efficiency of photocatalyst depends on how well one can prevent this charge recombination

So, this is again in a nut cell to show you, when light shines electrons go one way and protons should go the hole should go the other way. And the electrons on the surface can recombine and the holes and the surface can go and oxidize or they can also recombine, the electrons can recombine with holes or the they can go on the surface and reduce, you have to stop the electron whole recombination. So, this process and this process you want to stop to make an efficient photo catalyst. And the electron whole recombination is of the order of less than 30 p per seconds, hence efficiency is very low. So, this is the bottle neck you want to stop the electron hole recombination and you have only efficiency of around 5 to 6 percent in this water splitting reactions.

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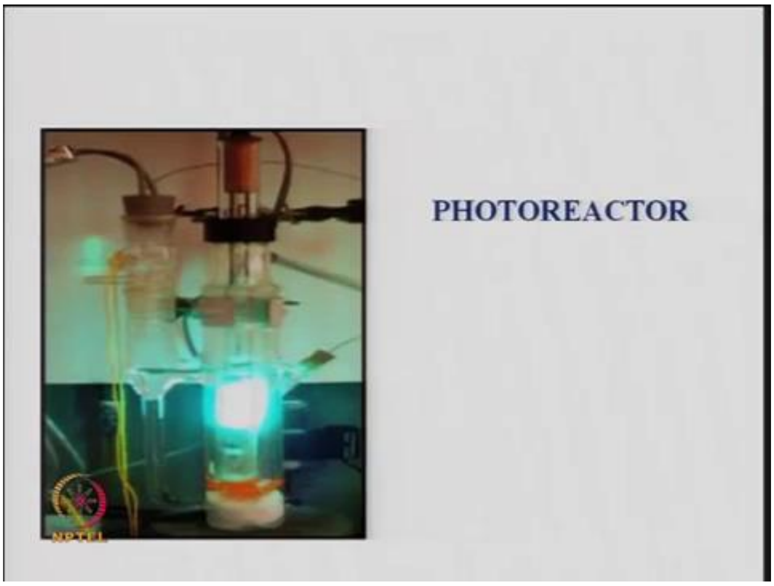

PHOTOREACTOR

So, finally, this is how the reaction looks when you are doing a photo catalysis, so this is the lamp, which I was talking to you a xenon lamp or mercury lamp is placed inside. And solution is there with the photo catalyst and electrodes are there the electrode assembly and you are doing photo catalytic reactions here. So, with that I come to the end of today's lecture and we have one more lecture on photo catalysis, which we will be doing in the next lecture.

Thank you.