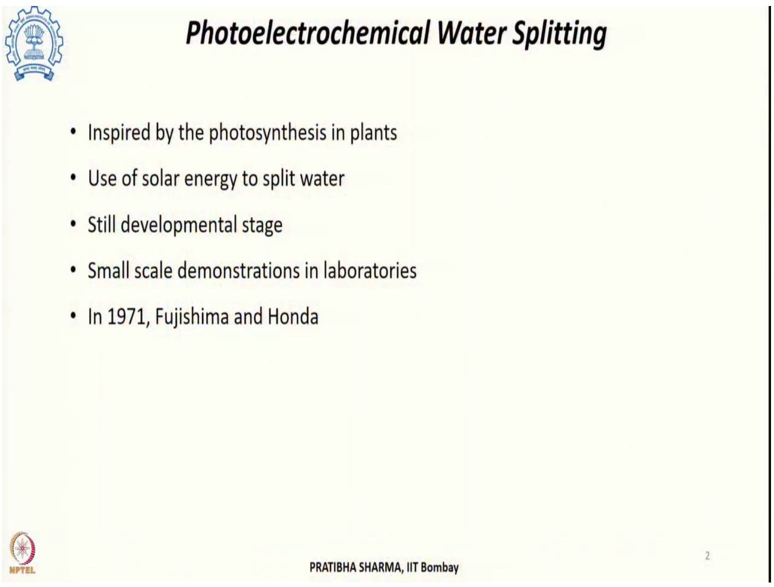
Hydrogen Energy: Production, Storage, Transportation and Safety
Prof. Pratibha Sharma
Department of Energy Science and Engineering
Indian Institute of Technology, Bombay

Lecture - 27
Photoelectrochemical Hydrogen Production

For sustainable Hydrogen Production, the energy required can come from renewables and feedstock or source could be water. In earlier classes, we have seen two different methods for water splitting; these were thermochemical cycles, where the required energy for water splitting comes from either waste heat from nuclear reactor or from solar thermal.

We have also seen in detail water electrolysis, where the required electrical energy can come from either solar photovoltaic or it can come from hydroelectric power or from wind. So, today we will see another method for water splitting, which is photoelectrochemical water splitting. The energy which is required again comes from solar energy to split water, but this technology is still at a developmental stage.

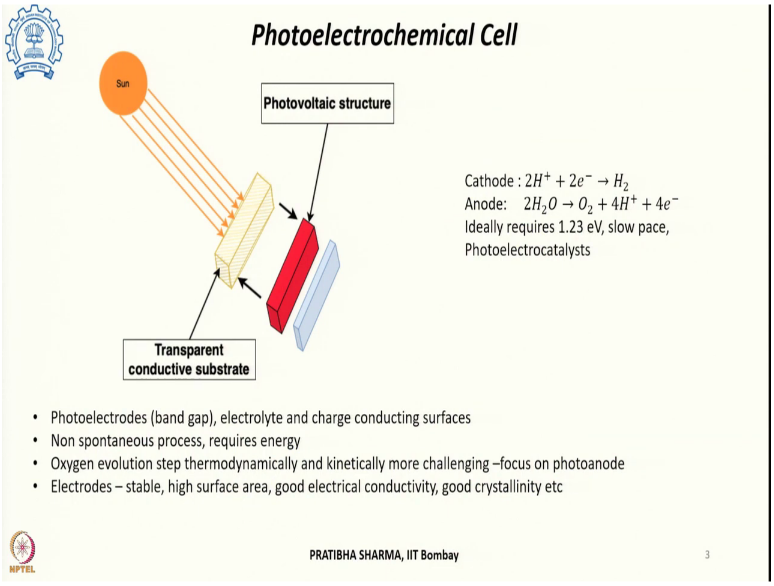
(Refer Slide Time: 01:10)



And there are very small scale demonstrations which have been there in the laboratories. So, we will be just very briefly looking at this technology; because in this particular course our inclination has been towards production methods which has been on commercial scale or on industrial scale for hydrogen production.

Now, this particular method of photoelectrochemical water splitting this is inspired by photosynthesis in plant, where the sunlight and water, plant uses that to produce chemical energy, this is using a biochemical process. So, water splits into hydrogen containing species and oxygen in different photo systems, which are separated; same logic was used for photoelectrochemical water splitting. And it was in 1971, when Fujishima and Honda, they came up with the photoelectrochemical reaction and that was using titanium dioxide as the material.

(Refer Slide Time: 02:17)



So, a very basic structure, although there are several other layers attached to it is where there is a transparent conducting layer; then there are semiconducting layer and then there could be current collectors or transport layers. So, basically a photoelectrochemical cell just like electrolyse has a basic unit of electrolytic cell; photoelectrochemical cell is the basic unit for the process.

And it has two electrodes, the two photo electrodes and the requirement for them to have is a appropriate band gap; then there is an electrolyte and then charge conducting surfaces can be there. Like electrolysis again this is water splitting, so it is a non spontaneous process. And it requires energy for the water to split into its constituents which are hydrogen and oxygen and that required energy can come from sun.

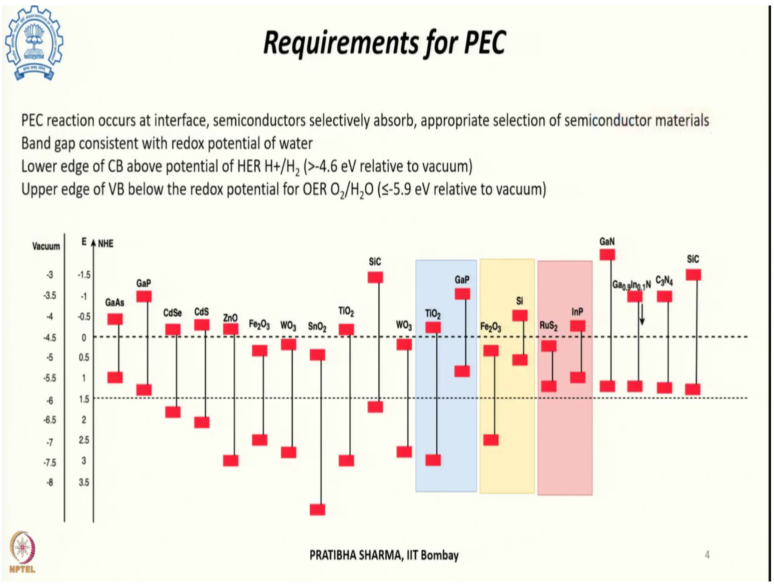
So, there are semiconductor materials which can absorb sunlight producing electron hole pairs and that electron can go through the external circuit reducing H+ ions into hydrogen.

The holes can go to anode side and then water get oxidized into oxygen releasing oxygen on the anode side. Now, typically this reaction requires a voltage of 1.23 electron volt; but when this much amount of energy is being supplied for the required reaction, the reaction occurs at a slower pace.

So, it has a activation energy which is higher and then if this much amount of energy is being provided; then it will still take place at a slower pace. So, for increasing or enhancing the rate of the reaction, photo electrocatalysts are required. At the same time the reaction that occurs on to the anode side which is oxygen evolution that is more demanding and thermodynamically and kinetically both it is more challenging.

So, if we see most of the literature or most of the research has been focused on towards developing the suitable material for photo anode. Now, these again the electrodes need to have certain characteristic; they should be stable under the irradiation condition, they should have high surface area to provide the required regions for the reaction to take place, it should have good electrical conductivity, good crystallinity.

(Refer Slide Time: 04:43)

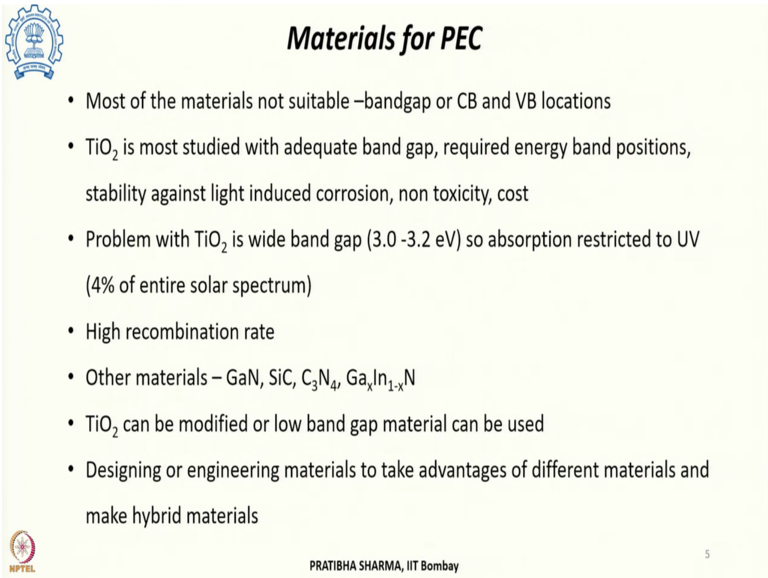


When it comes to photoelectrochemical reaction that occurs at the interface, electrode electrolyte interface. Now, there are several semiconductors which are available which absorb sunlight and then they can produce the charge carriers; but for photoelectrochemical reaction to occur, the band gap is a important measure. So, appropriate selection of semiconductor materials, such that the band gap matches with the redox potential of water is very essential for the process to happen.

And the requirement is that the lower edge of conduction band should be above the potential of hydrogen evolution reaction for this redox couple. So, it should be higher than minus 4.6 electron volt, which is relative to the vacuum level. At the same time the upper edge of valence band should be below the redox potential for the oxygen evolution reaction, which is corresponding to minus 5.9 electron volt.

Now, if we see both the conditions such that the conduction band lies above this and the edge of the valence band lies below this is satisfied by very few materials we can see that. So, rest of the materials like we can see silicon carbide, titanium dioxide; so there are very few materials that satisfies this condition.

(Refer Slide Time: 06:20)



Most of the materials they are not suitable for photoelectrochemical reaction to occur; this is because of both either they do not have the required band gap or the locations of the conduction band and valence band are not as per the desired condition. Now, among the materials which have been studied for photoelectrochemical cell, titanium dioxide is the most widely studied material and this is known to have the required band gap; it has the required band positions in terms of the conduction band edge and valence band edge.

And it is known to have a stability towards the light induced corrosion, it is at the same time, it is not expensive, it is non-toxic; but the major problems associated with this material titanium dioxide is, it is a wide band gap material. So, the band gap for this material lies in the range of 3 to 3.2 electron volt and if we convert that into wavelength, that comes out to be lying in the UV region ultraviolet region.

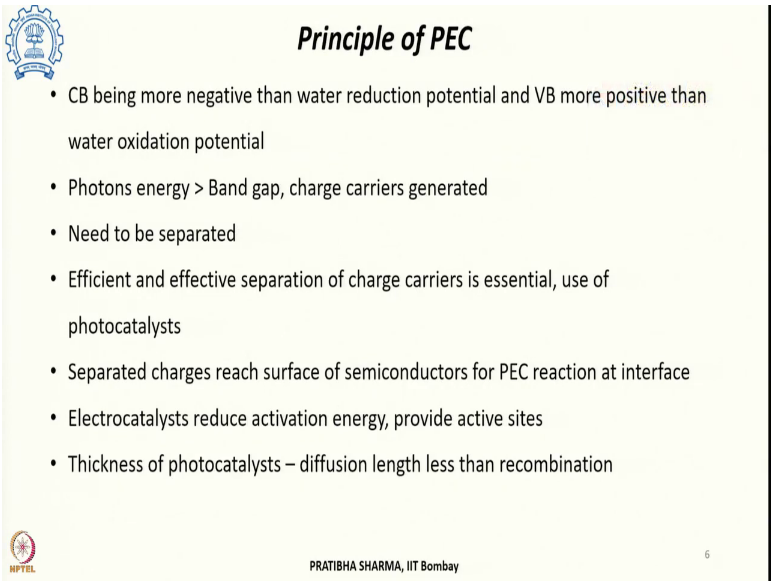
So, for this material, the absorption is restricted basically to the ultraviolet region. And this ultraviolet region if we look at the solar spectrum, that constitutes only 4 percent of the entire solar spectrum. As such a major portion of that remains unabsorbed if we use this material; at the same time the recombination of the charge carriers, so as the charge carriers are produced, they can even recombine.

And that recombination rate is higher for the titanium dioxide material. So, what can be done is, either we can modify that titanium dioxide; so we can have appropriate doping, we can have nano structuring, sensitizing. So, there are different ways of modifying titanium dioxide or else we can use a low band gap material, such that it can absorb the broader region in the solar spectrum.

Now, there are other possible materials which satisfy the two required conditions of band gap and the locations of the conduction and valence band and these are like the materials which can be used are gallium nitride, silicon carbide, C3N4, gallium indium nitride. So, these materials can also be used for photoelectrochemical reactions. Now, the important thing lies here is, there may be different materials which may have different advantages.

And if we can make a hybrid material out of that, if we can design a material; we can engineering tailor the material, so as to take benefit of the advantages of different materials to make hybrid materials which could provide a better efficiency, better stability for photoelectrochemical processes, then that will be that is the desired area for research.

(Refer Slide Time: 09:22)



Now, if you look at the basic principle of photoelectrochemical process, we have seen in the earlier figure the requirement is conduction band should be more negative than the water reduction potential and valence band should be more positive than the water oxidation potential. So, what is required is when the sunlight falls on to such material semiconductor material, the required energy of photon should be higher than the band gap.

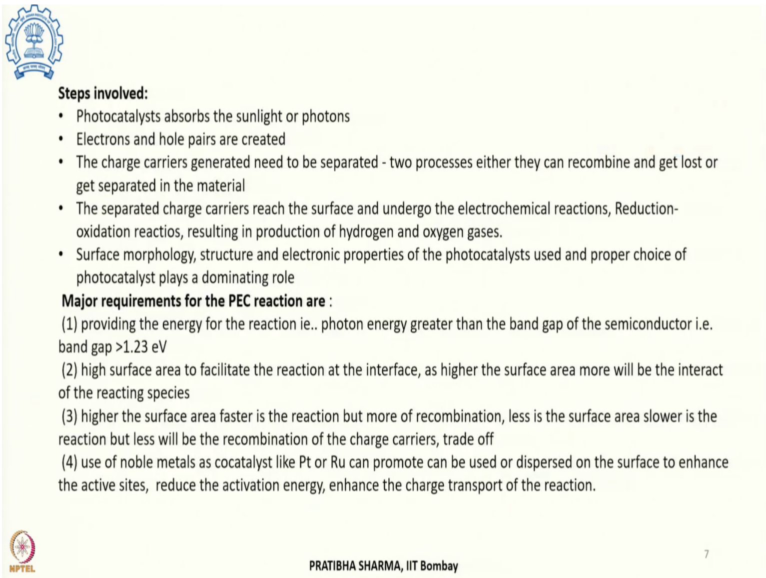
And once it is higher than the band gap, the electron hole pairs are created. So, these are the charge carriers which are generated; but at the same time the charge carriers which are generated, they need to be separated and that is very important that, efficient and effective separation of charge carriers is essential and we can use several photocatalyst for achieving that.

Once these separated charge carriers they can they reach on to the surface of the semiconductors; they are at the interface of the electrode electrolyte, the photoelectrochemical reaction will take place. Now, the role of these electrocatalyst or photoelectrocatalyst is to reduce the activation energy; because we know that water splitting has a very high activation energy, it also provides the required active site where the electrochemical reaction could take place.

So, at the same time the thickness of these photocatalyst that are deposited onto the surfaces that is very important. The reason being the diffusion length of the charge carriers if this is smaller than the thickness or the thickness is higher than the diffusion length; then the charge carriers which are produced in the process, they will recombine back and once they recombine, they will give back that reaction.

The they will give back the energy which is the electron has taken in moving from valence band to conduction band. So, there will be more of recombination. So, if this is the case, if diffusion length is less; then this will, the recombination's will take place in the process.

(Refer Slide Time: 11:29)



So, if we see the what are the major steps involved in photoelectrochemical process is the photocatalyst which are present they absorb the sunlight or photons. That energy is absorbed, with that energy the electrons move from the valance band to conduction band creating holes in the valance band. So, electron and hole pairs are created in the process; these charge carriers electrons and holes which are created, these require to be separated.

And there are two possibilities either they will recombine; so electron and hole pair will recombine giving the energy and get lost in the process or they can be separated in the material. Once they are separated, they reach on to the surface; at the interface they undergo the different electrochemical reactions, which is basically a reduction oxidation reaction that takes place at the interface producing hydrogen and oxygen gases, so hydrogen onto the cathode side, oxygen onto the anode side.

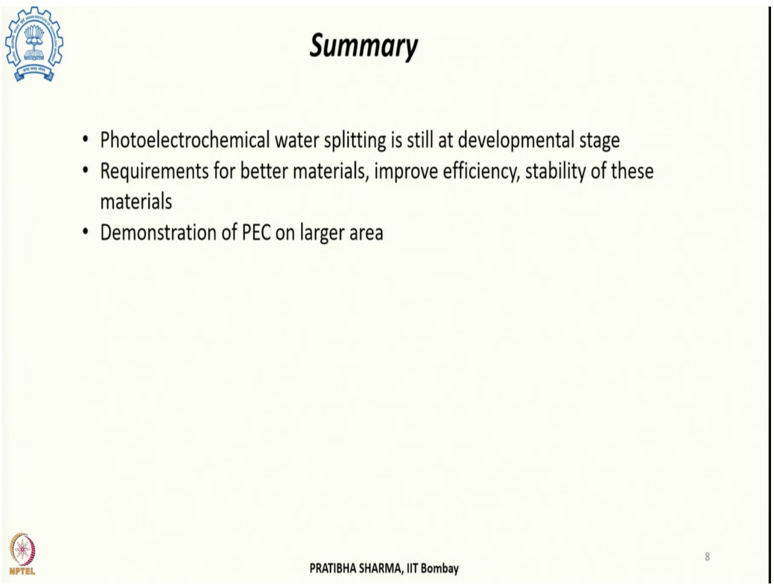
Here the important things are the surface morphology the structure, what are the electron transport properties of the photocatalyst which are used. So, as such a proper choice of photocatalyst plays an important role in photoelectrochemical water splitting. Now, the major requirement which are there for photoelectrochemical reaction to take place are the required energy which is the photon energy higher than the band gap and that value is 1.23 electron volt, which is minimum required energy for the reaction to take place should be provided by means of the photons.

A higher surface area is required, where the reaction should take place at the interface; this higher surface area will provide will be when it is higher, there will be more interaction region available for the reacting species. But at the same time the higher surface area although it promotes a faster reaction; but at the same time there is more of recombination that will result with the increase in the surface area.

So, less of surface area although the reaction is going to be slower, but the recombination of charge carriers will be less; so there lies a trade off between the surface area between the kinetics of the reaction, at the same time the separation of the charge carriers. So, for that like several co catalysts are also used like noble metal cocatalyst, including platinum or ruthenium.

And their use of these cocatalyst can be helpful towards enhancing the active sites, reducing the activation energy further; they can enhance the charge transport for the reaction and to have a to facilitate the photoelectrochemical reaction to take place.

(Refer Slide Time: 14:31)



So, today we have seen very briefly the photoelectrochemical water splitting process; although there are several materials which have been looked at several properties, their morphology which has been studied in the literature, but this we have seen in very brief.

Now, this photoelectrochemical process this is still at a very early level, at a developmental level; the requirement is of better materials which could be stable enough, which have a better efficiency and the demonstration of such photoelectrochemical cells on a larger area is required, at present this has been on very small scale laboratory development.

Thank you.