Bioelectricity
Prof. Mainak Das
Department of Biological Sciences and Bioengineering
Indian Institute of Technology, Kanpur

Lecture - 34

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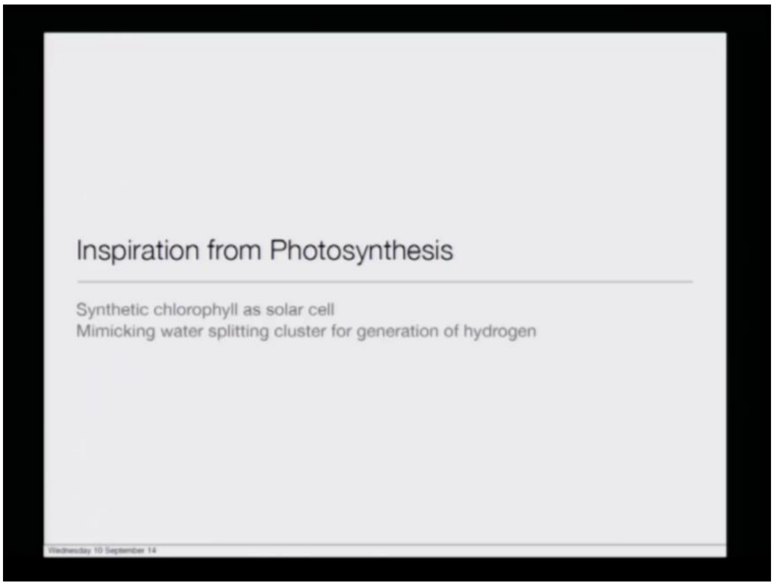

Welcome back to the lecture series in NP-TEL on bioelectricity. So, we are on the thirty fourth lecture. So, last lecture, we talked about photosynthesis. So, now we will be talking about to finish the photosynthesis. Now will be talking about the inspiration we have drawn from photosynthesis. And we will be talking about this topic at two level; one the inspiration which has led to the development of Gratzel's cells or dye sensitized solar cells; and the second one what will be talking about is the inspiration drawn from the manganese cluster. Just a brief recaps for those of you are joining in this lecture.

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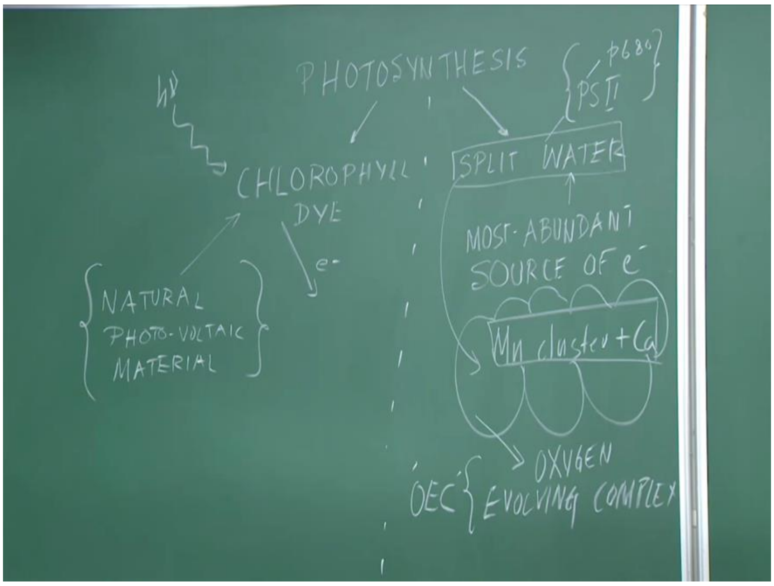

So, talking about photosynthesis in the last two lectures we talked about. So, there are two major things what we observed. One thing we observe that chlorophyll dye has the ability to absorb light and ejects an electrons. So, essentially this chlorophyll dye is a natural photovoltaic material. So, this is one thing what has inspired generations, since we know this thing. The second important thing about chlorophyll in terms of the inspiration is, it is the ability to split water, which is essentially, if you remember my last lecture, I told you the most currently in this current earth ecosystem most abundant source of electrons. And this water splitting cluster, which we talked about is present on just underneath PS 2 or photo system 2, or P 680. So, really we want to you know recollect it is is a manganese cluster plus calcium surrounded by a series of proteins, which is called the oxygen evolving complex - OEC.

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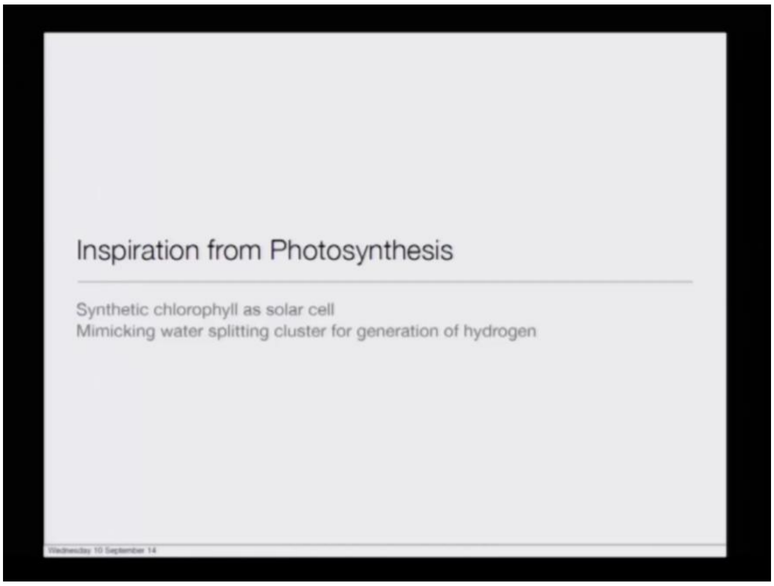

So, these are the two zones. So, if you look at the slide, these are the two zones where we have drawn inspiration. Synthetic chlorophyll as solar cells that is this part, and the second one mimicking water splitting cluster for generation of hydrogen.

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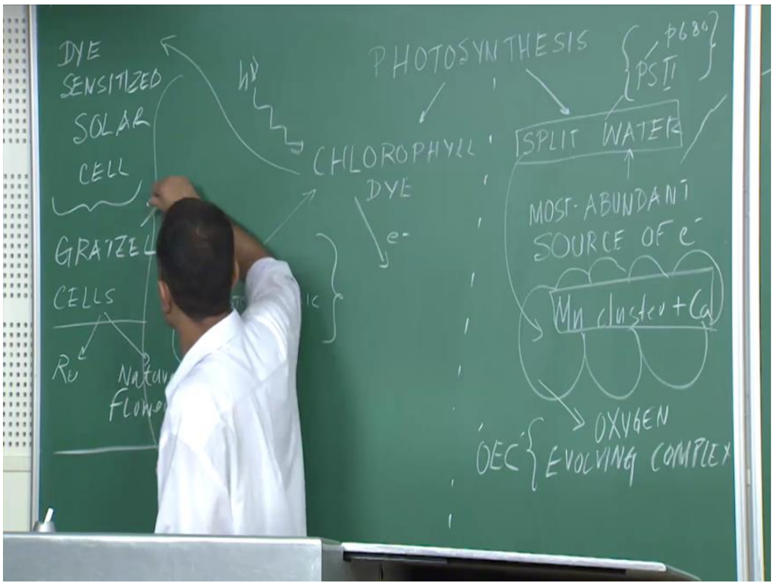

That is significant amount of hydrogen which is generated out here and this is what we call as hydrogen as fuel where you see all these hybrids and hybrid cars and everything. These are the two things. So, talking about the chlorophyll dye, there are several other dye and we will have a exclusive one lecture on this one which will fall under dye sensitized solar cells, will talk about this in detail which is also commonly called as after the name of its innovator gratzel, called gratzel cells. So, we have a totally separate one lecture on gratzel cell or dye sensitized solar cell what are the different dyes, and in that you will come across several dyes, you know ruthenium dyes and you will talk about natural flower dyes likewise and so and so forth. Today will be talking about hydrogen as a fuel by mimicking the manganese cluster what are or its not mimicking by deriving inspiration from the manganese cluster which is present in the photo system two of the thylakoid membrane.

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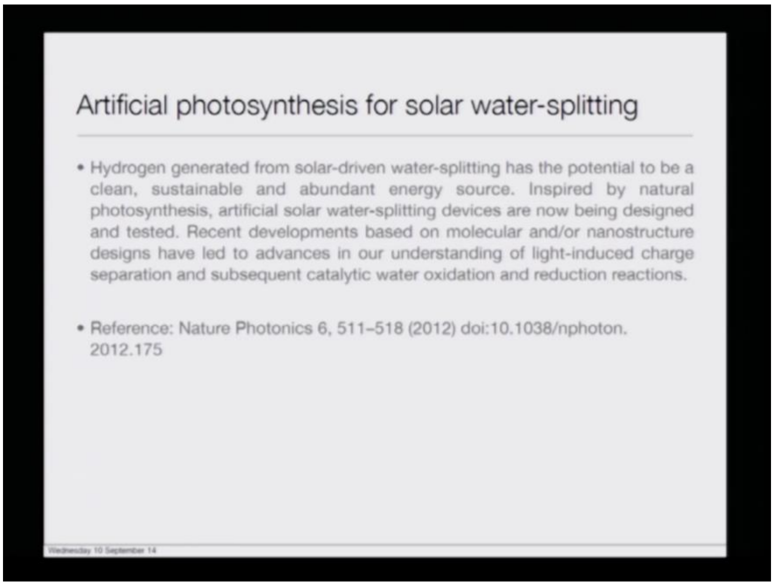

So, let us move on what we meant by the artificial photosynthesis for solar water splitting. So, essentially hydrogen is generated from the solar driven water splitting has the potential to be a clean, sustainable and abundant energy source. Inspired by natural photosynthesis, artificial solar splitting complex or devices are now being designed and tested. Recent developments based on molecular nano structure designs have led to advancement in order to understanding of light-induced charge separation and subsequent catalytic water oxidation and reduction reactions. There is a very nice review which I have sited here in the Nature Photonics came in the year twenty twelve; please go through this review, and most of the presentation which is which I will be doing today is from that specific paper.

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There are several good references and you will see the reference of Gratzel cell wonderful paper there is a paper by Gratzel in published nature. The title of the paper is photo electrochemical cell; please go through this paper, there is a cross reference of this paper in this particular paper what I am referring now. Go through this paper, this will help you to you know appreciate this whole thing far better than there is a wonderful review wonderful the good paper and that by Helmetro Buch, you will again see the reference in this nature photonics paper; go through the work of Helmotri Buch. So, these all will help you to get a very global idea how the world is now thinking where it is all moving.

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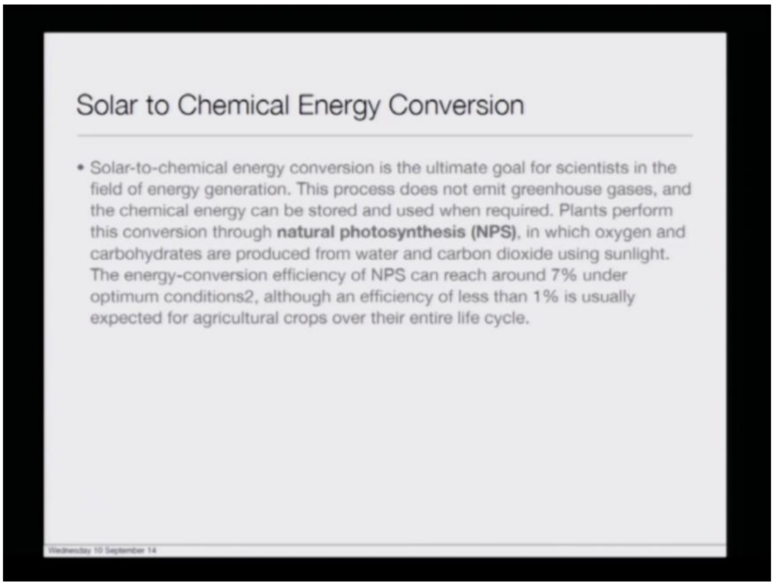

So coming to the solar to chemical energy conversion. Solar to chemical energy conversion is the ultimate goal for the scientist in the field of energy generation. This process does not emit any green house gases, and the chemical energy can be stored and used when required which is in the form of hydrogen. Plants form the conversion through natural photosynthesis which in abbreviated as NPS, in which oxygen and carbohydrates are produced from water and carbon dioxide using sun light that we have already discussed. The energy-conversion efficiency of NPS can reach around seven percent under optimum conditions, although an efficiency of less than 1 percent is usually expected for agricultural crops over their entire life cycle.

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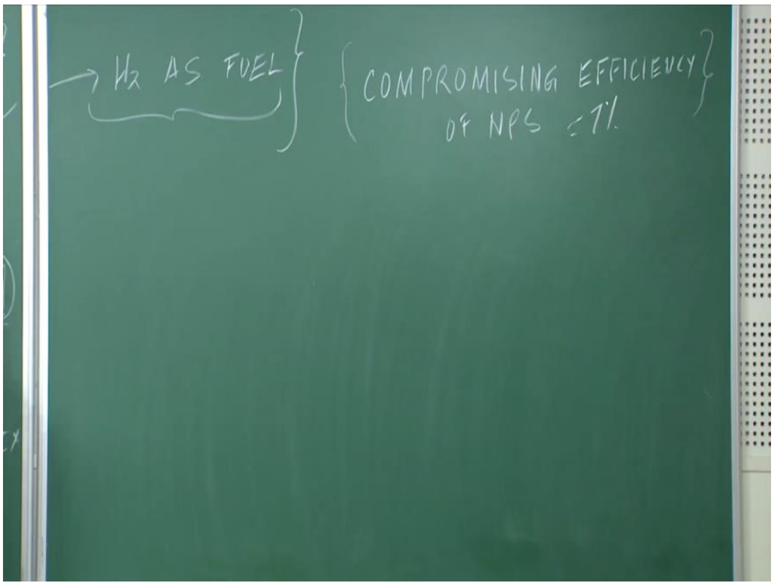

So, in the previous lecture, while I was talking to you about the efficiency of natural photosynthesis system, so you you can remember I was telling you that you are compromising efficiency of natural photosynthetic systems, which is approximately seven percent. The reason possibly you what I sited is in those one thylakoid complexes there are lot of when the chlorophylls are getting or exciting getting excited, and they are getting oxidized and they rejecting an electron. There are lots of free radicals which are preformed. Now in order to prevent free radical damage, this process is slow down and that is what, what you see this seven percent efficiency is in order to ensure that the free radicals, which are form there does not damage the system. So, that we feel to you know recuperate this system and it losses, its ages very faster possibly that could be one of the possible reasons.

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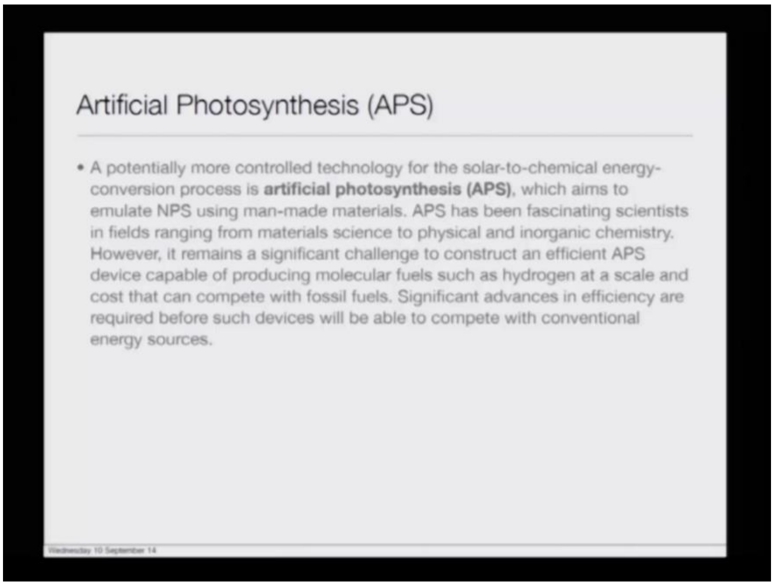

Now moving on to the next slide see the artificial photosynthesis, what we really went by that. So, you have two words which are coming for you know one is natural photosynthetic system and the other one is APS which is a stands for artificial N stands for the natural. So, coming back to the slide, a potentially more controlled technology for the solar to energy conversion chemical energy conversion process is artificial photosynthesis, which aims to emulate natural photosynthesis using man-made materials. APS has been a fascinating scientist in field ranging from material science to physical to inorganic chemistry. However, it remains a significant challenge to construct an efficient APS device capable of producing molecular fuels such as hydrogen at a scale and cost that can compete with fossil fuels. Significant advances in efficiency are required before such devices will be able to compete with conventional energy sources.

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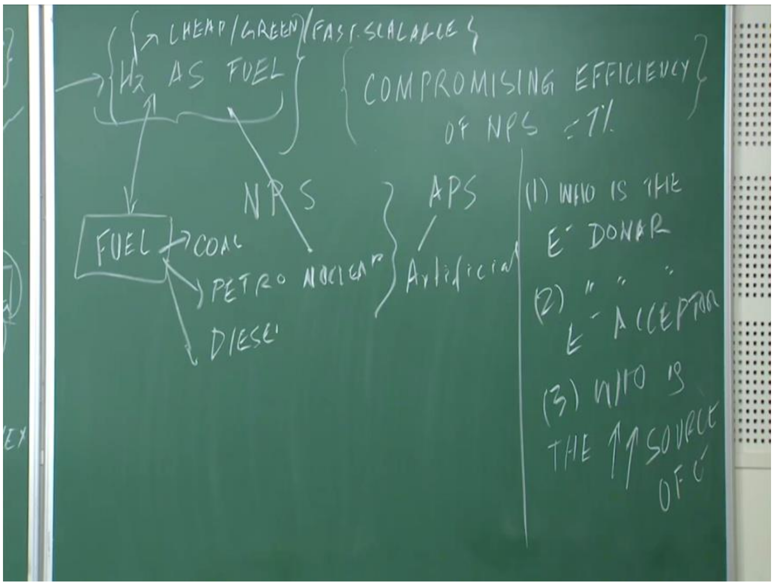

So, this is what is competing with the other fuels the like coal, petrol, diesel and of course, you have the nuclear. So, this process has to be cheap, green and fast and fast scalable. Without this, this cannot really be achieved, the way we are dreaming of a world of clean and green energy. Nature is already done it, nature is already doing electron donation and if you remember in the last thing I told you that if I have to put three words for the whole evolution to who is the electron donor, who is the electron acceptor. And third one, who is the abundant, very abundant source of electron that is it this is all about this how you really can manipulate this to the next level.

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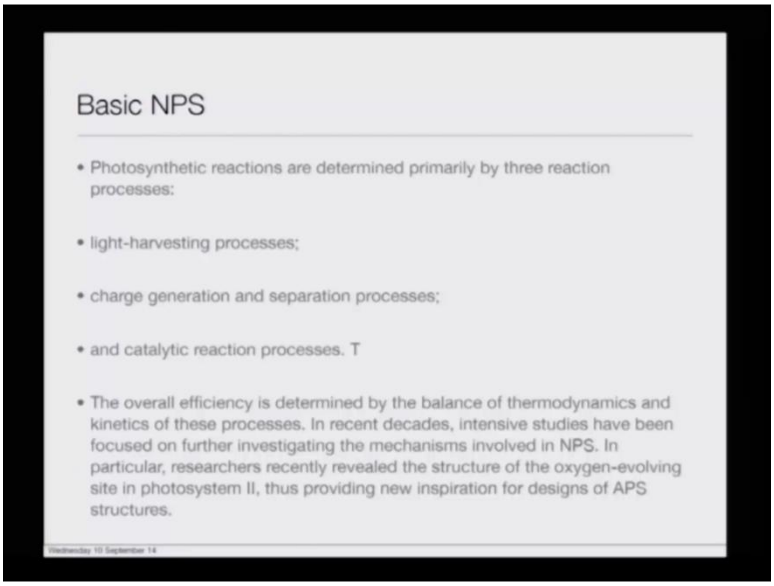

Coming back to the slide, so what are the basic of the natural photo systems. So, photosynthetic reactions are determined primarily by three reactions we looked at. There is a light harvesting process. If you remember it, there is a chlorophyll at P 680, P 700 which is essentially p photo system 2 and photo system 1 respectively, which is supported by series of molecules which is funneling the light and ejecting the electron this is the first foremost thing. So, you need a light harvesting because light energy is n ones of you come here who is the donor of electron. So, we are talking about what is the energy which will help you eject the electron. If you know the donor then that donor needs an energy which could, so this energy is provided by the sun and this energy is funneled through the antennae pigment to the light harvesting process.

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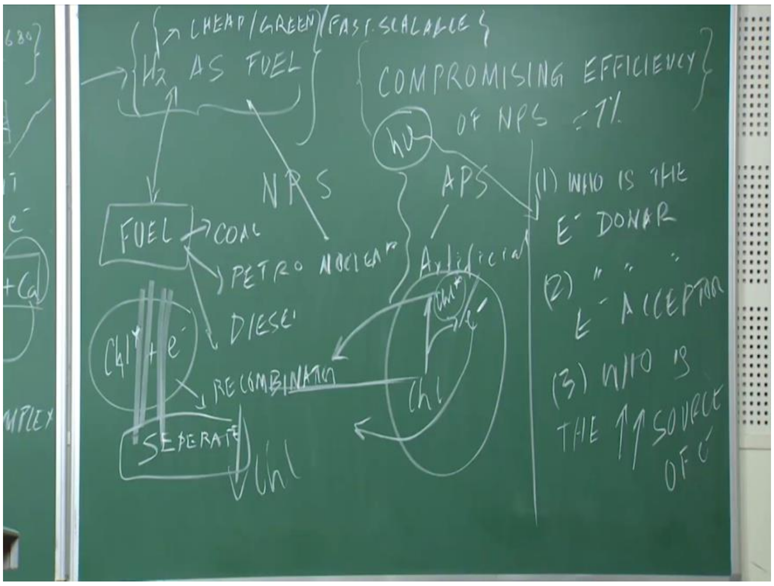

Second thing, if you go through this slide charge generation and separation process. So, what is the charge generation we talked about, talked about whenever there is chlorophyll molecules sitting here it ejects an electron and it becomes oxidized. So, this is the whole charge generation process and the combination electron hole paring. And the separation, you have to have a way by which you can separate these processes; otherwise, what will happen they will recombine back. So, the chlorophyll which is form the electron is closed to it. So, this is the problem. So, this chlorophyll which is there, which is divide of an electron plus the electron which is ejected, it will recombining then and there. They will be recombining combination process and it will bring it back to its ground state, it will reduce it. So, there has to be way by which you can separate the charges, you have to separate them; otherwise they will recombine.

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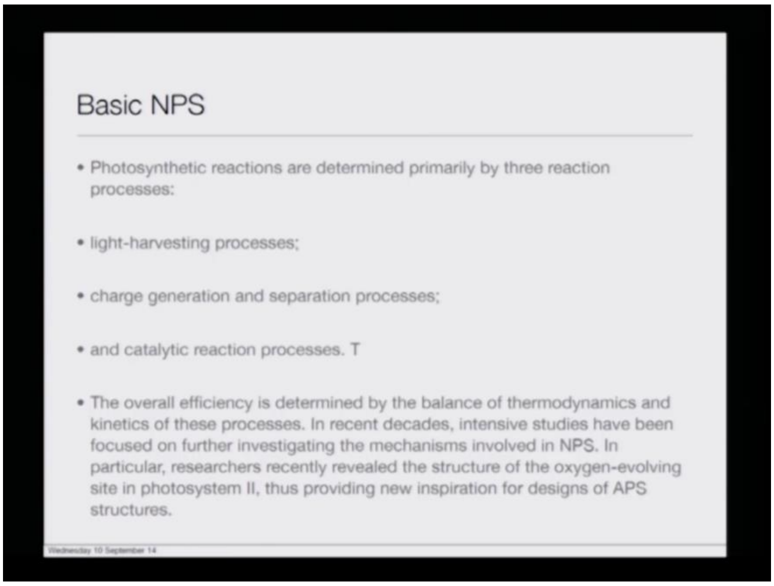

Then comes the catalytic process, which essentially is the splitting of water. Now the overall efficiency is determined by the balance of the thermodynamics, and the kinetics of all these processes. In recent decades, intensive studies have been focused on further investigating the mechanism involved in NPS; in particular researcher, recently revealed the structure of oxygen evolving complex site in photo system 2, thus providing new inspiration for design of NPS structures. So, I was talking to you about oxygen evolving complex - OEC, underneath P 680 or you know photo system 2. So, recently at least three years back this structure has been revealed. So, now since this structure is known, there is a lot of inspiration to design better oxygen evolving complex or better water splitting complexes.

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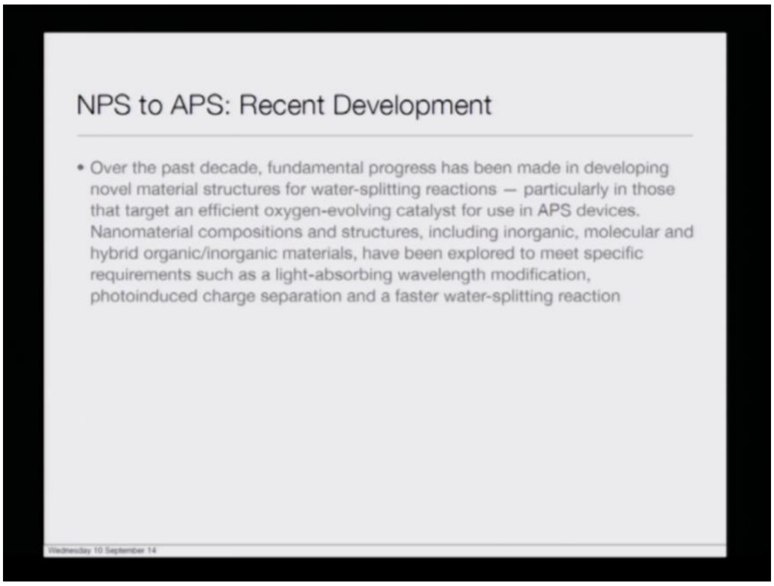

Now moving onto the next slide, NPS to APS, What are the recent developments? Over all the past decade, fundamental progress has been made in developing novel material structures for water splitting reactions - particularly in those that target an efficient oxygen-evolving catalyst for use in APS devices. Nanomaterial composition structuress including inorganic, molecular and hybrid organic or inorganic materials, have been explored to meet the specific requirements such as light-absorbing wavelength modification, photoinduced charge separation and faster water-splitting reaction.

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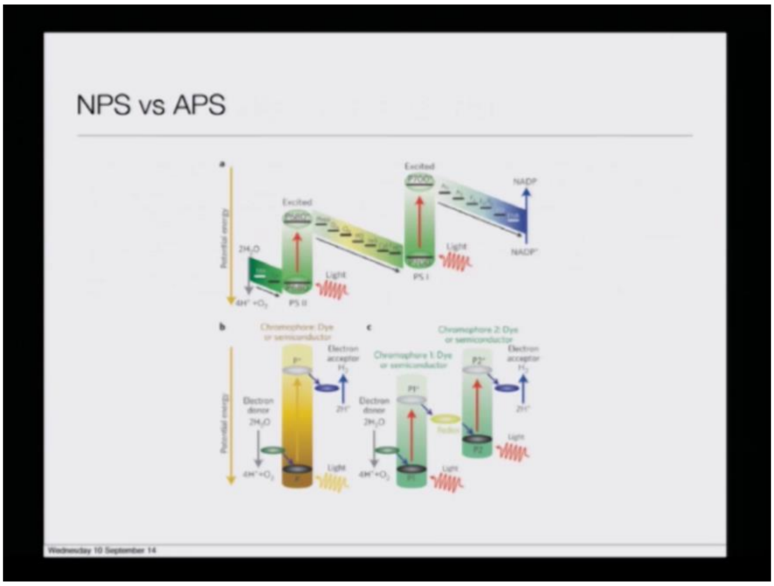

Now let us have a glims of diagrammatically what is happening, what are the difference between NPS and APS. The upper picture you see is the NPS, where you see the P 680 which is just in top of the water-splitting cluster which is manganese cluster on the right it is shown. Now P 680 electron gets excited that electron through phyofintine Q a to Q b to plastoquinine to iron sulphur to cytochrome b f to plastocynine moves on it is happing down down down down if you look at it. In the z scheme of things, it moves to P 700, where already there is another chlorophyll molecule which has oxidized, so that chlorophyll molecule which are oxidize has to be brought back to its ground state.

So, at P 700, this electron which brings back that P 700 excited molecule back to its ground state and the electron which is ejected by P 700 that moves to A o to A one complex to effects an f a f b complex. And eventually it will works with NADPH reductor is to make NADPH molecules. And in the mean time, on the left you see the manganese cluster is splitting the water into returns and oxygen is a byproduct and it is supplying the electron. The rich source of electron what I was kind of highlighting on the board.

Now if you look at the b and c, b and c are essentially these molecules, they are the dyes which have been mimicked. The chromophore of the dye or semiconductor which upon absorbing light gets excited, and donates an electrons. This electron is being accepted by protons. So, have to supply proton efficiency the b, have to supply protons, those protons forms hydrogen gas. Whereas you need a electron donor, so in the both cases electron donor is to H 2 O, so electron donor is the water, water-splitting and forming protons, these protons are filtered.

So, basically that two reactions which are happening here. So, you have this water-splitting cluster which is generating protons and oxygen. These protons are filtered through a proton membrane and added with the electron to form hydrogen gas. And on the other hand, this oxygen is a byproduct of this whole processs, when this light reaction is taking place. Whereas, you can do the same thing by having by mimicking or you know reducing the efficiency of the system by having two different dyes the chromophore one and chormophore two, and exactly follow the mechanism what the z scheme of things which is being followed by the natural photo system.

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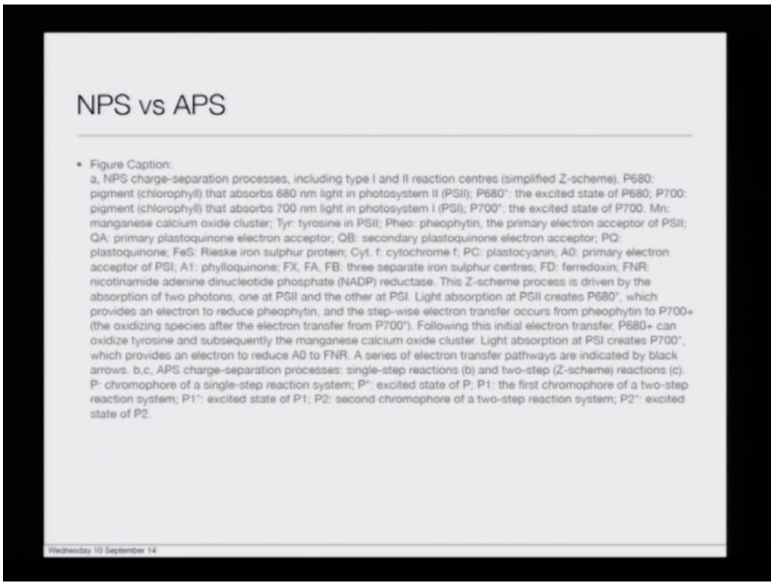

So, this is the overall a, and if you kind of go through the caption of this figure which has been derived from that nature photonics paper. So, this is exactly what it will tell you that and two steps of z scheme reactions of the P is a chromophore last two lines of a single step reaction P excited states. So, that is pretty much you can go through this and that will give you an idea that how this photo systems are working, now if you have emulate these kind of photo systems.

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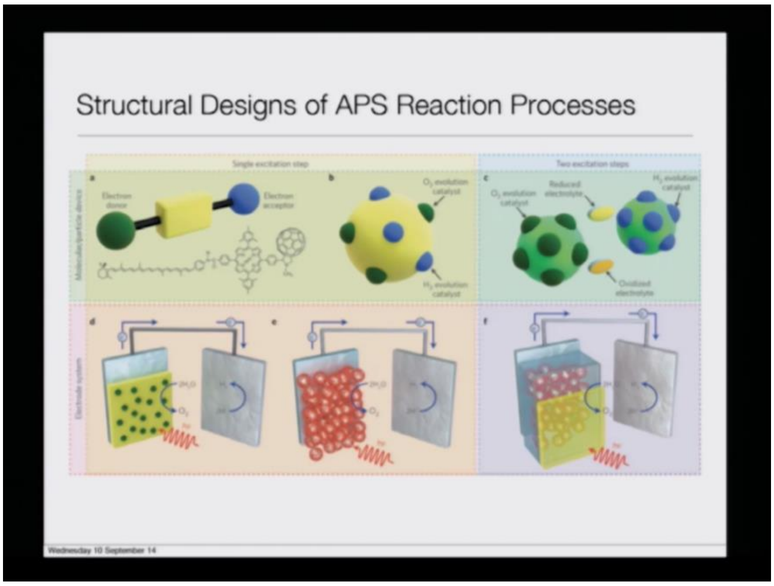

Now next I will coming to the structural designs of APS reaction processes. So, what you need essentially is, if you see the first picture which is the a and the b. So, will talk about a the structure of the carotenoid-porphyrin and fullerene molecular dyad system which is basically this one carotenoid-porphyrin and fullerene. So, where the carotenoid, you could see the long stretch molecule, long tail molecule at a. When you see the porphyrin which is sitting out there, which is an molecule which is the same molecule as your chlorophyll, and you have the fullerene ball on the other side. So, there is a single step semiconductor particle attached hydrogen oxygen evolving co-catalyst. So, this is the oxygen evolution catalyst and hydrogen evolution catalyst. So, these are the kind of geometries what are been followed if you go to the two excitation process where you have two different molecule.

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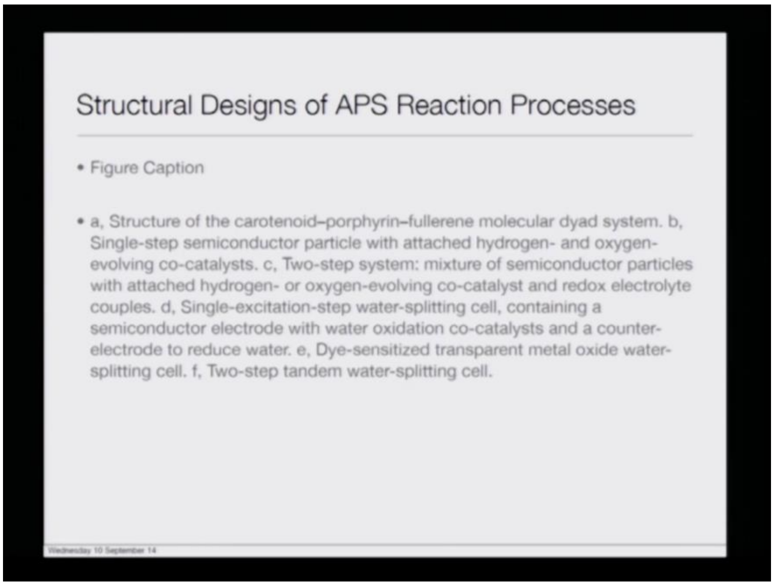

So, which you follow the c, you see at c, two-step system: mixture of semiconductor particle which attached hydrogen oxygen-evolving co-catalyst and redox electrolyte couples. So, this is very interesting out here where you two systems which is basically trying to emulate this kind of system where you see the one chromophore and the second chromophore mimicking the z scheme of things. Then you have the electrode system. So, this whole area has evolved at two different level. So, you need to develop high end electrodes for this and you need to develop molecules which will split the water as well as you need molecules which will in the by the action will absorb light and do this job. So, where this all started you have to go back in time.

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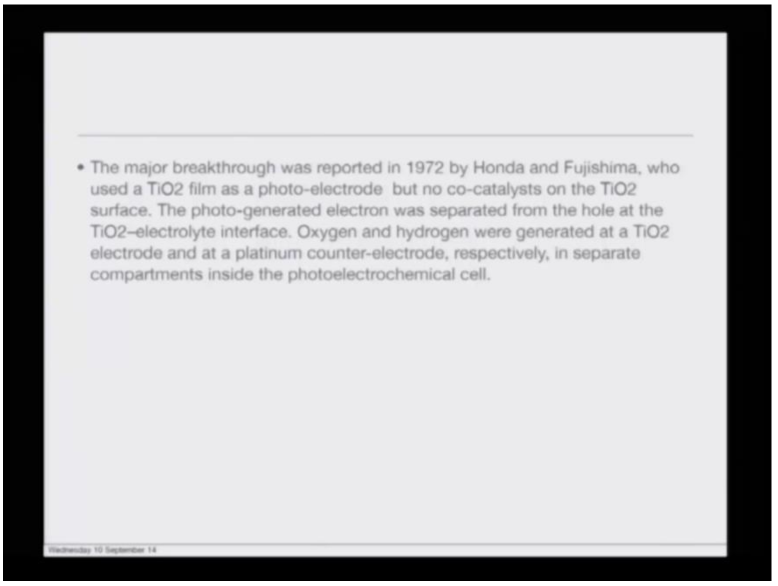

So, this is the major breakthrough in 1972 by Honda and Fujishima, who actually during this was a PAT problem and Tokyo university while he was doing it. What he was doing, he was developing titanium dioxide for ((Refer Time: 22:11)) purpose, and what he found out is that is pretty much lead the foundation stone of self-cleaning glasses. He was using, so now if you kind of go to the slide who used a titanium dioxide film as a photo electrode, but no co-catalyst on the titanium oxide surface, and this titanium oxide surface a photo generated electron was separated from the hole at titanium dioxide and electrolyte interface. So, this was the first evidence where titanium dioxide could split the water, the oxygen and hydrogen generated at a titanium dioxide electrode and a platinum counter-electrode respectively, in separate compartments inside the photo electrochemical cell.

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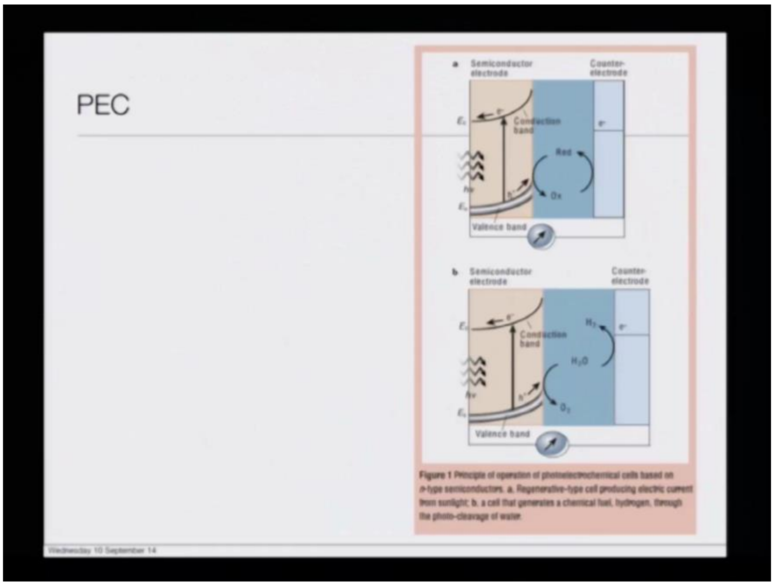

So, this was the first you can say that this was the first breakthrough, which lead the foundation stone for photo electrochemical cell, and what are photo electrochemical cell is I will give you the reference by just for your understanding here just for simple understanding. So, basically the principle of operation of based on the n-type semiconductors, and I will give you the exact reference you please go through what is PC, basically PCs are a hybrid device of semiconductor and electrolytes. It is these are not the pure dry kind of situations.

So, there is an electrolyte and there is semiconductor and I will give you a very nice reference which I have already highlighted here by Michael Gratzel on the photo electrochemical cell that is the title of the paper. Please go through that paper, I really wish you people to go through that I will be supplying the paper anyway; go through that paper because that paper will give you an idea about how this whole concept of photo electrochemical cell because that will be needed in order to understand the Gratzel cells or the dye sensitized solar cells.

So, before I come coming back to where I was, so there are two level, where these kind of things have to be developed. The other level is the. So, let us divide the problem. So, you need to develop the enumerated you need the water splitting chemicals which will split the water. You need an electrode system, which will capture the electrons, and then you have to put this whole thing in one assembly. So, the last two d, e, f what you see is essentially your the electrode system what has been developed. Single-excitation-step water-splitting cell, containing a semiconductor electrode with water oxidation co-catalysts and a counter-electrode to reduce water. So, have both the things on one electrode you are oxidizing the water; there is another electrode where reducing the water. Then you have dye sensitized transparent metal oxide water splitting cell and the two-step tandem water-splitting cell. So, these are some of the examples of it.

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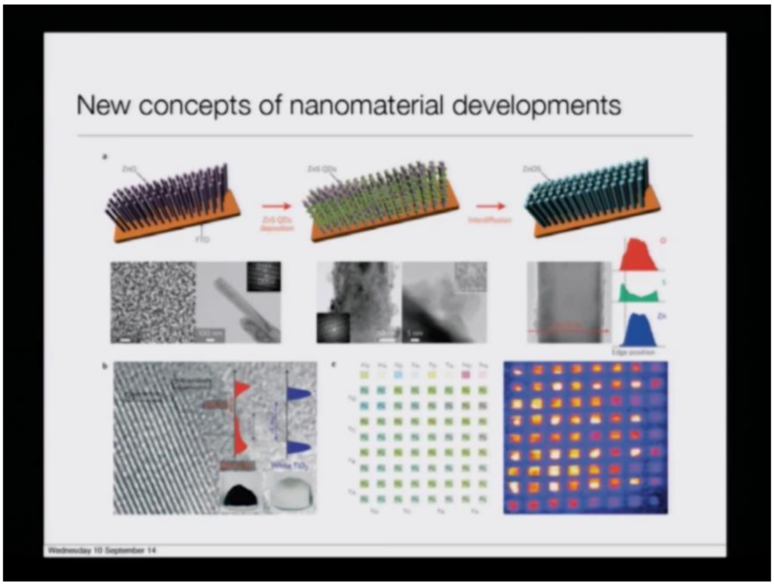

Now coming back to what are the new concepts of nanomaterial development.

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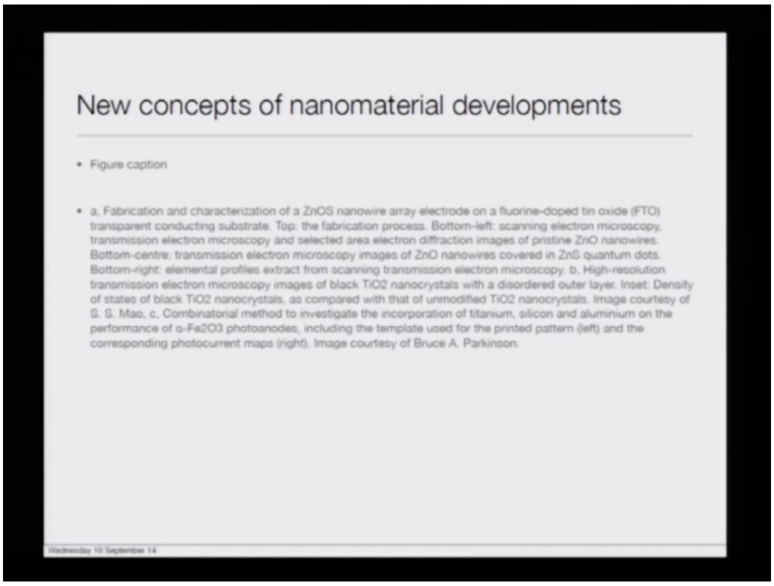

So, you follow this part one which is zinc oxide nanowire array electrode on the fluorine-doped tin oxide transparent conducting substrate. So, you need different kind of transparent conducting substrate, because this process is has to be light dependent; light is the source of energy in order to you know carry out this process. So, there are different kind of you know fluorine-doped tin oxide, which are been developed over a period of time which acts as a transparent conducting substrate. So, there is a lot of work which is kind of currently going on zinc oxide surfaces, and developing different kind of material which are transparent and to allow this process to take place. Please go through the paper reference what I have given you, because that will give you a better idea about what all development has happened in this area.

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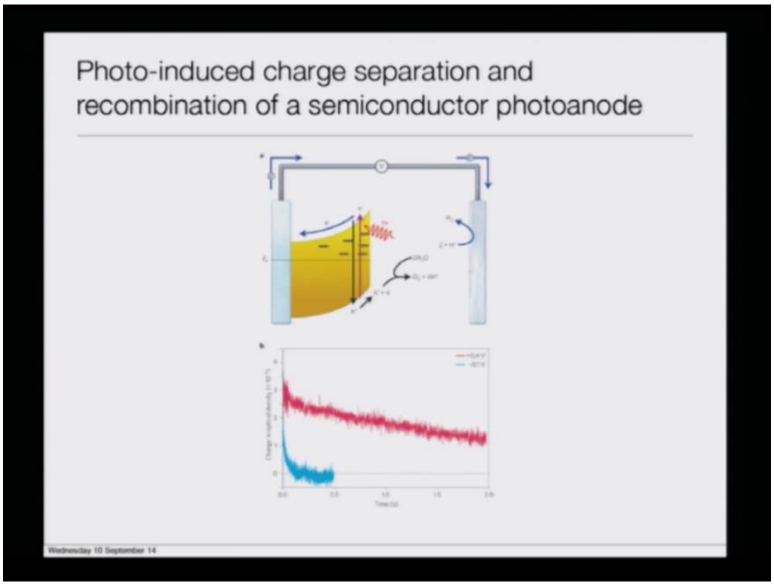

This is what will give you an idea of photo induced charge separation and recombination of a semiconductor photoanode. This is basically, the basic very fundamental principle of the photo electrochemical cell where you have a interface of a semiconductor and a electrolyte, and where the water-splitting is taking place.

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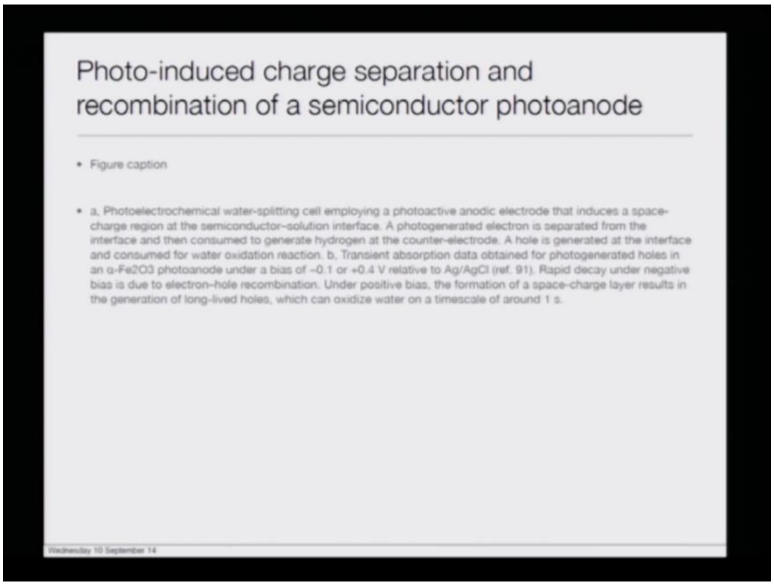

So, this is basically what is happening in a photo electrochemical, water-splitting cell, employing a photoactive anodic electrode that induces a space-charge region at the semiconductor-solution interface. The photogenerated electron is separated from the interface and then consume to generate hydrogen at the counter electrode. A hole is generated at the interface and consumed for water oxidation reaction. So, this is pretty much what is happening. So, you are splitting the water, you are getting the protons through a membrane on one side, where you are again reducing it by adding electron to make hydrogen. So, this is the overall kind of scheme of things.

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If some day, if this whole thing really works out that we are able to mimic the manganese cluster in near future on far future, these are some of the… So, if you look at this, this is kind of a dream where will have hydrogen power plants which will be present which will be generating hydrogen. And hydrogen will be supplied as the major energy source or for you know pretty much everything what you see all over apart from the other sources which are like photovoltaic power, and underground electron and the wind power and likewise and so on and so forth.

So, what I wanted to highlight here is that you have to realize a biology is no more just community where studying all these molecules. But biology is an inspiration now bio-mimicry bio-mimetic, it is an inspiration for generations now a physicist, chemist, electronics who are trying to emulate these wonderful structures what nature has already developed. Because even if you could understand as I always tell that you know ten percent of it, we can really, not only you can dream, we can really achieve clean and green energy all over the earth.

So, in that whole process, so as I told you the beginning of the lecture that we will be talking about the two set of development. One set of development is in terms of the hydrogen fuel. The other set of development will be where the chlorophyll dye has been mimicked or there are synthetic chlorophylls or the inorganic molecules like ruthenium and all which is the ability to behave like chlorophyll, but those things always needed. Whenever we talk about natural, whenever we talk about those kind of dyes they always needed a system again that what I was trying to tell you this one. You always needed a source of electron which will ensure that once they get oxidized by donating an electron, they should be brought back to their ground state.

So, this is very very essential for us to understand that this whole processes, if you follow these three lines very carefully, who is the donor of electron, who is the acceptor of electron, and who is the perennial source of electron, it is all about these things. While this whole photosynthesis, water-splitting, photo system two, photo system one, hydrogen generation and pretty much, all the power generation processes happening in biological systems are kind of govern. So, this is the overall scheme of things. In next lecture will be talking about the dye sensitized solar cells followed by one of the lectures probably the thirty eight lecture we will be talking about iron disulphide solar cells and iron disulphide. So, these are the different inspiration what has been which has been drawn over the period of time, in order to you know emulate some of the feed which nature has already achieved we are just trying to mimic nature.

So, with this, I will closing and please go through all the references what I am giving, because they really are very good references, please because within limits of a class you cannot explain everything. So, you have to really go through some of these references wherever it is needed I tried to you know who as much as I can. As a generic audience, I will have to be careful, but please read through those references, because they will help you to clear some of your basic, specially please read through this nature photo electrochemical cell references, this will be very helpful to understand gratzel cell as well as the hydrogen generation.

Thanks a lot.