Chapter 5

PHOTOELECTROLYIS OF WATER – HOLY GRAILOF ELECTROCHEMSTRY

5.1. Introduction

Historically, the discovery of photo-electrolysis of water directly into oxygen at a TiO_2 electrode and hydrogen at a Pt electrode by the illumination of light greater than the band gap of TiO_2 [~3.1 eV] is attributed to Fujishima and Honda [1] though photocatalysis by ZnO and TiO_2 has been reported much earlier by Markham in 1955. For more details of the origin of photocatalysis refer to ref.2.

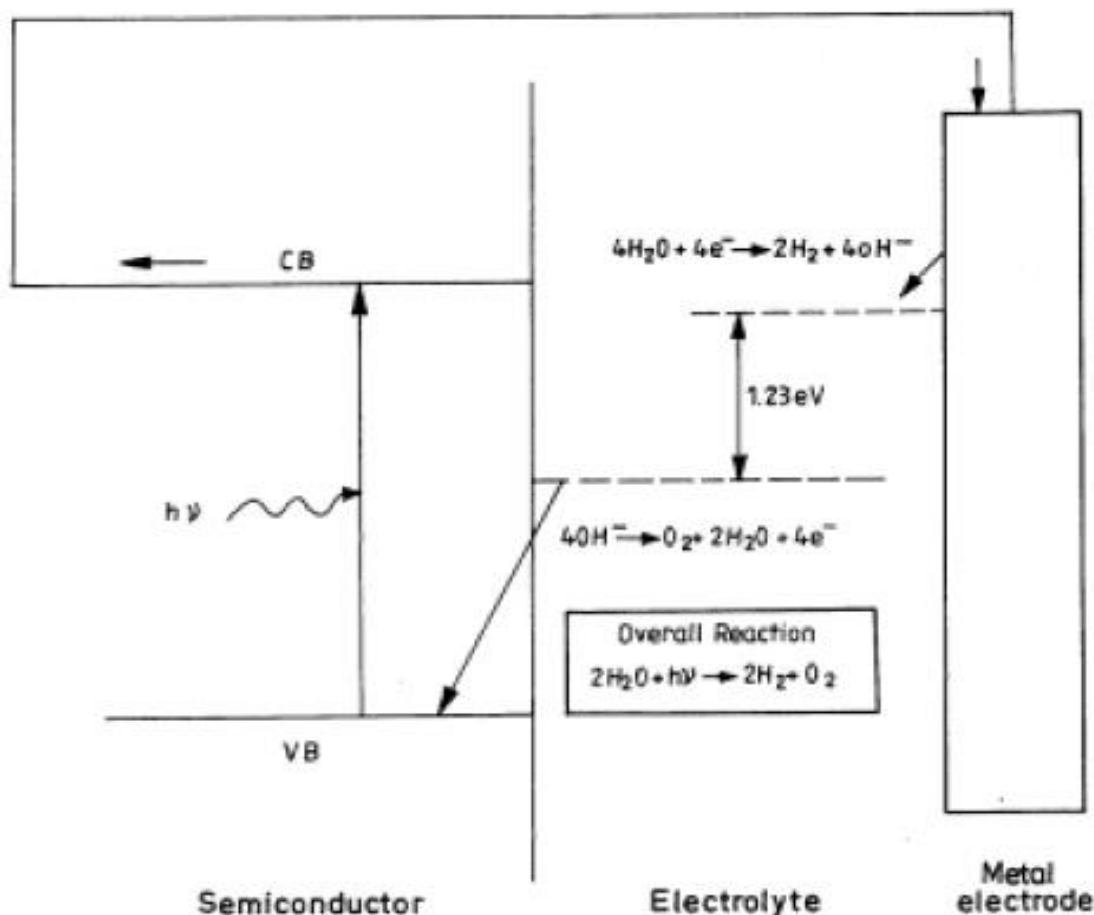In simple terms the essential reactions taking place are shown schematically in Fig.5.1.

Fig.5.1. Schematic simple representation of photo-electrolysis of water

Using these postulates, the known semiconductors and the possibility of water splitting reaction taking place on their surfaces are pictorially shown in Fig.5.2.
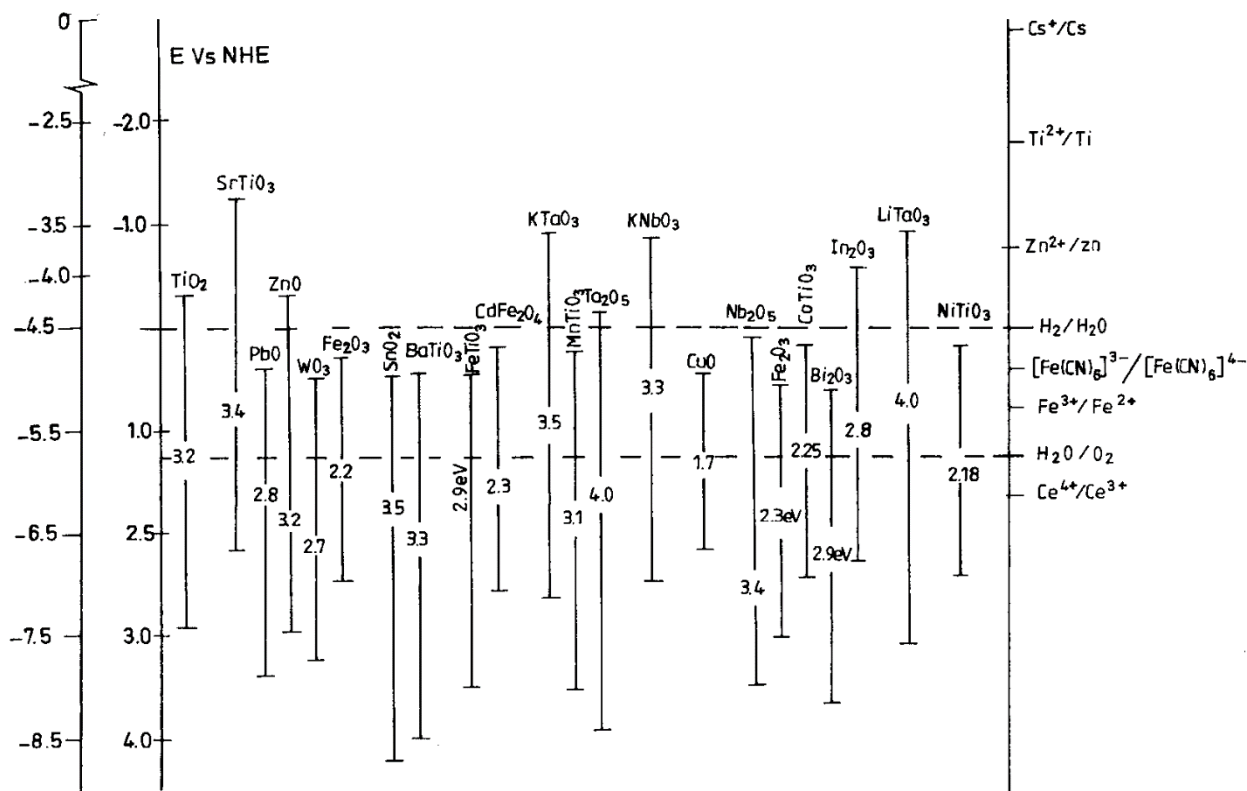

Fig.5.2 Some of the well-known semiconductors, their band gap values and hydrogen and oxygen evolution potential are shown. From these, one can make a choice of semiconductors which can decompose water. On the right side some other common redox potential values are also given to indicate which other redox reactions are possible. The left -hand side scale is the absolute energy scale and the electrochemical scale is also shown as second vertical axis in the left-hand side. On the right hand the redox potential values of selected redox reactions are given.

The H_2 production rate is normally measured in the units of micromoles of H_2 evolved per hour per gram of the catalyst employed and the photon current density in terms of mA cm^{-2}. The wavelength and intensity of the incident radiation are a few of the other parameters of relevance. However, the set up used to measure these data are mostly home-made and different from each other, varied results are obtained and hence, it is necessary to report the results in a consistent manner. In order to compare the results from different sources two parameters are often employed namely the quantum yield (QY) or apparent quantum Yield (AQY) and they are defined as follows:

(QY) % = (Number of electrons reacted / Number of photons absorbed) X 100... (1)

(AQY)%-(No of electrons reacted/No of incident electrons) X 100 …………(2)

AQY% = (No of evolved hydrogen moleculesX2/ no of incident photons) X 100 .(3)

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However, in the solar water splitting reaction, the incident radiation creates electron and hole pairs and these were to take part in the surface reaction, then high efficiency will be desirable. However, in this transport of charge carriers, there can be recombination and so the solar to hydrogen conversion efficiency may be different. Hence, another parameter is often used namely the solar to hydrogen conversion efficiency (STH) defined as follows:

STH% - (Output energy of hydrogen /energy of input solar light) $AM_{1.5G}$ X 100 .(4)

$= [(\text{m moles of hydrogen/s x 237kJ/mol})/(P_{incident}(mW.cm^2) \text{ X Area}(cm^2))] AM_{1.5G} X100$

5.2. Selection of Semiconductors for the decomposition of water

Various conceptual principles have been incorporated into typical TiO_2 catalyst system so as to make this system responsive to longer wavelength radiations. These efforts can be classified as follows:

- 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.

All these attempts are some kind sensitizations and hence the route of charge transfer has been extended and hence the efficiency could not be increased considerably.

The available opportunities include:

(1) Identifying and designing new semiconductor materials with considerable conversion efficiency and stability
(2) Constructing multilayer systems or using sensitizing species including dyes – increase of absorption of solar radiation
(3) Formulating multi-junction systems or coupled systems - optimize and utilize the possible regions of solar radiation
(4) Developing nano-size systems to efficiently dissociate water

These are mostly tried possibilities and there can be other avenues and these will come up in subsequent chapters. In these opportunities, the attempts so far made include:

- Deposition techniques have been considerably perfected and hence can be exploited in various other applications like in thin film technology especially for various devices and sensory applications.
- The knowledge of the defect chemistry has been considerably improved and developed.
- Optical collectors, mirrors and all optical analysis capability have increased which can be exploited in many other future optical devices.

- The understanding of the electronic structure of materials has been advanced and this has helped to our background in materials chemistry.
- Many semiconductor electrodes have been developed, which can be useful for all other kinds of electrochemical devices.

In spite of all these concerted attempts, there is only limited success in developing a viable semiconductor with maximum efficiency for the decomposition of water. The main reasons for this limited success in all these directions are due to:

- The electronic structure of the semiconductor controls the reaction and engineering these electronic structures without deterioration of the stability of the resulting system appears to be a difficult proposition.
- The most obvious thermodynamic barriers to the reaction and the thermodynamic balances that can be achieved in these processes give little scope for remarkable improvements in the efficiency of the systems as they have been conceived and operated. Totally new formulations which can still satisfy the existing thermodynamic barriers have to be devised.
- The charge transfer processes at the interface, even though a well-studied subject in electrochemistry, has to be understood more explicitly, in terms of interfacial energetics as well as kinetics. Till such an explicit knowledge is available, designing systems will have to be based on trial and error rather than based on sound logical scientific reasoning.
- Nanocrystalline (mainly oxides like TiO_2, ZnO, SnO and Nb_2O_5 or chalcogenides like CdSe) mesoscopic semiconductor materials with high internal surface area and can be made in nano scale and thus effectively absorb solar radiation.
- If a dye were to be adsorbed as a monolayer on the semiconductor surface, 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.
- Another aspect of the nano crystalline state is the alteration of the band gap to larger values as compared to the bulk material which may facilitate both the oxidation/reduction reactions that cannot normally proceed on bulk semiconductors.
- The response of a single crystal anatase can be compared with that of the 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 only 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. This increase is due to better light harvesting capacity of the dye sensitized nano crystalline material but also due to mesoscopic film texture favouring photo-generation and collection of charge carriers.
- It is clear therefore that the nano crystalline state in combination with suitable sensitization is one another alternative which is worth investigating.

- The second option is to promote water splitting in the visible range using Tandem ells. In this a thin film of a nanocrystalline WO_3 or Fe_2O_3 may serve as top electrode absorbing blue part of the solar spectrum. The positive holes generated oxidize water to oxygen

$$4h+ + 2H_2O \rightarrow O_2 + 4 H^+$$
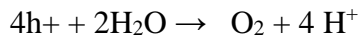
- The electrons in the conduction band are fed to the second photo-system consisting of the dye sensitized nano crystalline TiO_2 and since this is placed below the top layer it absorbs the green or red part of the solar spectrum that is transmitted through the top electrode. The photo voltage generated in the second photo system favours hydrogen generation by the reaction

$$4H+ + 4e- \rightarrow 2H_2$$
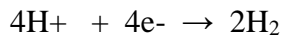
- The overall reaction is the splitting of water utilizing visible light. The situation is similar to what is obtained in photosynthesis.
- Dye sensitized solid hetero-junctions and extremely thin absorber solar cells have also been designed with light absorber and charge transport material being selected independently so as to optimize solar energy harvesting and high photovoltaic output. However, the conversion efficiencies of these configurations have not been remarkably high.
- Soft junctions, especially organic solar cells, based on interpenetrating polymer networks, polymer/fullerene blends, halogen doped organic crystals and a variety of conducting polymers have been examined. Though the conversion efficiency of incident photons is high, the performance of the cell declined rapidly. Long term stability will be a stumbling block for large scale application of polymer solar cells.[3,4]

5.3. New Opportunities

Thus, this field has given rise to new opportunities in science and these can be listed as follows:

1. New semi-conducting materials with conversion efficiencies and stability have been identified. These are not only simple oxides, sulphides but also multi-component oxides based on perovskites and spinels.
2. Multilayer configurations have been proposed for absorption of different wavelength regions. In these systems the control of the thickness of each layer has been mainly focused on.
3. Sensitization by dyes and other anchored molecular species have been suggested as an alternative to extend the wavelength region of absorption.
4. The coupled systems, thus giving rise to multi-junctions is another approach which is being pursued in recent times with some success
5. Activation of semiconductors by suitable catalysts for water decomposition has always fascinated scientists and this has resulted in various metal or metal oxide (catalysts) loaded semiconductors being used as photo-anodes.
6. Recently a combinatorial electrochemical synthesis and characterization route has been considered for developing tungsten based mixed metal oxides and this has thrown open yet another opportunity to quickly screen and evaluate the performances of a variety of

          systems and to evolve suitable composition-function relationships which can be used to predict appropriate compositions for the desired manifestations of the functions.

7. It has been shown that each of these concepts, though have their own merits and innovations, have not yielded the desired levels of efficiency. The main reason for this failure appears to be that it is still not yet possible to modulate the electronic structure of the semiconductor in the required directions as well as control the electron transfer process in the desired direction.

In spite of all these efforts, there is still no economically viable semiconductor material identified for the decomposition of water.   The success in this attempt will give a boost to the energy needs of this universe.

Semiconductors with high ionicity are stable against corrosion and passivation. However, they require the ultra violet region of the electromagnetic spectrum. As stated earlier, threshold behaviour is important in photo-electrochemistry to maximize the use of solar spectrum. In this sense, for water decomposition materials with band gap between 1.3 to 1.8 are the optimum type of semiconductors for maximizing the efficiency of the water decomposition reaction. This means one wishes to make use of the visible range of the solar spectrum.

Light absorption by a semiconducting solid is governed by Beer's law

$A = \ln (I/I_o) = \alpha l$ or $T = (I/I_0) = \exp (-\alpha l)$

Where I and I_0 – transmitted and incident light intensity and α is called the absorption coefficient. Semiconductors can be classified as direct or indirect band semiconductors. Direct band gap semiconductors have large absorption coefficient (10^4 -10^5 cm^{-1}).

The absorption coefficient for these materials is given by the equation,

   (Alpha) $\alpha = [A(h\nu)– E_g)^m] /h\nu$

In this equation m is a constant which depends on the optical transition, m=2 for an indirect band gap semi-conductor and ½ for a direct band gap semi-conductor.

Intrinsic carrier concentration in semiconductors is normally low and the equation concerning this parameter is given by

    $N_j p_i \propto \exp(-E_g/kT)$

Doping generally increases the conductivity of the semiconductor and able to control other electronic properties. Doping with other valent ions or even the crystal defects can also behave as dopants. Therefore, conductivity can be controlled by doping and is given by the expression

Sigma $= \sigma = qn\mu_n + qp\mu_p$

Where μ_n and μ_p are the charge carrier mobilities

The processes that take place on a semiconductor powdered material can be visualized as follows:
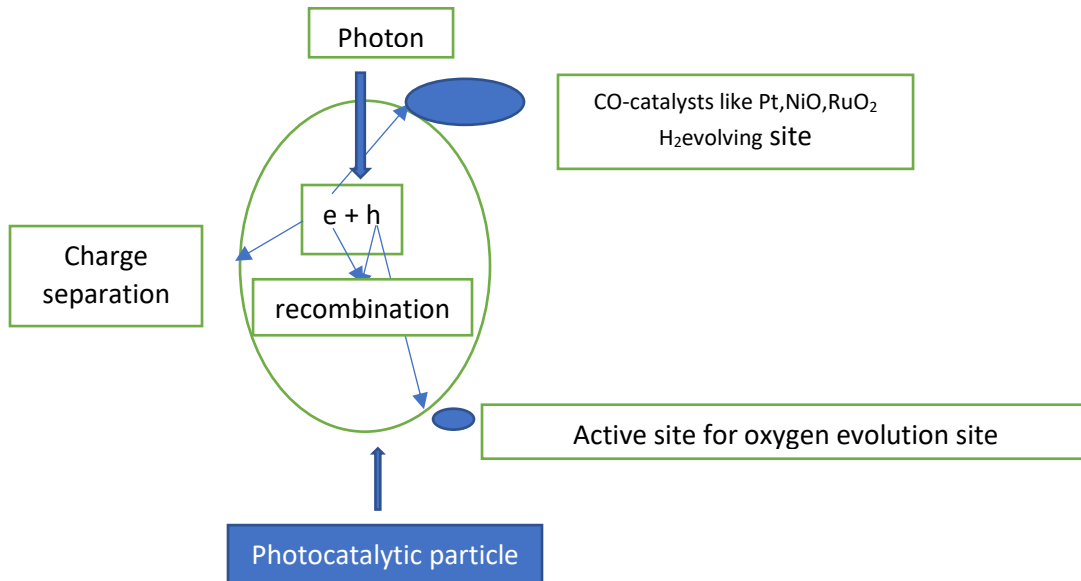

Fig.5.3. Typical processes that occur on photoactive semiconductor

At this stage, we need to understand the structure of electrode-electrolyte interface and the possibility of charge transfer when the electrode happens to be a semiconductor. The charge transfer depends on the relative energy positions of the donor and that of the acceptor. Flat band potential is defined no band as Flat bending situation and for highly doped semiconductors, this equals to the bottom of the conduction band. This is defined by the following equation:

$V_{fb} = E_0 - \chi + (1/2) E_g$ where χ is the value of electronegativity in Mulliken's scale.

The charge transfer abilities of a semiconductor electrode depend on whether there is an accumulation or depletion layer. If there is an accumulation layer – behaves as metallic electrode-since excess of majority charge carriers available for charge transfer.

If there is a depletion layer - there are few charge carriers available and the electron transfer reaction occurs slowly. However, if the electrode is exposed to radiation of sufficient energy. electron hole pairs are produced. If the processes occur within the interior of semiconductor, the heat and recombination take place. If it occurs in the space charge region, the electric field in this region will cause the separation of the charge. The suitable conditions can be

1, Sufficiently high (visible) light absorption

 2. High stability in dark and under illumination (no photo corrosion)

3. Suitable band edge positions to enable the reduction/oxidation of water by the photo generated holes /electrons

4. Efficient charge transport in the semiconductor

5. Low over potentials for the reduction/oxidation reaction (high catalytic activity).

5.4.. **Stability against photo corrosion**

Most important property that limits the usefulness of many photo-active materials is the stability of the semiconductor. Many non-oxide semiconductors (Si, Ga As, GaP, and so on) either dissolve or form a thin oxide film which prevents the electron transfer across the interface. Almost all M-O photo anodes are thermodynamically unstable! TiO_2 and SnO_2 show excellent stability over a wide range of pH and applied potential. ZnO always decomposes, Fe_2O_3 shows an intermediate case (pH and oxygen stoichiometry)

Requirement of band positions: Conduction and valence band edges should straddle the reduction and oxidation potential of water . Specifically, E_{CB} should be above or less in numerical value E_{red} and E_{VB} should be below or more numerical value of E_{ox}.

The exciton life time is a very important criterion is the hole transfer across the n type semi-conductor-electrolyte interface. It should be fast enough to compete with photo-corrosion and to avoid accumulation. Loading of metals like Cu, Ag, Au, Ni, Pd, Rh and Pt over a variety of metal oxide semiconductors results efficient charge separation! Pt is well known as an excellent co-catalyst for hydrogen evolution. The addition of carbonated salts or other electron mediators enhance the hydrogen production by preventing backward reaction.

Mixed metals oxide semiconductors [NiO over $SrTiO_3 – NiO(H_2)$, $SrTiO_3$ $(O_2$) RuO_2 over TiO_2 -30 times bigger activity than TiO_2 alone] But if the concentration of RuO_2 exceeds a limit-act as electron hole recombination centers !!! ⌉ In the presence of co-catalysts such as NiO –highly active niobates , titanates and tantalates are reported ($NiO/NaTaO_3$).

Visible light activity : There are methods by which photocatalysts can be fabricated, by which they respond in the visible light. Valence band formation using elements other than oxygen [BiVO4, AgNbO3, Ag3 VO4 , Ca2 Bi2 O4 ....]

Ion doping: Cation doping - transition metals (V, Cr, Fe, Mo, Ru, Os, Re, Rh, V, etc.) -rare earth metals doped ion create new (impurity) energy levels. metal ion dopants act as electron or hole traps

Doping of anions such as N, F, C, Si in metal oxides or mixed metal oxides can shift in photo response into the visible region ¬ little tendency to form recombination centers - remarkable thing Z-scheme construction.

 Dual semiconductor system Dye-sensitization Dye molecules absorb light with the transfer of an electron from the ground state to excited state. The excited electron goes to the conduction band of an appropriate metal oxide.

References

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