

CHAPTER 4

PHOTOCATALYSIS – WHY SEMICONDUCTORS AND WHAT TYPE OF SEMICONDUCTORS

This branch of science has become popular since 1970s due to the possibility of generating fuel hydrogen from water by the action of photons and on a surface of a semiconductor (TiO_2). The photon energy is utilized in altering the reduction potential of electrons and the oxidation potential of the positive holes of semiconductor.

A band gap is the energy difference between the electrons of the valence band and the conduction band. Essentially, the band gap represents the minimum energy that is required to excite an electron to a state in the conduction band where it can participate in conduction. The next lower energy level is the valence band, and thus if a gap exists between this level and the higher energy conduction band, energy must be input for electrons to change its potential. The magnitude, size and existence of this band gap allow one to visualize the difference between conductors, semiconductors and insulators. These differences can be seen in diagrams known as *band diagrams*, shown in Figure 1. For more detailed account the way bands are formed and other details, one should refer to a text book on solid state Physics [1].

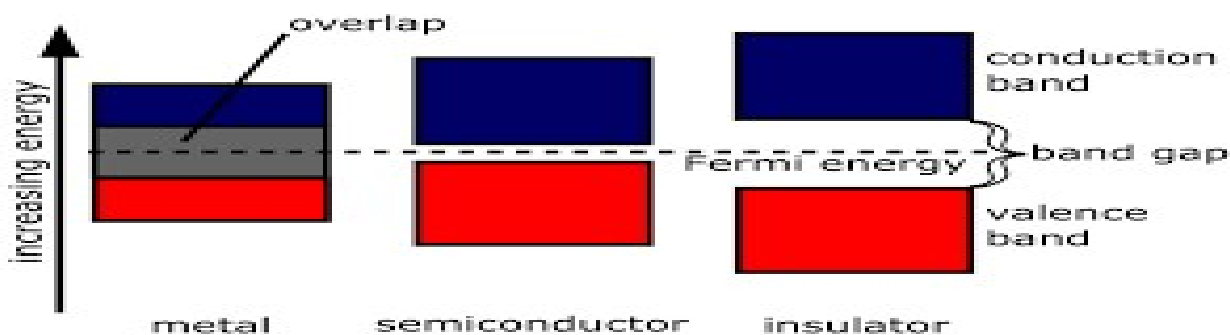


Fig.1. A band diagram with different values of band gaps for conductors (~ 0 eV), semiconductors (0-3 eV), and insulators (>4 eV)

The energy positions of the bottom of the conduction band should be more positive with respect to the reduction potential of the substrate and the top of the valence band should be more positive with respect to the oxidation potential of the

substrate. Here the potential scale used is the electrochemical scale not with respect to the absolute scale. This is pictorially shown in Figure.2.

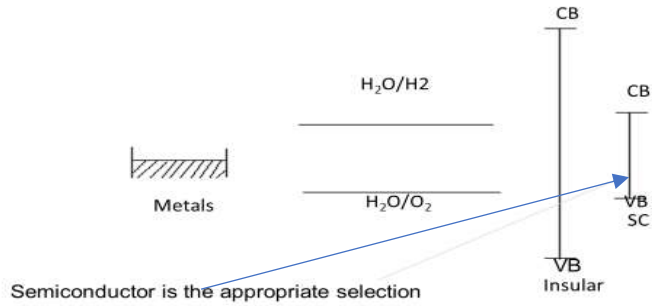


Fig.2 Water decomposition reaction and metals, semiconductors and insulators – why semiconductor band positions are favourable for this reaction.

Among the various semi-conductors, for water decomposition reaction which ones are suitable or not is shown in Fig.3.

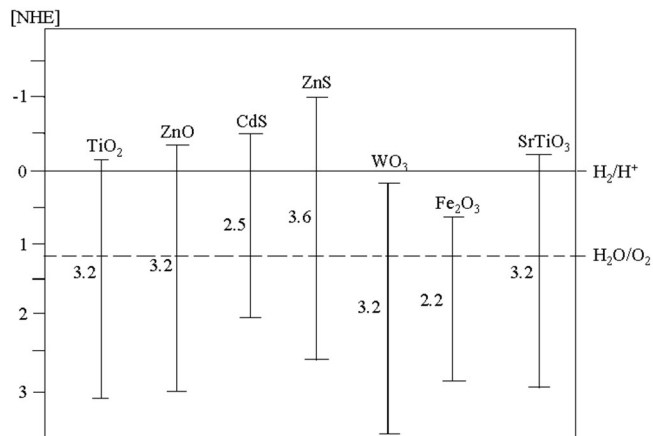
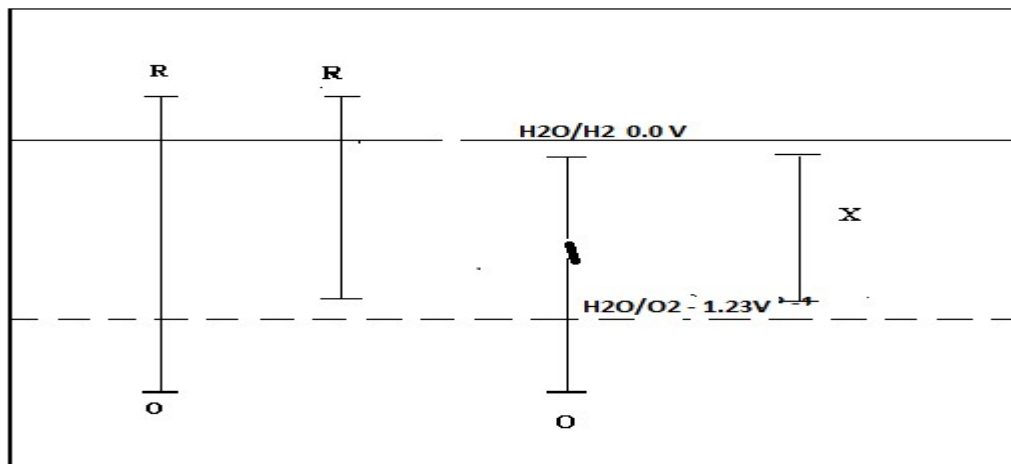


Fig.3. For water decomposition only those semiconductors whose conduction band bottom is more negative with respect to hydrogen evolution reaction and valence band maximum must be more positive with respect to oxygen evolution reaction. On this basis, the known semiconductors can be classified as reuction (R) type oxidation (O) type or OR type or X type where both the reactions are not possible.

This leads one to classify the known semiconductors into 4 different types, namely the ones that will promote both oxidation and reduction reactions simultaneously designated as OR type. If the chosen semiconductor promotes either of the reaction, then they are termed as O or R type and the systems that cannot promote either of the reactions is called X type. This classification is based on the relative positions of the redox potentials and the bottom of the conduction band and the top of the valence band. A pictorial representation of these 4 different types of semiconductors is shown in Figure 4.

Fig. 4. Types of semiconductors reduction (R) type; Oxidation type (O) Both reactions (OR) and neither of them (X) type



There can be competing reactions and instead of the water decomposition reactions these reactions will take place. For example, the case of ZnO semiconductor is considered here. If the dissolution potential of Zn^{2+} were to be more positive to hydrogen evolution reaction then this reaction will occur in preference to the hydrogen evolution. This process is called photo-corrosion and thus the material loss will take place. To prevent this type of degradation some deposits may be coated but it may adversely affect the photon absorption capacity of the semiconductor. These situations are shown in Figure 5 with respect to the energy scale with reference to Normal Hydrogen Electrode (NHE).

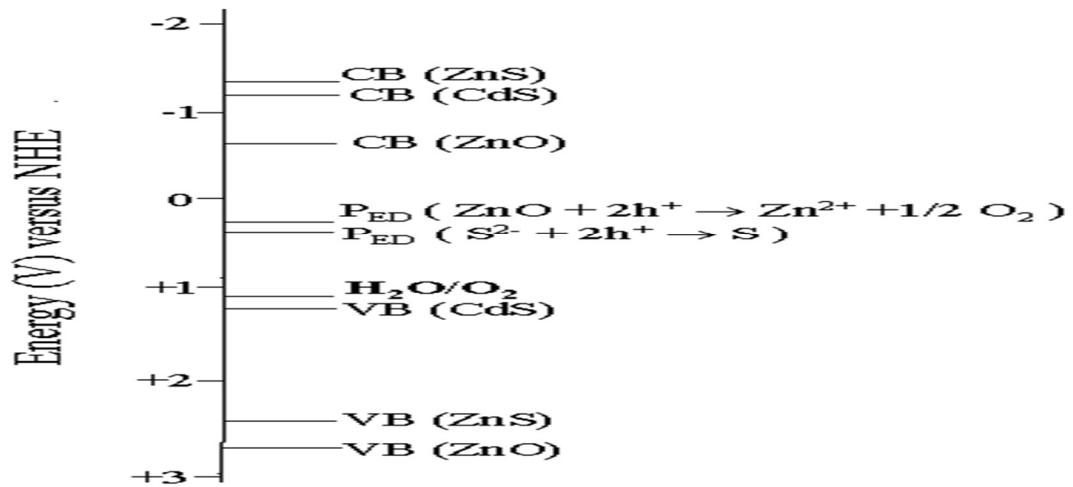


Fig.5. The energy scale for conduction band and valence band for a few semiconductors and the preferred photo corrosion reactions

When a semiconductor is irradiated with light whose wave length is equal to or shorter than the band gap value, an electron from the valence band will be excited and occupy an energy state in the conduction band. The positively charged state will remain in the valence band. Both these charged states can be utilized to promote a reduction reaction (electron) and an oxidation reaction (positive charged state) But for these reactions to take place, the charged states have to migrate to the surface. During this process, the charge states can recombine and thus not suitable for promoting the redox reaction. This recombination can take place in the bulk of the semiconductor or at the surface of the semiconductor.

These processes are pictorially shown in Figure.6.

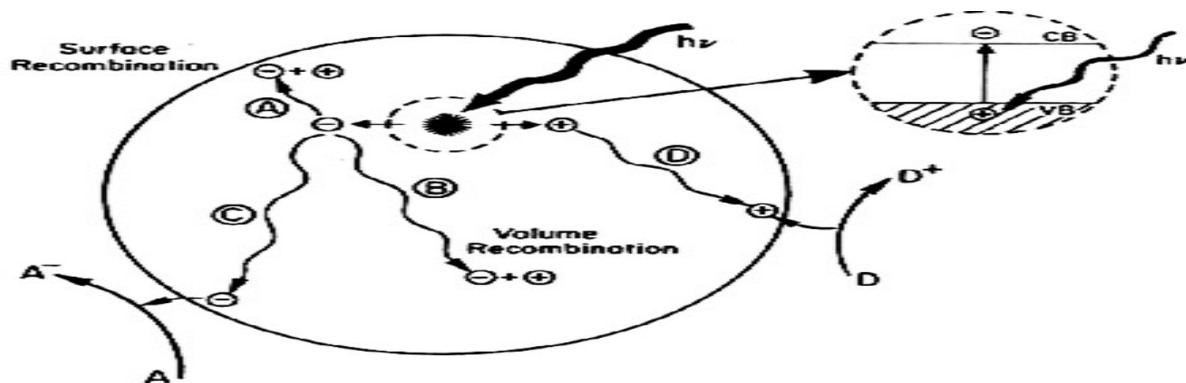


Fig. 6. Creation of exciton and their process in the semiconductor and the donor and the acceptor reactions with the substrate [reproduced from ref A. Millis and S. L. Hunte *J. Photochem. Photobiol. A: Chem* 180 (1997) 1; ref 2]

Many types of sensitization are possible to facilitate the charge separation and utilizing the charged states in the proposed redox reactions. One of the methods goes with the name “*doping*” which can be incorporation or inclusion of alter valent ionic species in the semiconductor. For example, in ZnO semiconductor. if either Li_2O is doped creating positive charged state and termed as p-type or doping with Ga_2O_3 (creates excess electronic states to facilitate the reduction reaction) and is termed as n-type doping.

One another striking way of sensitization, is called coupling of semiconductors. To make use of the radiation whose wavelength is longer than that is suitable for the semiconductor, then one can use a semiconductor whose band gap is suitable for the light radiation available the charge states can be created in the second semiconductor and if the energy positions of the excitation states are suitable for transfer to the original semiconductor then these charged states can be utilized in the redox reaction. The situation considered is shown in Figure 7.

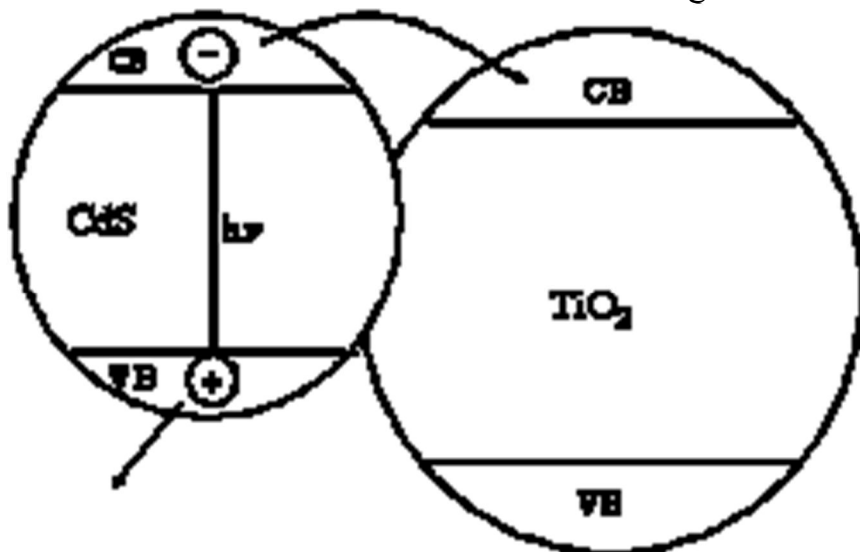


Fig.7. Coupling of semiconductors and the energy levels of the valence band and the conduction band positions facilitate the excited charged states to transfer to the original semiconductor.

For conventional redox reactions, one is interested in either reduction or oxidation of a substrate. In water decomposition, both the reactions have to take place at the rates corresponding to the stoichiometry of the molecule, namely for every mole of hydrogen evolved, half a mole of oxygen has to evolve.

For example, consider that one is interested in the oxidation of Fe^{2+} ions to Fe^{3+} ions then the oxidizing agent that can carry out this oxidation is chosen from the relative

potentials of the oxidizing agent with respect to the redox potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple.

The oxidizing agent chosen should have more positive potential with respect to $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple so as to affect the oxidation, while the oxidizing agent undergoes reduction spontaneously. This situation throws open a number of possible oxidizing agents from which one of them can be easily chosen.

Water splitting - carry out both the redox reactions simultaneously - reduction of hydrogen ions ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) as well as ($2\text{OH}^- + 2\text{h}^+ \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2$) oxygen evolution from the hydroxyl ions. The system that can promote both these reactions simultaneously is essential.

Since in the case of metals the top of the valence band (measure of the oxidizing power) and bottom of the conduction band (measure of the reducing power) are almost identical they cannot be expected to promote a pair of redox reactions separated by a potential of nearly 1.23 V.

Where the top of the valence band and bottom of the conduction band are separated at least by 1.23V in addition to the condition that the potential corresponding to the bottom of the conduction band has to be more negative with respect to the reduction reaction namely hydrogen evolution reaction, while the potential of the top of the valence band has to be more positive to the oxidation potential of the reaction $2\text{OH}^- + 2\text{h}^+ \rightarrow \text{H}_2\text{O} + 1/2 \text{O}_2$.

This situation is obtainable with semiconductors as well as in insulators.

Insulators are not appropriate due to the high value of the band gap which demands high energy photons to create the appropriate excitons for promoting both the reactions. The available photon sources for this energy gap are expensive and again require energy intensive methods. Hence insulators cannot be employed for the purpose of water splitting reaction.

Therefore, it is clear that semiconductors are alone suitable materials for the promotion of water splitting reaction.

Selection of the semiconductor materials

Essentially for photo-catalytic splitting of water, the band edges (the top of valence band and bottom of the conduction band or the oxidizing power and reducing power respectively) have to be shifted in opposite directions so that the reduction reaction and the oxidation reactions are facile.

Ionic solids (for example oxides) as the ionicity of the M-O bond increases, the top of the valence band (mainly contributed by the p- orbitals of oxide ions) becomes less and less positive (since the binding energy of the p orbitals will be decreased due to negative charge on the oxide ions) and the bottom of the conduction band will be stabilized to higher binding energy values due to the positive charge on the metal ions which is not favourable for the hydrogen reduction reaction.

More ionic the M-O bond of the semiconductor is, the less suitable the material is for the photo-catalytic splitting of water. The bond polarity can be estimated from the expression: Percentage ionic character (%) = $[(1 - e^{(\chi_A - \chi_B)^2/4})^2] \times 100$

Table 1 Percentage ionic characters of some of the commonly employed semiconductors

Semiconductors	M -X	Percentage ionic character
TiO ₂	Ti-O	59.5
SrTiO ₃	Ti-O-Sr	68.5
Fe ₂ O ₃	Fe-O	47.3
ZnO	Zn-O	55.5
WO ₃	W-O	57.5
CdS	Cd-S	17.6
CdSe	Cd-Se	16.5
LaRhO ₃	La-O-Rh	53.0
LaRuO ₃	La-O-Ru	53.5
PbO	Pb-O	26.5
ZnTe	Zn-Te	5.0
ZnAs	Zn-As	6.8
ZnSe	Zn-Se	18.4
ZnS	Zn-S	19.5
GaP	Ga-P	3.5
CuSe	Cu-Se	10.0
BaTiO ₃	Ba-O-Ti	70.8
BaMoS ₂	Ba-S-Mo	4.3
FeTiO ₃	Fe-O-Ti	53.5
KTaO ₃	K-O-Ta	72.7
MnTiO ₃	Mn-O-Ti	59.0
SnO ₂	Sn-O	42.2
Bi ₂ O ₃	Bi-O	39.6

It is seen that we have semiconductors of high ionic character (>40%) or of low ionic character (<20%) and the suitable semiconductor may be those that lie in between since high ionic character has large value of band gap and require ultra violet light and low ionic character systems will lead to more recombination.

The oxide semiconductors though suitable for the photo-catalytic water splitting reaction in terms of the band gap value which is greater than the water decomposition potential of ~ 1.23 V.

Most of these semiconductors have bond character more than 50-60 % and hence modulating them will only lead to increased ionic character and hence the photo-catalytic efficiency of the system may not be increased.

Therefore, from the model developed, the following postulates have been evolved.

The photo-catalytic semiconductors are often used with addition of metals or with other hole trapping agents so that the life time of the excitons created can be increased. This situation is to increase the life time of the excited electron and holes at suitable traps so that the recombination is effectively reduced. In this mode, the positions of the energy bands of the semiconductor and that of the metal overlap appropriately and hence the alteration can be either way and also in this sense only the electrons are trapped at the metal sites and only reduction reaction is enhanced.

Hence, we need stoichiometrically both oxidation and reduction for the water splitting and this reaction will not be achieved by one of the trapping agents namely that is used for electrons or holes. Even if one were to use the trapping agents for both holes and electrons, the relative positions of the edge of the valence band and bottom of the conducting band may not be adjusted in such a way to promote both the reactions simultaneously.

Normally the semiconductors used in photo-catalytic processes are substituted in the cationic positions so as to alter the band gap value.

Even though it may be suitable for using the available solar radiation in the low energy region, it is not possible to use semiconductors whose band gap is less than 1.23 V and anything higher than this may be favourable if both the valence band is depressed and the conduction band is destabilized with respect to the unsubstituted system. Since this situation is not obtainable in many of the available semiconductors by substitution at the cationic positions, this method has not also been successful.

In addition, the dissolution potential of the substituted systems may be more favourable than the water oxidation reaction and hence this will be the preferred path way. These substituted systems or even the bare semiconductors which favour the dissolution reaction will undergo only preferential photo-corrosion and hence cannot be exploited for photo-catalytic pathway. In this case ZnO is a typical example.

Low value of the ionic character also is not suitable since these semiconductors do not have the necessary band gap value of 1.23 V. - the search for utilizing lower end of the visible region is not possible for direct water splitting reaction. If one were to use visible region of the spectrum, then only one of the photo-redox reactions in water splitting may be preferentially promoted and probably this accounts for the frequent observation that non-stoichiometric amounts of oxygen and hydrogen were evolved in the photo-assisted splitting of water. At this point it is necessary to find the available photon sources. As is known the solar radiation is the best source of irradiation in terms of availability and also economic point of view. The available solar spectrum is shown in Figure 8. It is seen that only 5-7% radiation is in ultraviolet region and nearly about 40% is in the visible region. This is the factor for the anxiety to utilize the visible portion of solar radiation. Though this may be true. It has to be considered whether the available ultra-violet region is enough to harness energy for the consumption of earth's requirement. This is a question to ponder and to evolve a solution.

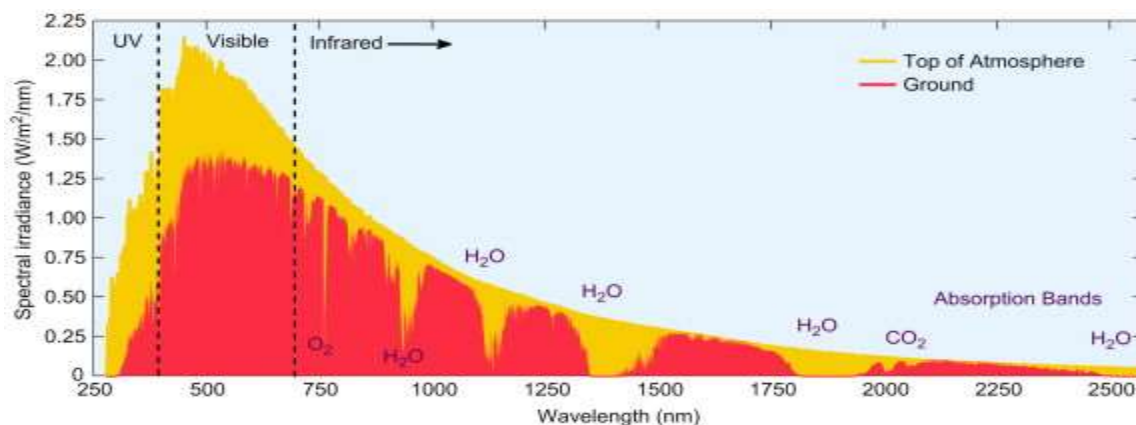


Fig.8 The solar spectrum as a function of wavelength [3]

There essentially a few reactions that are relevant to the society and which can be promoted by photons. These can be listed as follows:

- (1) Photo-assisted decomposition of water for the production of fuel hydrogen [4]
- (2) Photo-catalytic reduction of carbon dioxide to value added products [5]

- (3) Photo-catalytic reduction of dinitrogen to ammonia [6]
- (4) Photocatalytic process in pollution abatement [7]
- (5) Photocatalytic production of fine chemicals [8]

The listed are indicative and in each category, there can be many manifestations.

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