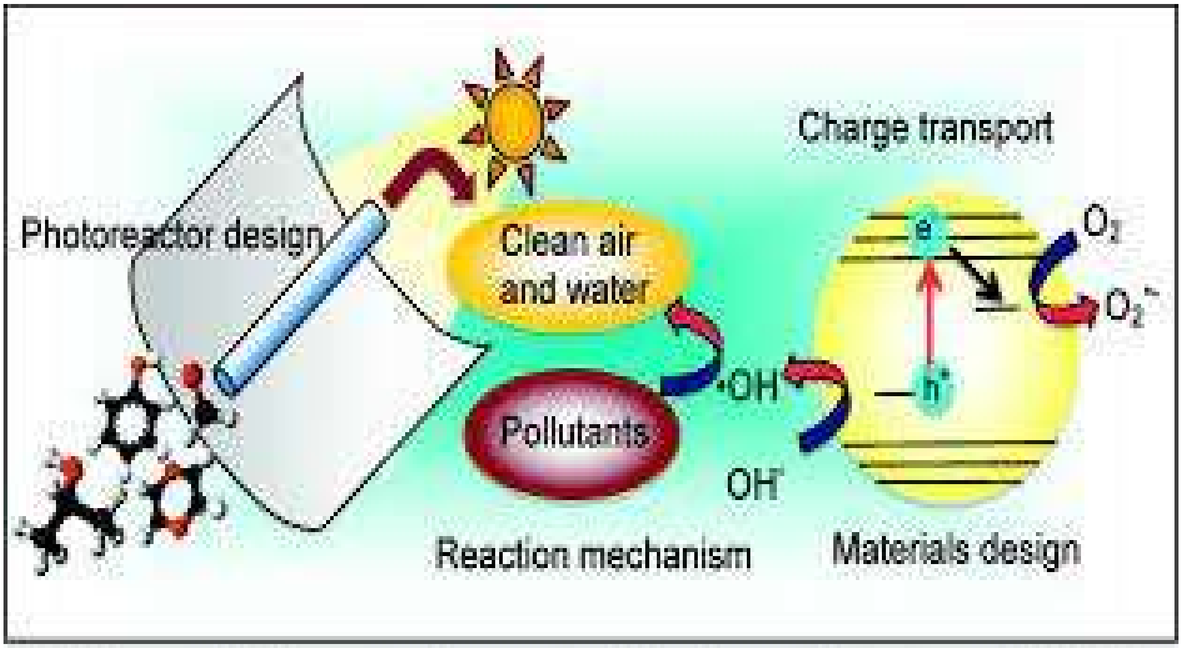
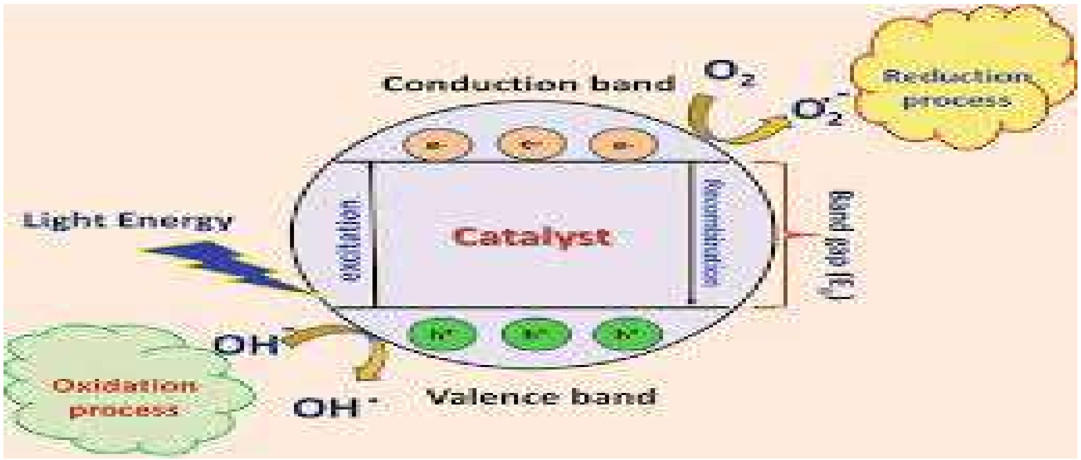
PHOTOCATALYSIS



B. Viswanathan



NATIONAL CENTRE FOR CATALYSIS RESEARCH
INDIAN INSTITUTE OF TECHNOLOGY, MADRAS
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PREFACE

The idea to compile a book on Photocatalysis originated in handling a class for a course on this subject to master degree students for a decade from 2010. However, it must be stated that this compilation is in the draft mode and there can be some figures repeated but they have been retained so that the reader can choose any portion one wants to go through. We are aware there are limitations in this compilation and would like to improve on them and hence the persons who can suggest these steps to improve, we shall be grateful. The author of this compilation has to thank a number of his fellow scholars and to all of them a big thank you since you have been the motivation for attempting this compilation.

We can only assure you that we will refine this compilation in due course. The presentation may not be the best in order of sequence this also can be suggested to improve.

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National Centre for Catalysis Research

March19th,2022

PREFACE

Photocatalysis is an evolving subject on day-to-day basis and this subject has already started as part of our learning curriculum. This branch of science started to grow from the report by the Japanese team announcing the photoelectrochemical decomposition of water on TiO_2 surfaces in the early part of 70s. In this past 50 years this subject has seen many developments, new results, concepts, and applications are evolving on daily basis. This is a field that has revolutionized our approach to energy conversion process and pollution abatement processes have seen new solutions and remedies.

In this past half century, this subject has been responsible for the development of Photo-electrochemistry, the remarkable developments in harnessing solar radiation, the so-called solar cells, and has given rise to many daily use materials like self-cleaning tiles, hydrophobic wind screens and many more. Though the initial enthusiasm to produce fuel (hydrogen) by the photoelectrochemical decomposition of water has not seen great success, this has not hampered the hope and so there are still attempts to make this process viable commercially.

The learning process of this subject has some requisites, namely the subject requires knowledge of solid-state physics, material science, chemical engineering, analytical and synthetic chemistry, and many other disciplines. This situation imposes great barriers, and the learners find it difficult. In addition, non-availability of suitable and concise textbooks is yet another issue in this connection.

The present exercise is an attempt in this direction and the text has been evolved liberally borrowing from the literature available and as stated, this is still an evolving subject and hence the coverage as on-date cannot be completely satisfactory. This text has been evolved as a teaching resource and can have many short comings. The learning community will do a great service if these shortcomings can be brough to attention, so that the text can be improved further. The author is grateful to many members of the scientific community for contributing to the growth of this division of science.
Grateful thanks are due to many of our colleagues who have spent hours of their time in attending these presentations and also contributed substantially to the development of this text version.

Chennai
3rd September 2021 B. Viswanathan

Chapter 1
INTRODUCTION

Catalysis Today

Scientific research has been changing its emphasis every decade and accordingly the manufacturing and processing sectors have been adopting new materials and concepts in their manufactured products. The developments in design strategy and introduction of new synthetic methodologies have thrown open a number of choices and it has become a tough proposition to select the material for a given application. One such area, where material selection has been a demanding proposition in the last four to five decades is the selection appropriate anode material for the photoelectrochemical cells [1] for the following:

1.Especially for the decomposition of water [2]

2. Reduction of carbon dioxide [3]

3 Photo-catalytic reduction of dinitrogen
4 Decontamination of water and air and pollutants removal

are a few reactions of great relevance in the context of energy carrier or conversion. Even though the governing principles [4] for each of these reactions have been postulated and their applicability established beyond doubt, the selection and application of the most appropriate material that can be employed for commercial endeavour for these reactions so as to be economically viable is still eluding [5]. The primary purpose of this monograph is to address this aspect even though it is the realized that a complete and fully satisfactory solution may not evolve so easily, at least one can formulate a path in finding the solution.

Catalysis has been the corner stone of chemical manufacturing industry. The corner stone of a successful catalyst development depends on the identification and generation of adequate number of so-called active sites [6]. A simple one component catalyst system itself can give rise to a variety of sites (both active and possibly inactive sites on the surface (refer to Fig.1 for a typical conceived defect surface) and this so-called heterogeneity makes the catalyst selection most often cumbersome.

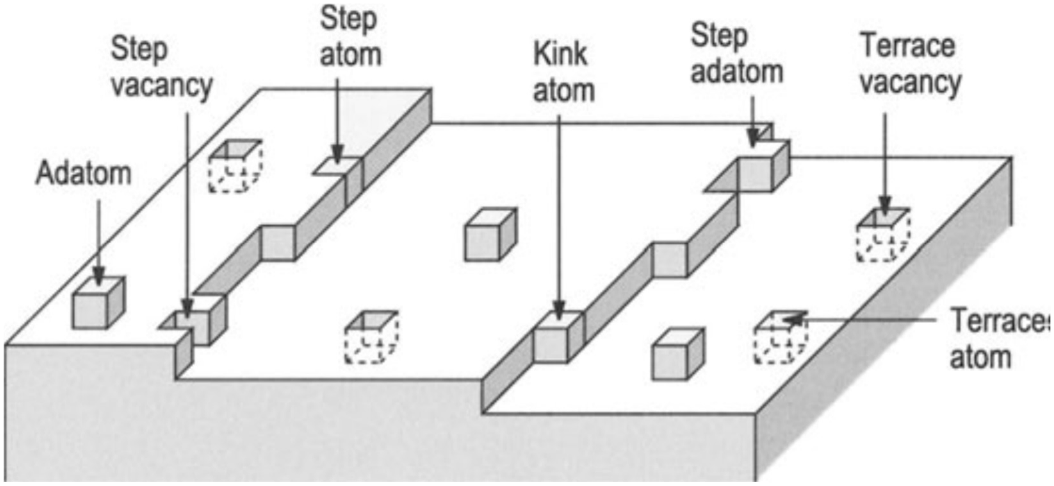

Figure 1.: Representative model of a one component surface with possible defect (active) sites indicated.

Among the various manifestations of catalysis, Photocatalysis has taken a dramatic revolution these days. In simple terms a catalyst (usually a semiconductor or possibly an insulator) is irradiated with light of suitable wavelength corresponding to the energy of the band gap, electrons normally present in the usually or mostly filled energy levels of the valence band will be transferred to the allowed unoccupied energy levels of the conduction band and thus creating a hole in the valence band and an active electron in the conduction band. This photo-generated electron-hole pair can be directed to perform both reduction and oxidation reactions simultaneously and in doing so the photon is technically consumed in the reaction. The photon can also be absorbed by the substrate, thus generating an excited state of the substrate and the science that follows is conventionally termed photochemistry. It may become obvious that the term photocatalysis is possibly misleading since catalysis means the catalyzing species has to be regenerated at the end of the catalytic reaction. A simple pictorial representation of photocatalytic decomposition of water (the details of this process will be considered subsequently) is shown in Fig.2.

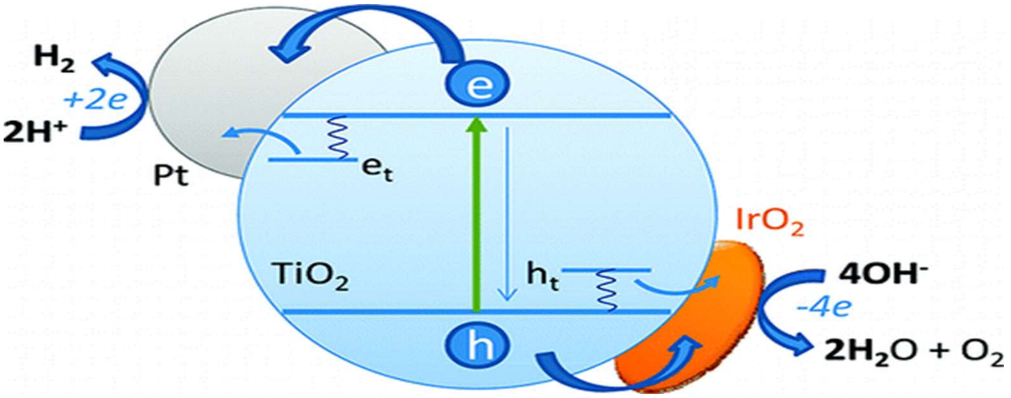

Figure 1.2: Schematic representation of charge transfer across a semiconductor-substrate interface indicating both reduction and oxidation reactions taking place [7]

The advent of this possibility has given rise to a change in face of the field of catalysis. It is generally considered that the energy position of the bottom of the conduction band and the top of valence band of the semiconductor respectively denote the reducing and oxidizing power of the semiconductor and thus facilitating the selection of appropriate substrates that can undergo decomposition. This interesting reaction sequence as a result of photon absorption by the semiconductor has been exploited in a number of ways like decontamination of water and air, [8] or generation of chemicals by p8otocatalytic routes [9]. A typical general scheme is shown in Fig.3 for the use of photocatalysis for pollutant removal.

Heterogeneous photo-catalysis is thus evolving as a versatile low-cost, environmentally benign technology and these applications can be expected to be exploited in many ways in the coming days.

This changing face of catalysis not only introduced a new branch of science called photocatalysis but also added new challenges in addition to the various challenges that are already present in the field of catalysis like the use of alternate feed stocks for the production of value-added chemicals [10]. The main challenge of this new face of catalysis namely photocatalysis is to provide the governing principles for the selection of catalysts.

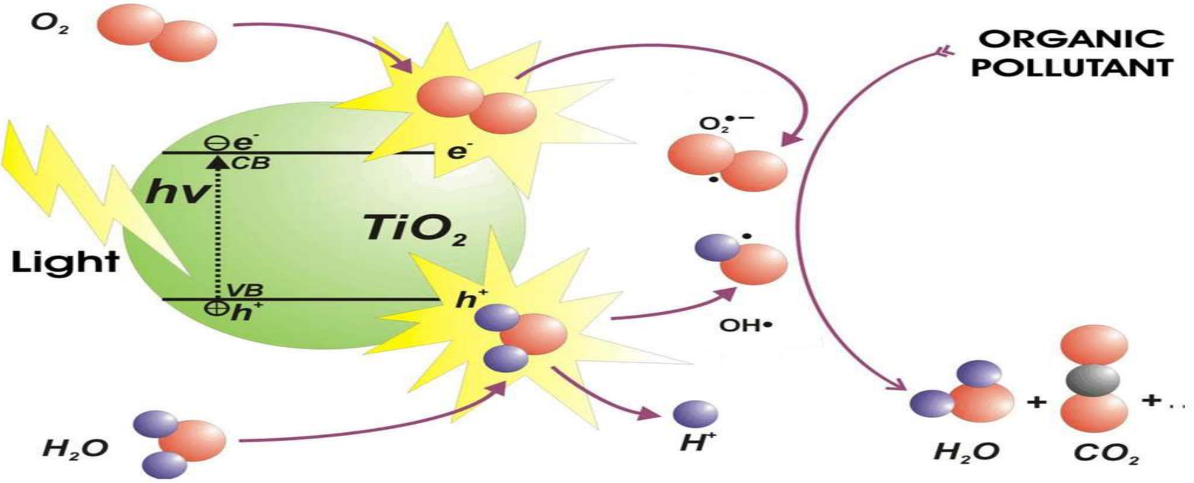

Figure 1.3: A typical representative scheme of pollutant removal by a photocatalysis [Reproduced from A.O.Ibhadon and P.Fitzpatrick, Catalysts, 3,189 (2013)].

1.2. Photocatalysis Today

For some obvious reasons, like the possibility of utilizing the solar radiation and the amount acquired knowledge on the physics, semiconductors (among them TiO_2 based systems especially) have been the material of choice, though of late nano metals have also been proposed as possible candidates for the new phenomenon called Plasmonic Catalysis [11]. The motivation for modifying semiconductors [like doping (both anionic and cationic sites), coupling (two or more semiconductors and inclusion of co-catalysts), and compounding (generating ternary and other quaternary systems) is probably to mimic natural photosynthesis and also the anxiety to utilize major portion of the available solar radiation which is nearly in the visible region. Even though nearly four decades of research has been expanded in search for the suitable and viable semiconductor material and nearly more than 400 semiconductors with all possible modifications have been screened, it must be admitted that still the appropriate material which can satisfy all the desired characteristics is yet to be identified.

This presentation therefore attempts to address this particular question. This possibly requires an understanding of the physics of semiconductor-electrolyte interface. Interested readers can refer to authoritative documents on this topic elsewhere [12]. There are also other questions relating to this topic which require careful examination of the possibilities. Some of them are:

1.Is it necessary to look for materials which will absorb photons in the visible region or is it sufficient or is it advisable to try other materials which will absorb only in the UV region? This question arises due to the fact that the energy available in the UV region of the solar radiation may be more than sufficient for the requirements of earth.

2, In photoelectrochemical cells, thin films and in photocatalysis, powdered polycrystalline samples are normally employed. It may be worthwhile to examine if these are the appropriate geometry for harnessing maximum efficiency?

3. In the modification of the semiconductors, doping is most often resorted to and it may be necessary that these methods of alteration of the electronic properties of the semiconductors have been standardized so that interpretations can be within one framework.

4. The selection of the semiconductor is mostly based on the value of the band gap, nature of the semi-conductivity (direct or indirect) and possibly photon absorption coefficient but it is not clear all these parameters are enough and how weightage has to be given to each of these parameters.

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Chapter 2

OVERVIEW OF PHOTOCATALYSIS

1.1. Introduction

There is generally a conception that Photo-catalysis originated with the discovery of Photo-electrochemical decomposition of water by Fujishima and Honda [2] in the 70s. Photo-catalysis which is a phenomenon wherein an acceleration of a chemical reaction in the presence of photons and catalyst has been reported in the literature in 50s (possibly even earlier to this) by Markham and Laidler [20]. Sister Markham followed this with a publication in chemical education [19] wherein she reported the photo-catalytic properties of oxides. In fact, Sister Markham reported that the absorption of photons by the solid generates electron hole pair which are utilized in the generation free radicals (hydroxyl radicals (.OH)). The chemical consequence of this process today goes with the name of Advanced Oxidation Process (AOP; which may or may not involve TiO2 and Photons). Markham had a number of subsequent publications on the photo-catalytic transformations on irradiated zinc oxide [12]. Photo-catalysis deals with the Photochemistry has been an integral part of life on earth. One often associates photo-catalysis with photosynthesis. However, the term photo-catalysis found mention in an earlier work by Plotnikov in the 1930's in his book entitled Allaemeine photochemie. The next major systematic development as stated earlier was in the 1950's when Markham and Laidler performed a kinetic study of photo-oxidation on the surface of zinc oxide in an aqueous suspension. By the 1970's researchers started to perform surface studies on photo-catalysts like Zinc Oxide and Titanium dioxide. The most commonly employed photo-catalyst is Titanium dioxide. TiO_2 exists mainly in three crystallographic forms, namely Brookite Anatase and Rutile. There have been a number of studies on the three modifications of titania. The energetics of the titania polymorphs were studied by high temperature oxide melt drop solution calorimetry. It has been shown that relative to bulk rutile, bulk brookite is 0.71±0.38 kJ/mol and bulk anatase is 2.61±0.41 kJ/mol higher in enthalpy. [21]. The effect of particle size on phase stability and phase transformation during growth of nanocrystalline aggregates and has been shown that mixed phases transform to brookite and/or rutile before brookite transforms to rutile. [13] Among these three forms, the most often used photo-catalyst is the anatase phase either in pure form or in combination with rutile form. There are various reasons for this preference of TiO_2 as photo-catalyst. These reasons include that it was the first system studied by Fujishima and Honda and TiO_2 exhibits possibly maximum photon absorption cross section (i.e., it absorbs maximum number of photons of correct wavelength). This preference over TiO_2 is seen from the data given in Table 1.

Table 1 Statistical distribution of scientific publications focused on nanomaterials for PEC/Photo-catalysis hydrogen production [15]

Materials	percentage of study
TiO_2	36.2
Non-TiO_2Oxides	10.9
Oxy-sulphides	18.8
Oxy-nitrides	5.1
Other semiconductors	5.8
Composites and Mixtures	17.4
Non-semiconductors	5.8
Total	100

Degussa P25 Titanium dioxide generally employed as catalyst in many of the studies reported in literature and hence, considered as standard for photocatalytic activity comparison, contains both anatase (about 80 percent) and rutile (about 20 percent). It is in general impossible to completely trace the history of Photo-catalysis. Even Fujishima and his coworkers [3] have expressed concern on completely outlining the history of photo-catalysis. The main difficulty appears to be that photo-catalysis unlike other chemical reactions involves simultaneously both oxidation and reduction reactions on a surface possibly assisted by photons of appropriate wavelength corresponding to the band gap of the semiconductor employed as catalyst. In 1921 Renz reported that titania was partially reduced when it was illuminated with sunlight in the presence of organic substrates like glycerol [24]. In 1924, Baur and Perret [E. Baur, A. Perret. Helv. Chim. Acta, 7 (1924), p. 910] probably were the first to report the photodecomposition of silver salt on ZnO to produce metallic silver. Probably Baur and Neuweiler [5] were the first to recognize that both oxidation and reduction are taking place simultaneously on the production of hydrogen peroxide on ZnO. This was followed by the work of Renz in 1932 [25] who reported the photocatalytic reduction of silver nitrate and gold chloride on TiO_2. Goodeve and Kitchener [6] studied the photo-catalytic decomposition of dye on titania surfaces and even reported the quantum yields. In 1953, it has been recognized that the organic substrate was oxidized and oxygen was reduced. Unfortunately, these studies have been carried out on ZnO surfaces and hence could have been hampered because of the inevitable problem of photo-corrosion of ZnO [20]. There were few attempts in between for the production of hydrogen peroxide and decomposition of dyes on illuminated semiconductor surfaces. There were attempts to study the photo-catalytic oxidation of organic substrates on a variety of oxide surfaces from other parts of the world in and around this period. In the 1960s photo-electrochemical studies on ZnO with various redox couples were started. All these studies culminated in the photo-electrochemical decomposition of water by Fujishima and Honda which opened up means for solar energy conversion and also for the generation of hydrogen fuel. Subsequently Bard and his coworkers [16] have demonstrated that illuminated TiO_2 could be used for the decontamination of water by photo-catalytic decomposition. This has led to new photo-catalytic routes for environmental clean-up and also for organic synthesis. These aspects will be dealt with separately. Fujishima et al., have provided a more detailed and authentic write-up on the history of photo-catalysis [3].

1.2. Basic Principle of Photocatalysis

According to the glossary of terms used in photochemistry [IUPAC 2006 page 384] photo-catalysis is defined as the change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infra-red radiation in the presence of a substance the photo-catalyst that absorbs light and is involved in the chemical transformation of the reaction partners. When a semiconductor (or an insulator) is irradiated with light of suitable wavelength corresponding to the energy of the band gap, electrons occupying the usually or mostly filled energy levels in the valence band will be transferred to an allowed energy states in the normally empty conduction band thus creating holes in the valence band. This electron-hole pair is known as exciton. These photo-generated electron-hole pairs promote the so-called redox reaction through the adsorbed species on the semiconductor or insulator surface. However, the band gap of the insulators will be usually high and as such generating of such high energy photons will not be comparatively easy and hence insulators are not considered as possible candidates for Photo-catalysis. Generally, metals cannot be employed as photo-catalysts since their occupied and unoccupied energy states are overlapping with respect to energy and hence the recombination of electron-hole pair will be the most preferred process and hence the conversion of photon energy to chemical energy using metals will not be advantageous. The choice of semiconductors for photocatalysis is clear from Fig.2.1. It is generally considered that the energy position of the top of the valence band of a semiconductor is a measure of its oxidizing power and the bottom of the conduction band is a measure of its reducing capacity. It is therefore necessary one has to know with certain level of accuracy the energy positions of the top of the valence band and bottom of the conduction band so that the reactions that these excitons can promote can be understood. One such compilation is given later in this chapter in Table 3.

Photo-catalytic destruction of organic pollutants in water is based on photochemical process involving semiconductors. When a semiconductor is irradiated with UV light (usually but it can be any other radiation as well) light of wavelength appropriate for excitation from valence band to the conduction band of the chosen semiconductor, an exciton is created. The photochemical oxidation of the organic substrate normally proceeds by the adsorption of the substrate on the surface of the semiconductor with transfer of electrons with the hole generated. However other possible oxidation processes can also take place with radicals generated (OH radical if the solvent is water) at the surface of the semiconductor surface. Thus, a variety of surface reactions will take place on the photo-excited semiconductor surface, the preferred reaction depends on the nature of the substrate under consideration and its nature of adsorption and activation on the semiconductor surface. In Fig 2.2 a simple representation of these possible processes is shown by considering simple general reactions water giving hydroxyl radicals and organic substrate being oxidized all the way to carbon dioxide and water in order to get an idea of what can takes place on the surface of semiconductor as a result of photoexcitation and catalysis. Since it is possible that the organic substrate can be completely degraded to carbon dioxide

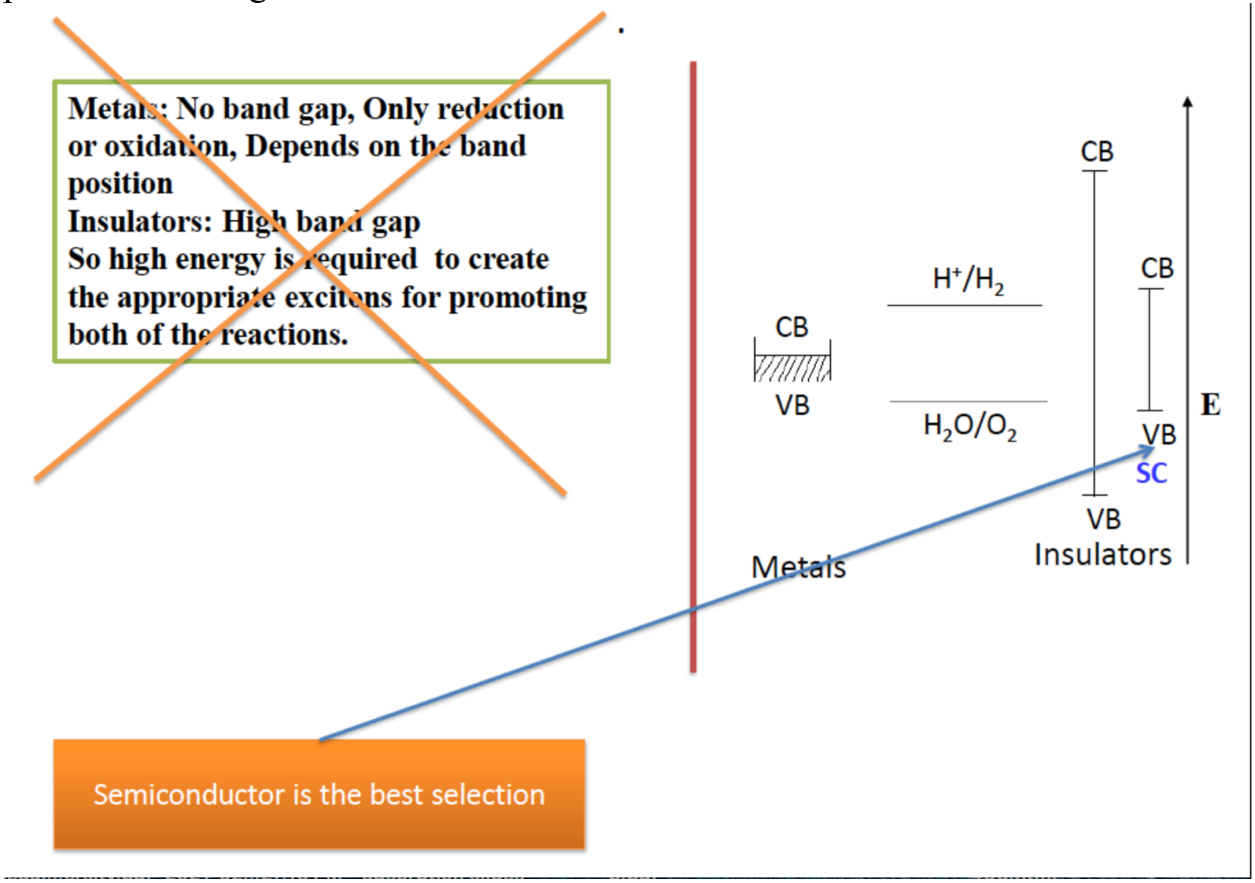

Fig 2.1. The choice of semiconductors for photo-catalysis is pictorially represented.

and water, this process has been considered to be a viable method for the decontamination of water. In addition, it should be kept in mind that hydroxyl radical is a powerful oxidizing agent as compared to other common oxidizing agents as can be seem from the data given in Table.2. It is clear from the data given in Table.2 that the aqueous phase reactions will still be preferred in Photo-catalyst

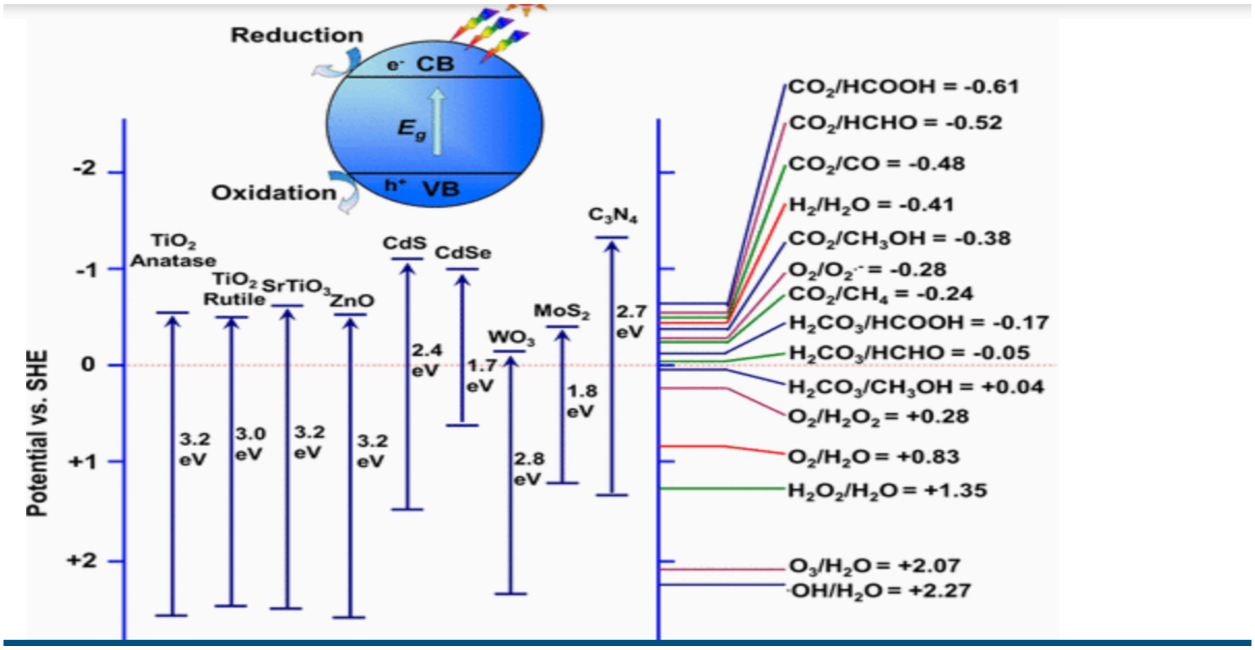

Figure 2.2.: Schematic representation of the principle of photocatalysis showing the energy band gap of a semiconductor particle. Typical reactions considered water → hydroxyl radical; organic substrate + hydroxy radical→ carbon dioxide + water + mineral acid

Table 2 Oxidizing power of some of the commonly employed oxidizing agents.

Oxidant	Oxidation Potential(V)
Hydroxy Radical	2.80
Ozone	2.07
Hydrogen Peroxide	1.77
ClO_2	1.49
Chlorine (Cl_2)	1.35

1.3. **Limitations of photo-catalysis**

Though Photo-catalytic technology has been emerging as a viable technology for the remediation of pollutants from water, it can be applied to a variety of compounds. One of the factors to be considered is the possibility of mass transfer limitations due to the characteristics imposed in the reaction chamber by the existence of the catalyst in various forms in dispersed state. In fact, the construction of an appropriate photo-chemical reactor itself has been a major issue and various designs have been proposed in literature. A simple reactor design conventionally employed is shown in Fig.2.3. Sclafani et al. [4] postulated external mass transfer limitations to interpret their results in a packed bed reactor filled with spheres of semiconductor catalyst (in this case pure titanium dioxide (ca. 0.12 cm in diameter)). Chen and Ray [8] studied internal and external mass transfer limitations in catalytic particles of photo-catalytic reactors and concluded only mild mass transfer restrictions since the effectiveness factor observed was near 0.9 and hence rotating disc photo reactor when the spherical particles of the semiconductor fixed on a solid support. The specific role of mass transfer was analyzed in terms of one of the dimensionless Damkhler numbers. In other reactor configurations, particularly films and membrane reactors other quantitative observations of internal mass transfer limitations have been published. [9], [7] and many others (see for example one of the reviews on this topic in Legrini et al. [22]). Unfortunately, these limitations have not been examined with other type of reactors like slurry reactors. In addition, since photons are coupling with a heterogenous system, this can result in gradients in concentration or the coupling of the photon field with the scattering particles. The points that emerge from the data presented in these two tables are that the top of the valence band is nearly the same for the oxide semiconductors and the bottom of the conduction band depends on the cation involved and hence the oxide semiconductors will be more or less behaving in a similar manner. The other chemical limitations involved in the photo-catalytic degradation of pollutants from water are: The adsorption of the pollutant species on the surface of the semiconductor. This fact has been recognized in the literature but still not many quantitative relationships have emerged indicating the importance of this step in the photo-degradation processes. However, the importance of this step is apparent since the charge transfer from the semiconductor to the substrate and hence cause their degradation is possible only in the adsorbed state of the substrate since charge transfer has restrictions with respect to distances involved. In addition, the adsorption is directly related to the surface area of the photo-catalyst and hence it is conventional to optimize the surface area of the photo-catalyst. The pH may also have an effect on the photo-degradation of organic pollutants since the nature of the species involved can change with respect to pH. In addition, in aqueous medium the potential changes by 59 milli-volts per pH unit and this also can affect the process of degradation. In solution phase, the presence of both type of counter ions namely, anions and cations can affect the photo-degradation process due to reasons like photon absorption by the ions and also the type of species that will be generated as a result of photon absorption. When the composite solar radiation is employed for photo-degradation process, the temperature of the system can affect all the reactions (normally increase is noticed) except for the electron hole creation step. However, the solubility of oxygen will decrease with increase in temperature and this can also affect the rate of photo-degradation reaction. In a subsequent chapter, the studies reported on the application of photo-catalysis for the decontamination of water will be considered. This field seems to assume importance in these days due to various reasons. However, the studies reported in this area have to be considered with care since the products of oxidation and their effects have not yet been established though it is generally assumed to be carbon dioxide. As seen earlier that one of the areas in which photocatalysis has been extensively employed is the decontamination of water. Water covers over two thirds of earth's surface and less than a third is the land area. Oceans, rivers and other inland waters are continuously polluted by human activities leading to a gradual decrease in the quality of water. There are specified limits of concentration beyond which the presence of some substances is considered as polluting water. In Table 5, the recommended tolerance limits of pollutants are given. The common pollutants in water are classified as inorganic contaminants and organic pollutants. The main inorganic contaminants are the metal ions, nitrates, nitrites, nitrogen dioxide, ozone, ammonia, azide and halide ions. There are various studies reported in literature that deal with the photocatalytic decomposition or transformation of these inorganic contaminants. Photocatalytic decomposition (mostly oxidation) of organic pollutants has been of great interest. In these studies, the reaction is carried out in presence of molecular oxygen or air for complete oxidation to carbon dioxide and water and possibly inorganic mineral acids as the final products. It has been shown that many of the organo-chlorides, pesticides, herbicides and surfactants are completely oxidized to carbon dioxide, water and hydrochloric acid. It may be worthwhile to realize the effect of some of the pollutants on human health. The data collected from literature are given in Table.6. It is to be remarked the effects of pollutants generally affect the human health in a variety of ways basically affecting the nervous system.

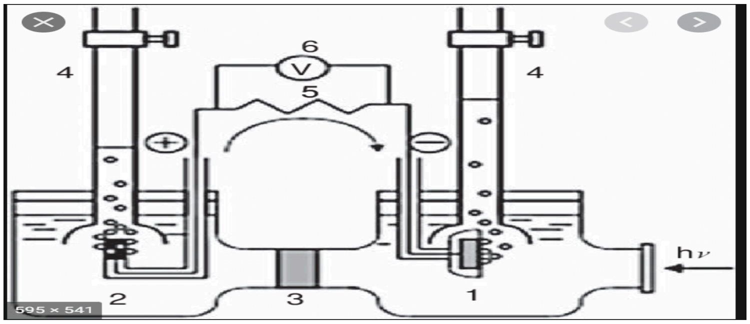

Figure 2.3. Typical reactor design conventionally employed for the photo-splitting of water. This is termed as Fujishima Honda cell.

Table.3. Electro-negativity, [χ], Band gap, (Eg) energy levels of the conduction band bottom (ECB) and energy position of the top of valence band (E V B) [data extracted from Y. Xu and M.A.A. Schoonen, American Mineralogist, 85, 543-556 (2000)]

Substance oxide	Electronegativity (χ)	Band gap (E_g)	Conduction band E_{CB}	Valence Band E_{VB}
$BaTiO_3$	5.12	3.30	-4.58	-7.88
Bi_2O_3	6.23	2.80	-4.83	-7.63
$CoTiO_3$	5.76	2.25	-4.64	-6.89
CuO	5.81	1.70	-4.96	-6.66
Fe_2O_3	5.88	2.20	-4.78	-6.98
Ga_2O_3	5.35	4.80	-2.95	-7.75
$KNbO_3$	5.29	3.30	-3.64	-6.94
$KTaO_3$	5.32	3.50	-3.57	-7.07
$MnTiO_3$	5.59	3.10	-4.04	-7.14
Nb_2O_5	6.29	3.40	-4.59	-7.99
NiO	5.75	3.50	-4.00	-7.50
$NiTiO_3$	5.79	2.18	-4.70	-6.88
PbO	5.42	2.80	-4.02	-6.82
SnO_2	6.25	3.50	--4/50	-8.00
$SrTiO_3$	4.94	3.40	-3.24	-6.64
TuO_2	5.81	3.20	-4.21	-7.41
V_2O_5	6.10	2.80	-4.70	-7.50
WO_3	6.59	2.70	-5.24	-7.94
ZnO	5.79	3.20	-4.19	-7.39
ZrO_2	5.91	5.00	-3.41	-8.41

Table.4. Band positions of some semiconductor photo-catalysts in aqueous solution at pH =1 and positions are given in volts versus NHE.

Semiconductor material	Valence Band V vs NHE	Conduction band V vs NHE	Band Gap (eV)	Band gap (wavelength)
TiO_2	+3.1	-0.1	3.2	387
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	387

ZnS	+1.4	-2.3	3.7	337
WO_3	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	490
CdSe	+1.6	-0.1	1.7	729

In addition, there are some Persistent Organic Pollutants (POP) like aldrin, chlordane DDT, hexachlorobenzene, furans, polychlorinated biphenyls, Polycyclic aromatic hydrocarbons (PAHs) and so on. These substances some of which are called the dirty dozen cause many disorders including cancer breast cancer, damage to reproductive system, neuro-behavioural disorders and health related concerns.

Table 5 Recommended tolerance limits of pollutants in water [Data collected from K.C. Agarwal, Industrial power engineering and Applications, Butterworth-Heinemann, pp.565 (2001)

S. No	Parameter	Recommended Tolerance level
1	Biological Oxygen Demand (BOD)	30 mg/l
2	Chemical Oxygen Demand (COD)	250 mg/l
3	Alkali traces	maximum upto pH 9
4	Acid	Not less than pH 5.5
5	Total suspended solids	100 mg/l
6	Oil and Grease	10 mg/l
7	Dissolved phosphates as P	5 mg/l
8	Chlorides as Cl	600 mg/l
9	Sulphates (as SO_4)	1000 mg/l
10	Cyanides as (CN)	0.2 mg/l
11	Total Chromium	2 mg/l
12	Hexavalent chromium	0.1 mg/l
13	Zinc as Zn	0.25 mg/l
14	Iron	3 mg/l
15	Total heavy metals	7 mg/l
16	Total Phenolic compounds	1 mg/l
17	Lead (Pb)	0.1 mg/l
18	Copper as Cu	2 mg/l
19	Nickel as Ni	2 mg/l
20	Bioassay test	89% survival after 96 hours

1.4. **Advanced Oxidation Processes**

Irrespective of the method of generation of hydroxyl radicals, the methods which utilize hydroxyl radicals for carrying out the oxidation of the pollutants are grouped as Advanced Oxidation Processes. Hydroxyl radicals are extraordinarily reactive species and have one of the highest oxidation potential (2.8 V). The values of rate constants in reactions with organic substrates are in the range of $10^6 - 10^9$ M^{-1} s^{-1} [23,1,14] (Table 7). In addition, hydroxyl radicals do not show any selectivity with respect to the position of attack on the organic substrates which is useful aspect for the treatment of water. The fact that the production of hydroxyl radicals can be made by a variety of methods adds to the versality of Advanced Oxidation Processes thus allowing a better compliance with the specific treatment requirements. An important consideration to be made in the application of AOP to waste water treatments is the requirement of expensive reactants like hydrogen peroxide and /or ozone. Hence, AOP cannot replace the application of more economical treatment methods such as biological degradation whenever possible. A list of the different possibilities offered by AOP are briefly given in Table 8.

Table 6 Possible pollutants in water and their effect on human health

Pollutant	Adverse effect on human health
Atrazine	Cancer, damage to nervous system
Benzene	Cancer anemia
Pentachlorophenol	Liver and Kidney damage and Cancer
Trichloroethylene	Cancer
Trichloroethane	Damage to Kidney, liver and nervous system
Bromoform	Damage to nervous system and muscle
Carbofuran	Damage to nervous system, kidney reproductive system
Carbon tetrachloride	Cancer
Chlorobenzene	Damage to nervous system, kidney and liver
Dichloroethane	Damage t0 nervous system muscle and cancer
Eridriin	Damage to nervous system, kidney, liver anemia and cancer
Ethylbenzene	Damage to nervous system, liver and Kidney
Heptachlor	Cancer
Heptachlor epoxide	Cancer
Hexa-chloro-cyclopentadiene	Damage to Kidney and stomach

Lindane	Damage to nervous system liver and kidney
Simazine	Damage to nervous system, Cancer
Styrene	Damage to nervous system, liver
Tetrachloroethylene	Damage to nervous system, Cancer
1,2,4-trichlorobenzene	Damage to liver and Kidney
Xylene pesticides	Damage to nervous system kidney lungs and membranes
Toluene	Damage to nervous system, liver and kidney

,

Table.7. Values of second order rate constants for the oxidation by ozone and hydroxyl radical for a variety of compounds [data from [23]]

Organic compound	value of rate constant M−1 s −1	
	Ozone[a]	OH radical[b]
Benzene	2	7.8 X 10^9
n-butanol	0.6	4.6 X 10^9
t-butanol	0.3	0.4 X 10^9
Chlorobenzene	0.75	4 X 10^9
Tetracholoroethylene	<0.1	1.7X 10^9
Toluene	14	7.8X10^9
Tricholorethylene	17	4.0X10^9
		a.

a- from Hoigne and Bader, 1983; b- from Farhataziz and Ross, 1977.

Table 8 Sources involved in the various Advanced Oxidation Processes

Source of Oxidants	Name of the processes
H_2O_2/Fe^{2+}	Fenton
H_2O_2/Fe^{3+}	Fenton like
$H_2O_2/Fe^{2+}, Fe^{3+}/UV$	photo-assisted Fenton
TiO_2 hν/O_2	Photocatalysis
O_3 or H_2O_2/UV	Photo-assisted oxidation

Heterogeneous Photo-catalysis

Among the AOPs mentioned, photo-catalysis is the promising method. This is attributed to its potential to utilize energy from the sun without the addition of others forms of energy or reagents. The reactions carried out by the photo-catalysts are classified into two categories namely homogeneous or heterogeneous photo-catalysis. Heterogeneous photo-catalysis is based on the semiconductors which are employed for carrying out various desired reactions in both liquid and vapour phases. Photo-catalysis involve the formation of highly reactive electrons and holes in the conduction and valence bands respectively. The electrons are capable of carrying out reduction reactions and holes can carry out oxidation reactions. There are also other processes that take place in the semiconductor. The electron and hole can react with acceptor or donor molecules respectively or recombine at surface trapping sites. They can also be trapped at bulk trapping sites and recombine with the release of heat. The electron hole can be exploited in a number of ways: (i) For producing electricity(solar cells)-Photo-voltaic; (ii) For decomposing or removing pollutants-Photo-oxidation; (iii) For the synthesis and production of useful chemicals-Photo-catalysis; (iv) For the photo-electrolysis of water-photo-electro-chemistry. As the recombination of the photogenerated electron and hole occurs on a pico-second time scale, electron transfer at the interface can kinetically compete with recombination only when the donor or acceptor is adsorbed on the surface of the semiconductor before irradiation. Hence adsorption of the substrate prior to irradiation is important for efficiency of the heterogeneous photo-catalytic process. [18]. Hydroxyl groups or water molecules adsorbed on the surface can serve as traps for the photogenerated hole, leading to the formation of hydroxyl radicals in the case of metal oxide suspensions. Strong adsorption of acetone and 2-propanol on ZnO has been observed during temperature programmed desorption [17]. Metal oxide surfaces have a surface density of about 4-5 hydroxy groups /nm^2 as has been shown by the continuous distribution of adsorption energies in the Freundlich isotherm. Many organic substrates were found to play the role of adsorbed traps for the photo-generated holes. For example, in a colloidal suspension of TiO_2 in acetonitrile, radical ions are detected directly during flash excitation [17]. Apart from materials derived from TiO_2 by modifications like doping, coupling with an additional phase or morphological changes different compounds with distinct composition and structure have also been examined. Various tantalates, [10] [11], niobates [26], Oxides of bismuth like $Bi_2W_2O_9$, Bi_2MoO_6, $Bi_2MO_3O_{12}$ and oxides of Indium as In_2O_3, $Ba_2In_2O_5$,MIn_2O_4, (M=Ca, Sr) were found to be capable of photo-splitting water. Tantalum nitride and tantalum oxynitride were also found to be effective catalysts for water splitting.

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Chapter 3

GENERAL PRINCIPLES OF PHOTOCATALYSIS

The scope of photocatalysis is increasing day by day. However, the field of decontamination of pollutants (including some drug and dye molecules) has received considerable attention. This aspect will be dealt with in detailed manner in a separate chapter. The activation and conversion of stable molecules like water. Carbon dioxide and dinitrogen still attract the attention of scientific community. In Figure 1, the various processes promoted by photocatalysis by semiconductors are shown.

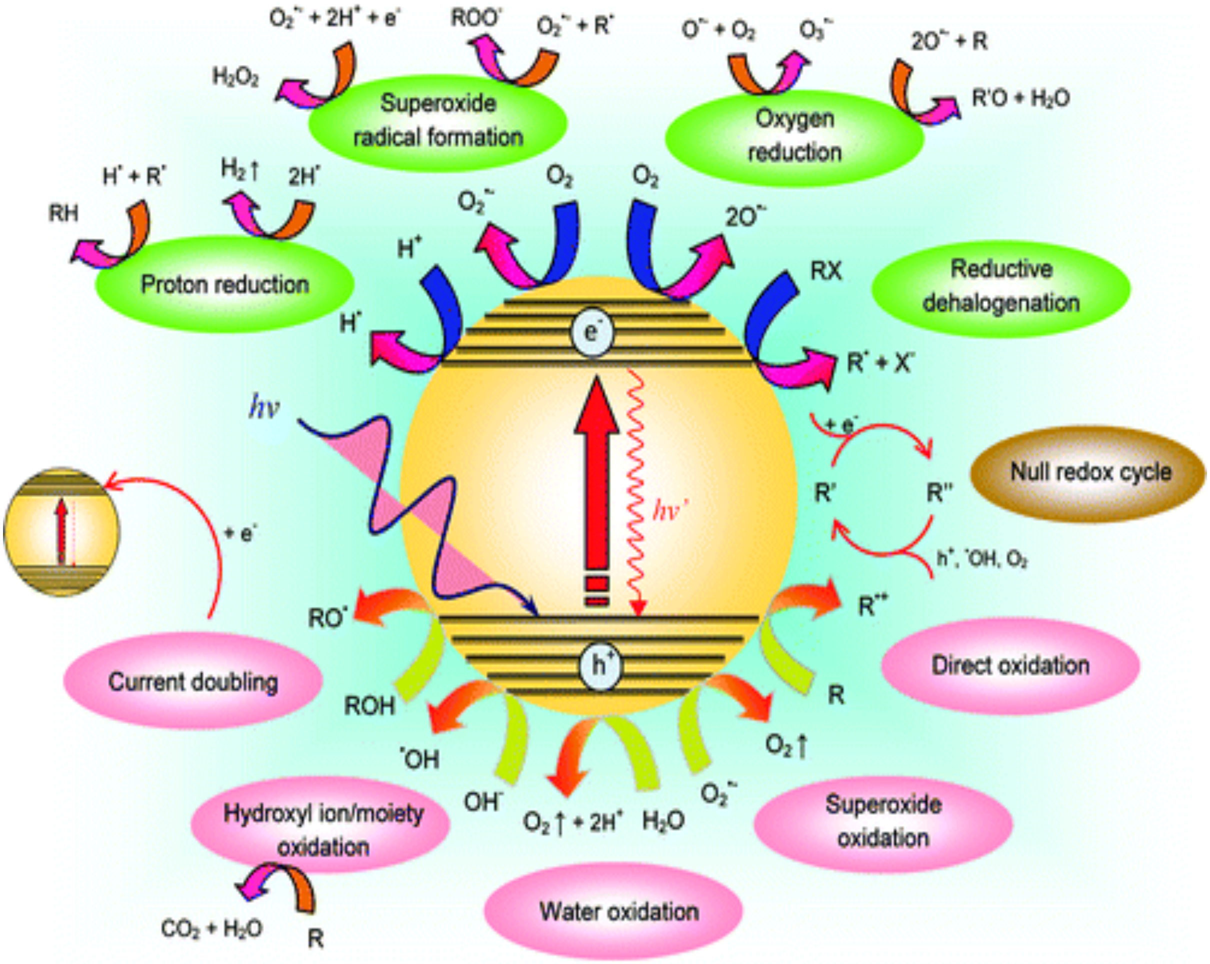


Fig. 1 Various light induced reactions involved in semiconductor photocatalysis [Reproduced from reference Tech et al., J. Phys. Chem. Lett., 3, 629-639 (2012)].

It is seen a variety of oxidation and reduction reactions can be carried out as a result of photo-catalysis. In addition, a host of organic reactions and radical induced inorganic transformations can be promoted in this field. The basic principles involved in this type of photocatalytic reactions are shown in Figure 2 using TiO_2 as a typical photocatalyst. The photon absorption gives rise to an energic electron in the conduction band which can be utilized for the reduction (acceptor) reaction and the hole formed in the valence band can be utilized in the oxidation (donor) reaction.

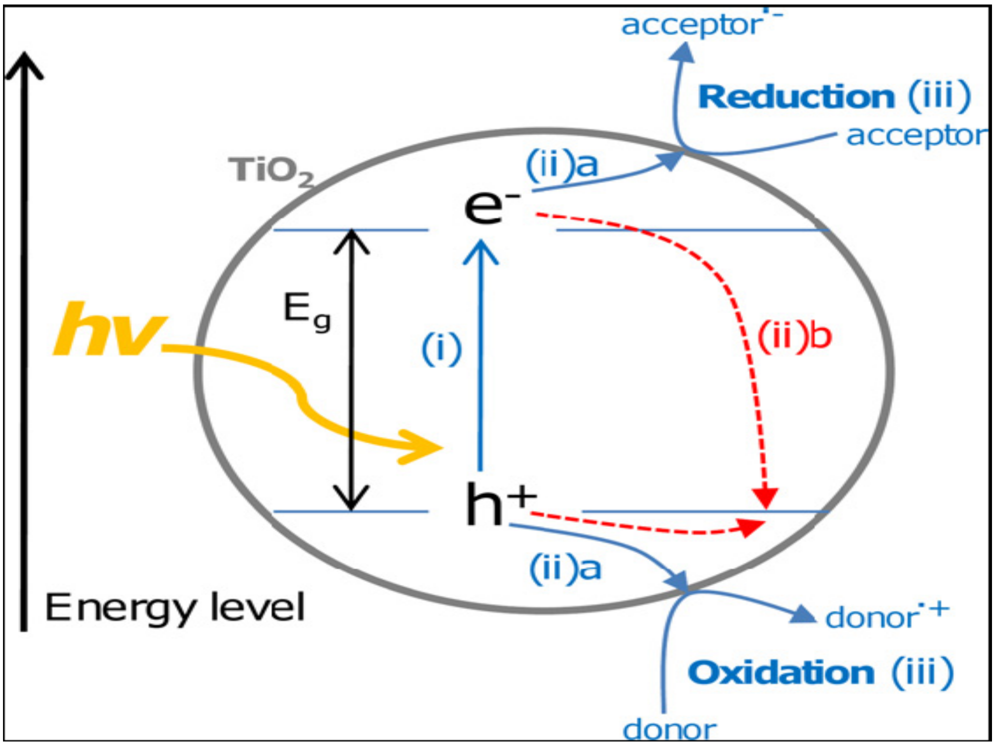


Fig. 2. Various processes involved in semiconductor photocatalysis. (i) Photon absorption and electron–hole pair generation. (ii) Charge separation and migration; (iia) to surface reaction sites or (iib) to recombination sites. (iii) Surface chemical reaction at active sites.[Leary et al carbon, 49. 741-772 (2011)].

Various Methods for Improving the Efficiency of Photocatalyst

These attempts are mainly concerned with facilitating the charge transfer efficiency/. This can be achieved in many ways. Among them, is to alter the energy position of Fermi level of the semiconductor. In addition. it is possible to introduce the electron transfer agents or hole trapping species. For electron transfer process, one has to use agents which have high electron affinity and these are mostly noble metals. Like Au, Pt and so on. This situation is pictorially shown in Figure 3.

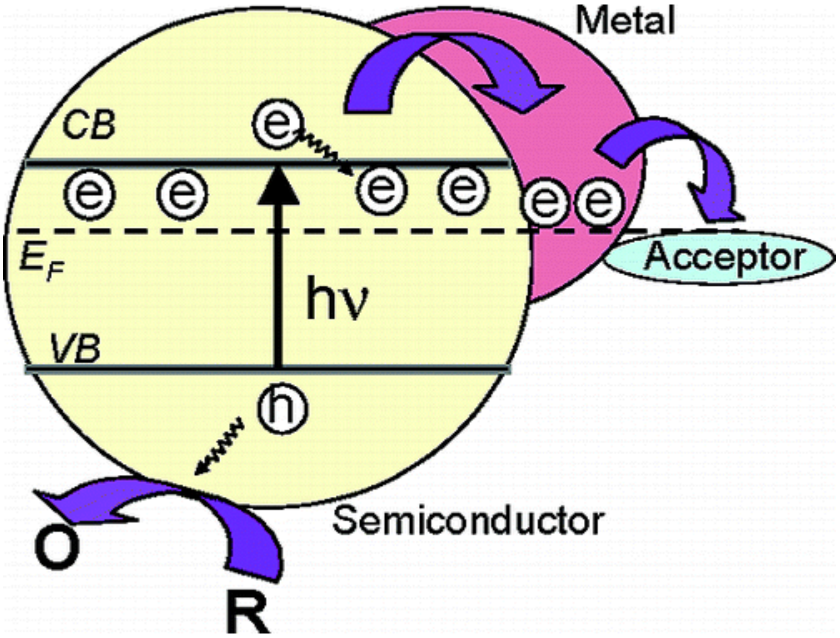


Fig. 3 Metal deposited semiconductor to facilitate electron transfer to the acceptor species. Refer to Subramanian et al., J. Am. Chem. Soc. 2004, 126, 4943-4950.

2. **Coupling of two Semiconductors**:

Another way to achieve efficient electron traanfer and decrease recombination of charge carriers is coupling two semiconductors. This can also be useful to use longer wavelenth radiaation that is shifting the photon source from UV to visible range. This has to satisfy that interfacial electron transfer between two semiconductors with different conduction band edges will facilitate and also minimize electron-hole recombination. The possibility is illustrated in Figure 4.

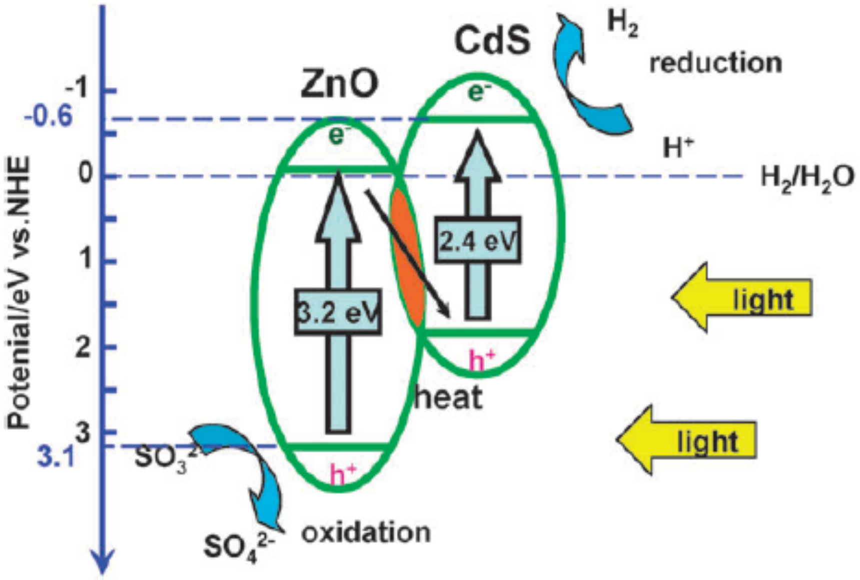


Fig. 4. Coupling of two semiconducotrs. Note the relative positions of the conduction band minima of the two semiconductors. See for example Wang et al. *Chem. Commun.*, **2009**, 3452–3454.

3.**Sensitization**

Usually this is done by employing substances (Dyes or other photoactive materials) which will absorb radiation. The separation and transfer of the charges like in splitting of pure water was achieved with dye-coated photocatalyst which is attributed to good electronic contact between dye and photocatalyst. This is pictorially shown in Figure 5.

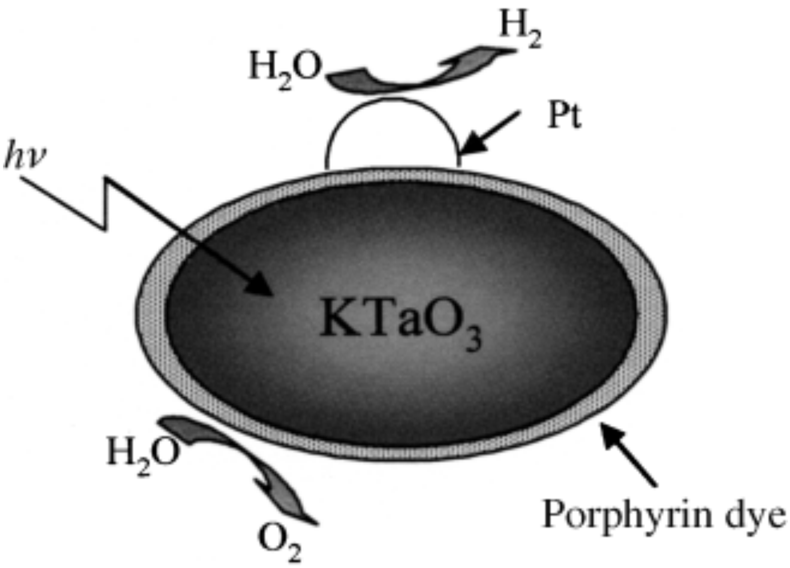


Fig.5 Dye coated semiconductor and the dye absorbs radiation or facilitate the charge transfer See for example Hagiwara et al. *Angew. Chem. Int. Ed.*, 2006, 45, 1420–1422.

4. Doping with metal ions (Fe^{3+}, V^{5+} etc.) and non-metals (N, C, S etc.)

The doping process helps to introduce additional states in the semiconductor eg.TiO_2 thereby reducing the band gap and improving the visible light absorbing properties. The main drawbacks of these systems are (1) The new energy states introduced into the composite material can also act as recombination centers for excitonic species especially when dopant concentration is high and (2) the thermal stability of the material will be affected.

There are other possibilities of activating and facilitating charge transfer process which will be taken up subsequently.

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].

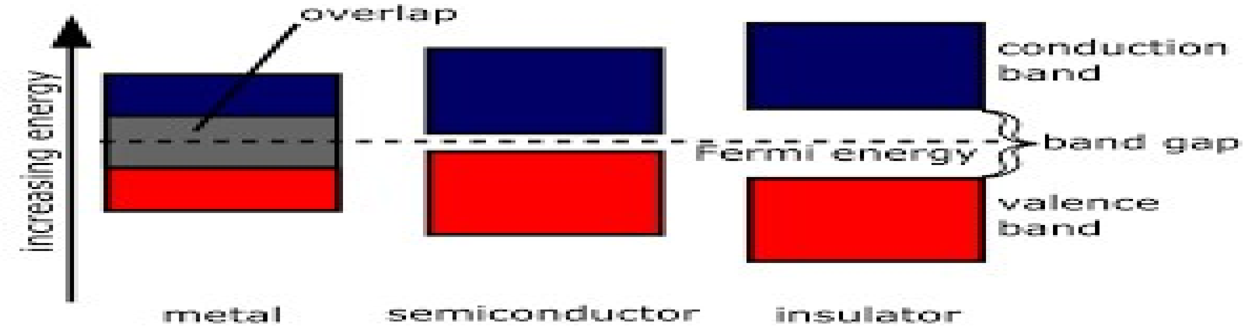


Fig.1. A band diagram with different values of band gaps for conductors (~0 eV), semiconductors (0-3 eV), and insulators (>4eV)

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.

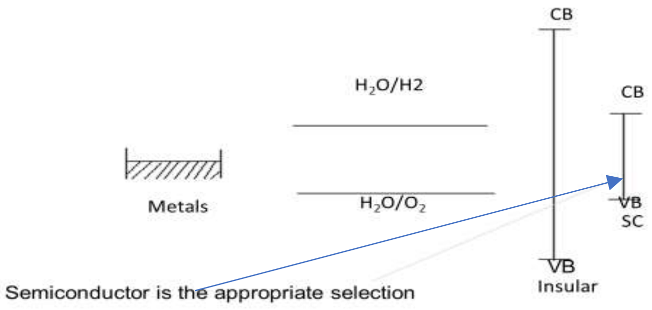


Fig.2 Water decomposition reaction and metals, semiconductors and insulators – why semiconductor band positions are favourable for this reaction.

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

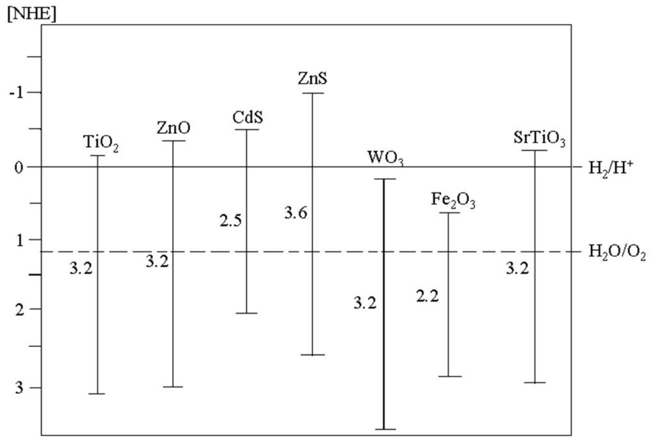
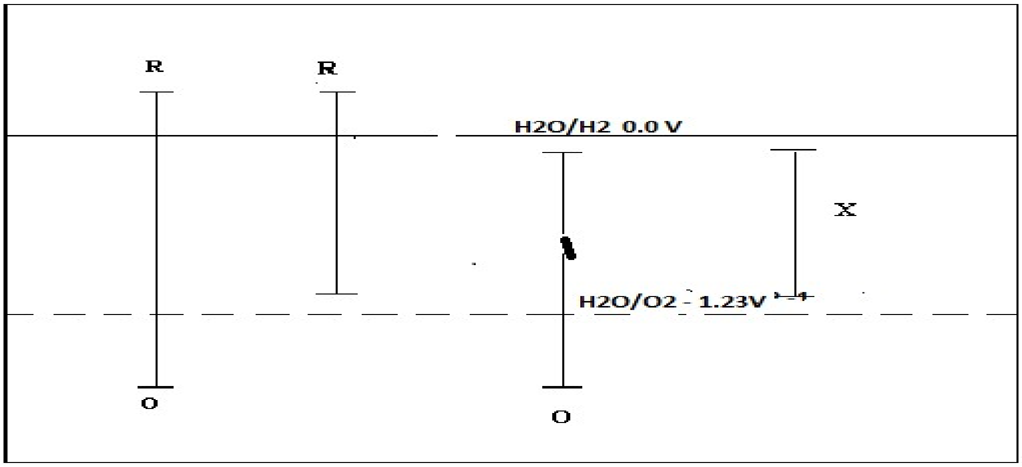


Fig.3. For water decomposition only those semiconductors whose conduction band bottom is more negative with respect to hydrogen evolution reaction and valence band maximum must be more positive with respect to oxygen evolution reaction. On this basis, the known semiconductors can be clasified as reuction (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 simutaneously 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 pictoral 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 niether 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 me 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).

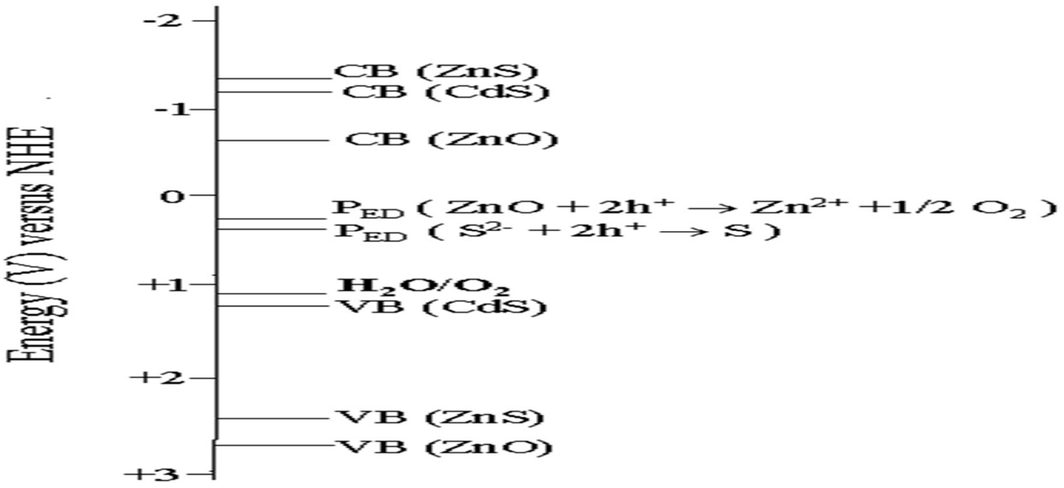


Fig.5. The energy scale for conduction band and valence band for a few semiconductors and the preferred photo corrosion reactions

When a semiconductor is irradiated with light whose wave length is equal to or shorten 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.

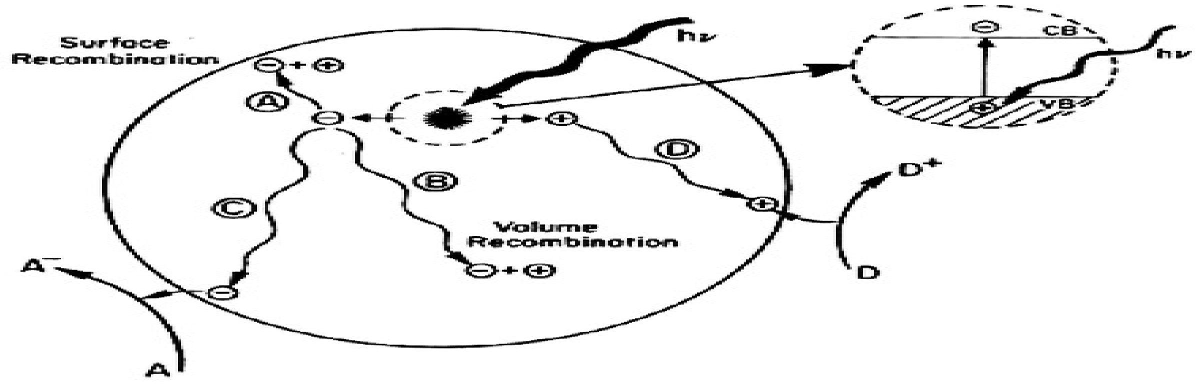


Fig. 6. Creation of exciton and their process in the semiconductor and the donor and the acceptor reactions with the substrate [reproduced from ref A. Millis and S. L. Hunte *J. Photochem. Photobiol.* A: *Chem* 180 (1997) 1; ref 2]

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 $Ga_2 O_3$_ (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.

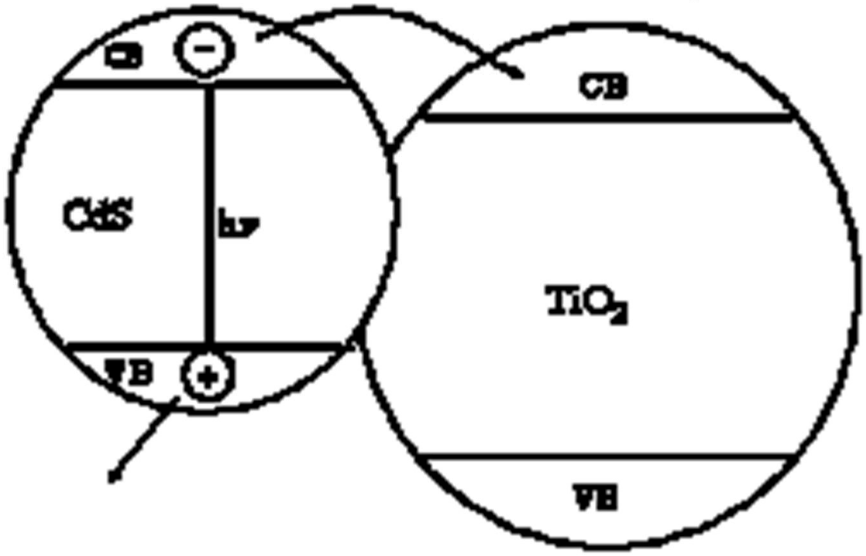


Fig.7. Coupling of semiconductors and the energy levels of the valence band and the conduction band positions facilitate the excited charged states to transfer to the original semiconductor.

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 Fe^{2+}/Fe^{3+} redox couple.

The oxidizing agent chosen should have more positive potential with respect to Fe^{3+}/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 ($2H^+ + 2e- \rightarrow H_2$) as well as ($2OH^- + 2h+ \rightarrow H_2O + 1/2O_2$) 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 $2OH- + 2h+ \rightarrow H_2O + ½ O_2$.

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 (%) = $[(1-e^{(\chi_A-\chi_B)^2/4}]$X 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_2O_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_2O_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.

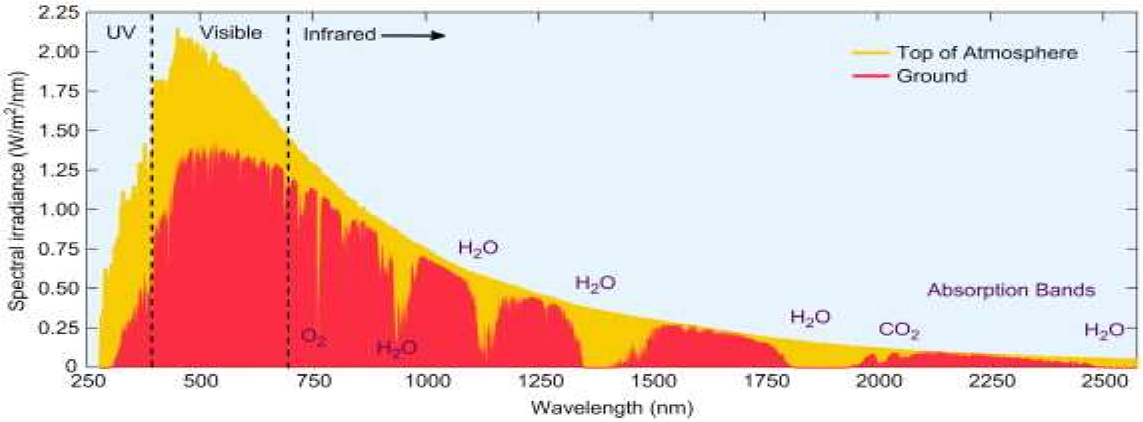


Fig.8 The solar spectrum as a function of wavelength [3]

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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CHAPTER 5

Photo electrolysis of Water-Holy Grail of Electrochemistry

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 photo catalysis by ZnO and TiO_2 has been reported 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.1.

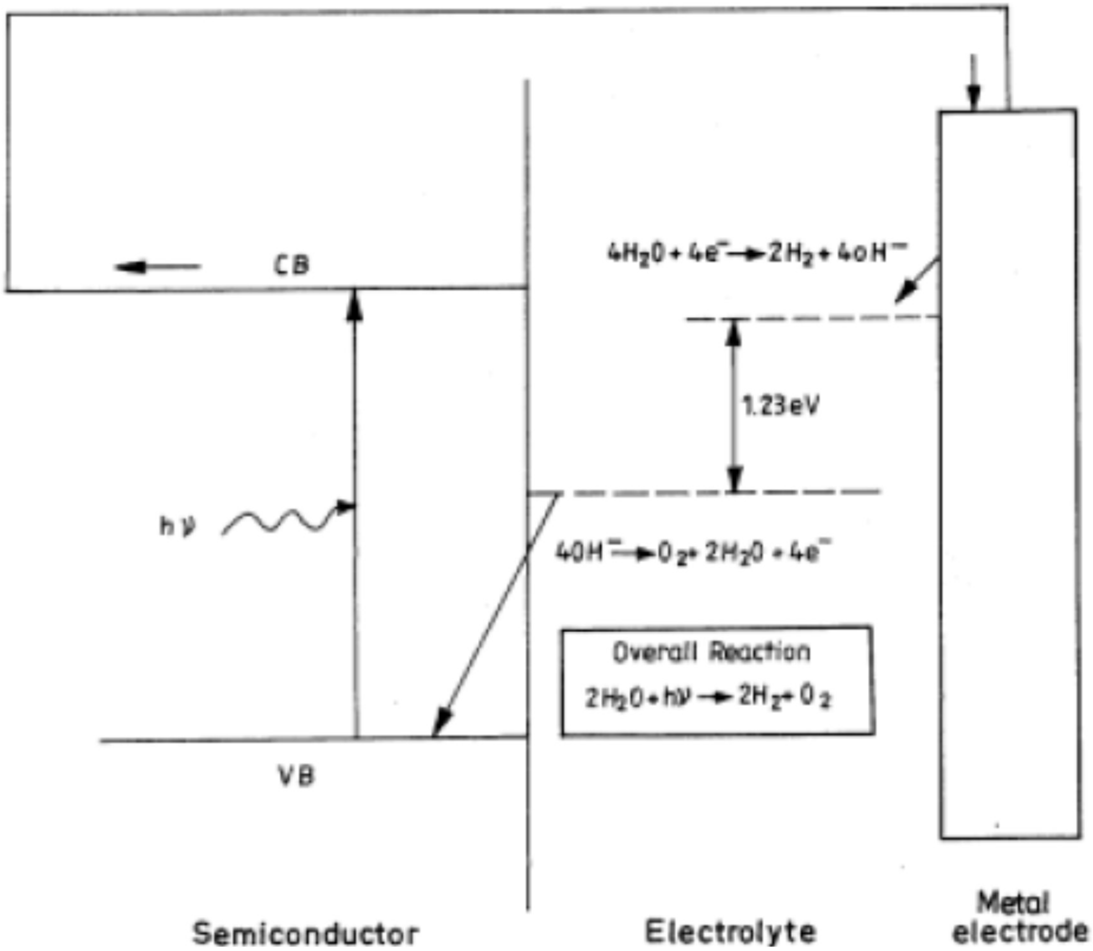

Fig. 1. Schematic representation of photo-electrolysis of water

Using these postulates the known semiconductors and the possibility of water splitting reaction taking place on their surfaces are pictorially shown in Figure 2.

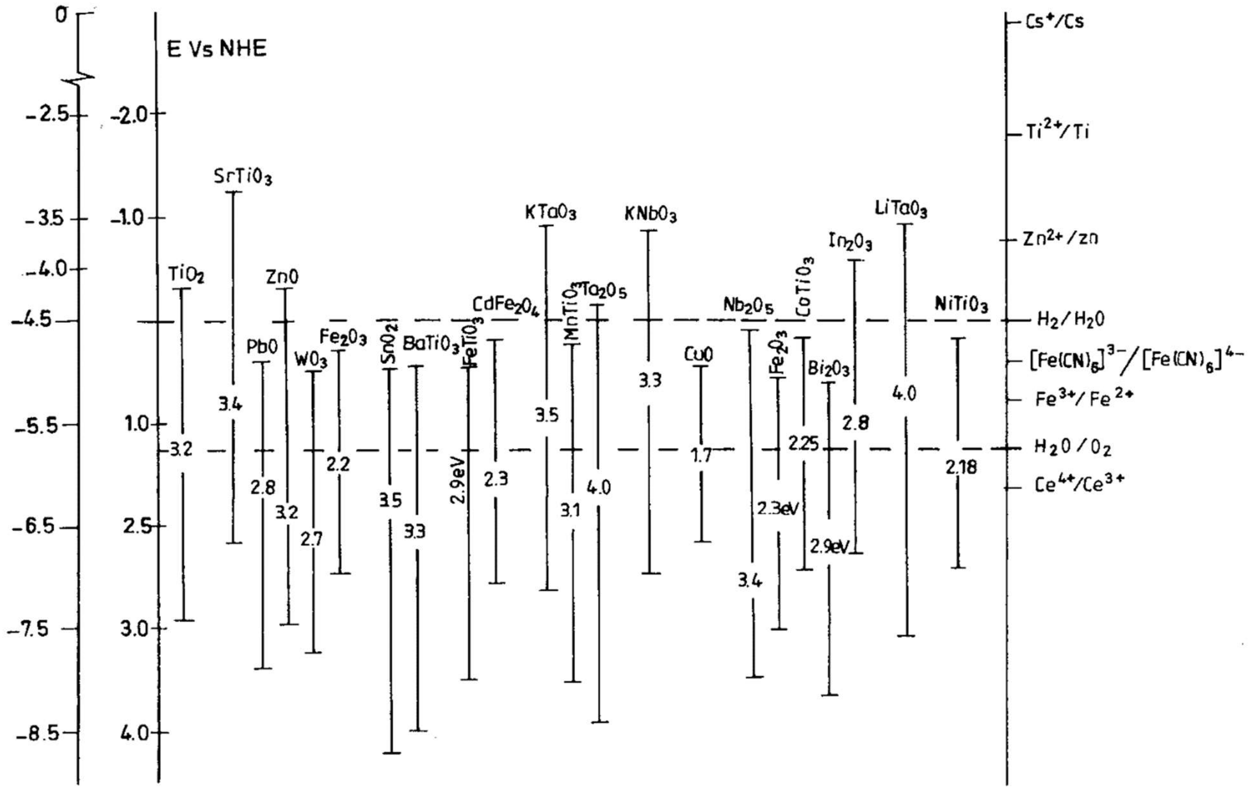

Fig. 2. Some of the well-known semiconductors, their band gap values and hydrogen and oxygen evolution potential are shown. From these, one can make a choice of semiconductors which can decompose water. On the right side some other common redox potential values are also given to indicate which other 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)

However, in the solar water splitting reaction, the incident radiation creates electron and hole pairs and if these were to take part in the surface reaction, then the 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)

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

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 sort of sensitization and hence the route of charge transfer has been extended and hence the efficiency could not be increased considerably. Sensitization of semiconductors will be taken up in a subsequent chapter.

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 have to be made available 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 mesoscpic 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

  $4h+ + 2H_2O \dashrightarrow O_2 + 4\ H^+$

- 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

  $4H+\ + 4e-\ \dashrightarrow\ 2H_2$

- 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.

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 has 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 identified for the decomposition of water. The success in this attempt will give a boost to the energy needs of this universe.

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CHAPTER 6
SOME FUNDAMENTAL ASPECTS OF PHOTOCATALYSIS

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

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

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 are given by the equation,

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

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

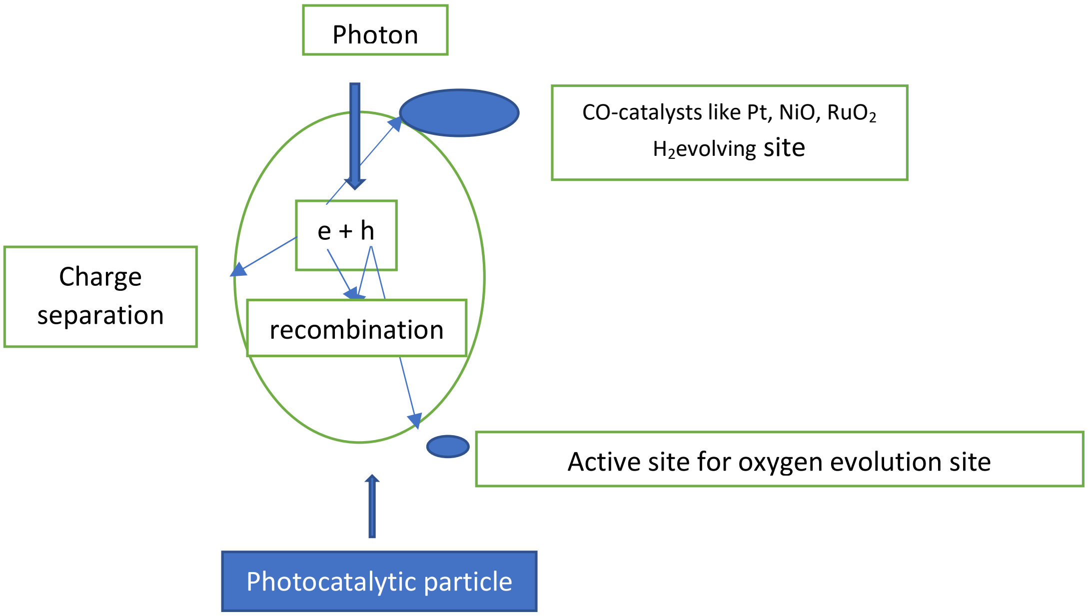
$$N_j p_i \ \alpha \ \exp(-E_g/kT)$$

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. Therefor conductivity can be controlled by doping and is given by the expression

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

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:



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 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.

Typical model calculation is shown below. Let us consider for model calculation the semiconductor TiO_2. The band gap of this semiconductor was taken as 3.2 eV. The values of electron affinity and ionization energy of Titanium and oxygen are respectively, 0.08 and 1.46 eV and 6.81 and 13.6 eV. The elements electronegativity is given by arithmetic mean values and are respectively 3.44 and 7.53 respectively. The semiconductor electronegativity is given by geometric mean and there are three elements in the semiconductor chosen is given as $[3.44 \text{ X } (7.53)^2]^{1/3} = 5.79$. The value of the conduction band minimum is given by $\chi - E^e - 0.5 \text{ X } E^g = 5.79-4.5-(0.5\text{X}3.2) = -0.31$ eV. The valence band position can be -0.31+3.2 = 2.89.

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

If there is a depletion layer then 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.

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).

Stability against photo corrosion

Most important property which limits the usefulness of many photo-active materials. 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.

Most of the M-O photo anodes are thermodynamically unstable. Eg: 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 an important criterion that 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- acts 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. Some other oxygen containing multicomponent systems are also useful typical examples are $BiVO_4$, $AgNbO_3$, Ag_3VO_4, Ca_2 Bi_2 O_4.

Ion doping

Cation doping - transition metals (V, Cr, Fe, Mo, Ru, Os, Re, Rh, V, etc.) -rare earth metals and these doped ions 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. These systems show little tendency to form recombination centers. Another remarkable thing is construction of Z-scheme systems. Dual semiconductor systems, and Dye-sensitization are other methods to shift the photon absorption wavelength. Dye molecules absorb light with the transfer of an electron from the ground state to excited state. The excited electron may then transfer to the conduction band of an appropriate metal oxide participate in the reduction reaction.

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CHAPTER 7

PHOTO-CATALYTIC DEGRADATION OF DYES: AN EVALUATION

Introduction

Photo-catalytic degradation of dyes or other organic pollutants is a recent research exercise intensively pursued [1-7]. Synthetic dyes are nowadays extensively used in the products like clothes, leather accessories, furniture, and plastic products. However, nearly 12% of these dyes is wasted during the dying process and ~ 20% of this wastage enters the environment [8]. Dye degradation is a process in which the large dye molecules are broken down chemically into smaller molecules. The resulting products are water, carbon dioxide, and mineral byproducts that give the original dye its color. During the dyeing process, not all of the dye molecules are used. The water waste that the industry releases contain a percentage of these dye molecules.

Heterogeneous photo-catalysis is one of the modern methods widely employed for the degradation or bleaching of the dyes [9]. The process mainly involves transfer of electrons from the valence band to the conduction band of a semiconductor surface (mostly oxides and sulfides) on illumination with appropriate wavelength of light. These generated excitons react with oxygen or water to yield superoxide anions and hydroxide radicals. These species have increased oxidizing and reducing power to degrade numerous molecules including those present in industrial dyes. The decontamination processes by these species and some other species like various forms of Fenton processes are called in scientific parlor Advanced Oxidation Process (AOP). Even though AOP is an important research area in the contemporary literature, we shall restrict only to those dye degradation processes promoted by semiconductors photo-catalytically [10-12].

It is necessary at this stage to point out the need to review this topic at this stage. The reasons include [13]:

(1) There are number of research groups working on this area and it is better to assimilate the literature at frequent periodicity

(2) Photo-catalytic degradation of pollutants is one of the methods which has some advantages including total degradation and possibly the less expensive method.

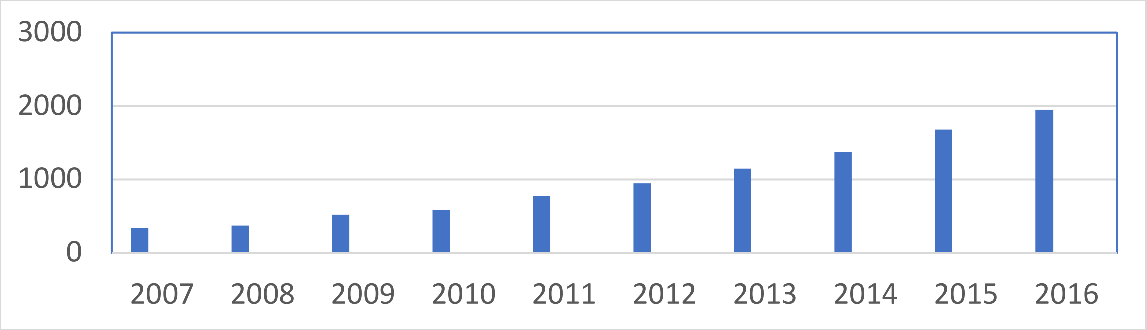
(3) The degraded components like water and carbon dioxide are non-toxic.

(4) The feasibility of degradation of any pollutant can be *a priori* decided from the numerical values of the oxidation potential of the pollutant and the reagent (like $OH^{\bullet}$ radical; standard reduction potential value is around 2 V [14]).

There are various kinds of dyes that are employed for coloring objects. These materials are classified according to the structure of the molecule component, color, the method that is adopted to apply these dyes to objects. The chromophore group attached to the dye molecule specifies the group to which the dye belongs and these can mainly be classified as acridine dyes, azo dyes, anthroquinone dyes, nitro dyes, xanthene dyes and quinine-amine dyes and so on [7]. The studies reported on photocatalytic dye degradation mainly concerned with the variables like concentration of the dye, the amount of catalyst employed, the effect of the intensity of the light irradiation and the time of irradiation and the effect of dissolved oxygen and other species. The kinetics of photocatalytic degradation of dyes are usually considered to be a pseudo first order reaction with the kinetic data fitted to the equation $-\ln (C/C_0) = kt$. The relevance of this kinetic data fit will be considered separately in a subsequent section.

Though extensive studies are reported on the photo-catalytic degradation of pollutants in water, there are certain aspects that have not yet received careful attention. The purpose of this presentation is to focus on these issues and to point out what is required in this direction. The literature in this area is increased five times or more during the last 10 years as seen from the data shown in Fig.1. It is noticed that the number of publications is doubling or more every five-year period. It is therefore natural that people attempt to review the literature at periodic intervals [5-7]. However as said earlier, the research is pursued mostly around oxides (especially TiO_2) and the variables studied are mostly the same, whether it is required or not.

Fig.1.Number of publications falling under the category of Photo-catalytic degradation of dyes (source: Web of Science)



Before we embark on the limitations of the studies so far reported, it is necessary to briefly review the available literature though not comprehensively but representatively. A few selected publications from literature are summarized in Table 1. Majority of the studies reported in literature deal with the effect on degradation activity on variables like the amount of the catalyst, the concentration of the dye employed, pH, effect of the radiation source and time of irradiation and also the effect of dissolved oxygen and others**.** The kinetics of degradation of dyes on most of the catalyst systems studied follows first order [15].

Conventional chemical, physical and biological processes have been extensively employed for treating waste water containing dye molecules. These methods have the following disadvantages like high cost, requirement of high energy, generation of secondary pollutants in the treatment process. The Advanced Oxidation Process (AOP) has received considerable attention in recent times for the decomposition of organic dyes [16].

1. The literature so far

This is an area of research which is carried out throughout the world unlike other areas of science. Research in certain areas of science is confined to certain regions of the world but degradation of dyes has been studied in almost all the countries and regions including almost all the developing countries around the world. This is reflected in the data assembled in Table 1**.** Scientifically the process involved in the degradation of dyes can be pictorially represented as shown in Fig2**.**

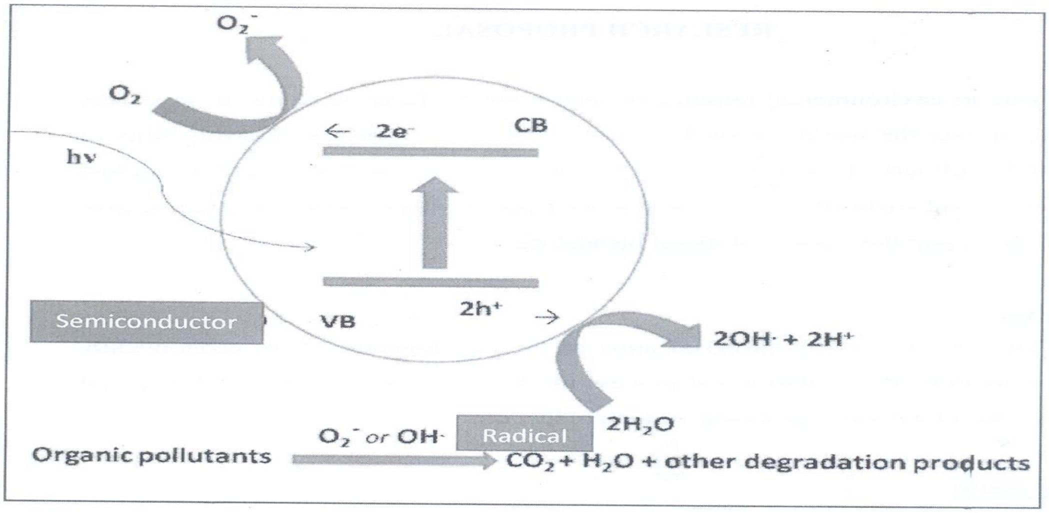


Fig.2. Pictorial representation of the process taking place in the photocatalytic degradation of dyes on semiconductor surfaces.

Most of the photocatalytic dye degradation studies reported have been with Titanium dioxide as photo-catalyst. However, the major disadvantage of TiO_2 that it absorbs only in the UV regions since it has a band gap of around 3.2 eV. Among the different phase of TiO_2, anatase form of TiO_2 is mostly employed due to its higher photon absorption characteristics. It is clear that the phase composition of TiO_2 has a role to play in degradation of dyes. Among the most prominent phases of TiO_2 namely Anatase, rutile and Boookite, the first two phases are most studied systems as seen from the data given in Table.1. The position of oxygen ions on the anatase surface exhibits a triangular arrangement which allows significant absorption of organic molecules, whereas, the orientation of titanium ions in the anatase phase creates an advantage's reaction condition with the adsorbed organic pollutants [17-24]. Interestingly, these favorable structural arrangements of oxygen and titanium ions are not present in the rutile phase. It is also believed that pure anatase phase with small proportion of rutile phase is conducive for meso-porosity and thus favourable for dye adsorption [17-28].

Mechanistically, the photon excites an electron from valence to the conduction band and the excitons (free electron in the conduction band and hole in the valence band) generate radical species which is responsible for the degradation of organic dyes to carbon dioxide and water and other degradation species.

Even though large surface area is recommended for effective dye degradation, (P-25 Degussa TiO_2 is a mixture of 80% anatase + 20% rutile phase and this combination alone makes this system active. In most of the studies this system is used as standard for comparison), dye adsorption may precede the degradation and this can affect the interpretation of the kinetics of degradation of dye. This aspect will be taken up subsequently.

Among the various waste water treatment procedures, dye removal has occupied a prominent place. Because of aesthetic and environmental concerns, the degradation of dyes in the effluent water of textile dyeing and finishing industry has been most important [29]. The semiconductors especially TiO_2 and ZnO are employed as nanorods, nano-spheres, thin porous films, nanofibers and nanowires or supported on polymeric films [30]. These systems exhibit high activity, low cost and environmentally acceptable [31-33].

Apart from TiO_2 and ZnO, various other semiconducting systems like CdS, ZrO_2 and WO_3 have been employed in the photocatalytic degradation of dyes. These studies and other reports on ternary oxides are included in Table.1. The drawback of most of these systems like TiO_2 is the high value of band gap and they require UV photon sources to be able to decolourize waste-water.

Table 1. Representative literature data on the photocatalytic degradation of dyes

Catalyst systems studied	Dyes employed	Conditions and variables studied	Reference
Graphene – gold Nano composite (GOR/Au)	Rhodamine B Methylene blue Orange H	Visible light - Rate of degradation of methylene blue is greater than Rhodamine B even though the redox potential is highest among these three dyes. Adsorption is identified as the reason	A1
Nanocrystalline anatase and rutile TiO_2	Acetophenone Nitrobenzene Methylene blue Malachite green	The activity of Anatase is higher than that observed with Rutile. The reason for this difference is not indicated in this communication	A2
TiO_2, ZnO, SnO_2	Crystal Violet Methyl Red	ZnO exhibited highest activity. Even better than Degussa P-25 and loading silver on ZnO resulted in 20% increase in photocatalytic activity	A3
Mg-TiO_2	Methyl Orange	The catalyst has better activity than the undoped TiO_2- Dye sensitization and injection of the excited electron is considered as the cause	A4
TiO_2 Impregnated ZSM-5 (TiO_2-ZSM = 0.15:1)	Reactive Black-5	This ratio system shows high adsorption capacity and degradation activity	A5
ZnO-nanoflowers	Methyl Orange Congo Red Eosin B Chicago Sky Blue	The catalyst prepared from asymmetric Zn(ii)dimeric complex showed good photocatalytic activity towards methyl Orange compared to other dyes	A6
ZnO Nano powder	Rhodamine B	95% degradation of the dye was observed under solar light irradiation	A7

TiO_2	Methyl Orange Methylene Blue	The photocatalytic activity is found to be greater in the presence of solar light than in UV.	A8
Nano-sized $GdCoO_4$	Rhodamine B Rhodamine Blue (RBL) Orange G(OG) Remazol Brilliant Blue (RBBR)	The catalyst (3nm) is more efficient than P-25. Size dependence is shown. The intermediates in both $GdCoO_4$ andP-25 are the same	A9
TiO_2	Methylene Blue Methyl Orange Congo Red	The size and Phase (Anatase) are important. Adsorption of the dye on the catalyst surface is also important (Freundlich isotherm)	A10
TiO_2	Indigo Indigo Carmine	Complete mineralization of the dyes Irradiation with visible light only produced color removal	A12
TiO_2 immobilized on polyvinyl alcohol (PVA) or polyacrylamide (PA)	Methylene Blue, Anthraquinone, Remazol Brilliant Blue R (RBBR), Reactive Orange (RO16).	TiO_2 loaded on PVA appears to be better than that loaded on PA	A11
Nanostructured TiO_2	Mono, di and tri azo class of dyes. Classes of indigoid, anthraquinone triaryl methane and xanthene dyes	Degradation depends on the chemical structure of the dye, the nature of functional groups. Mono-azo dyes degrade faster than anthraquinone dyes. Presence of nitrite group promote the degradation activity.	4
High surface area TiO_2	Methylene Blue Congo Red	Sol-gel method preparation of TiO_2 is suitable for degradation of Dyes.	2

		Freundlich Isotherm is employed.	
N-doped TiO$_2$	Methylene Blue Methyl Orange	Visible light source was employed and depends on nitrogen content of the catalyst	1
Nanometer sized TiO$_2$	Acid Orange 10(AO10) Acid Red 14 14ARI14)	The azo and sulphonate groups are determining factors for degradation	A13
SiO$_2$ nanoparticle dopes with Ag and Au	Methyl Red	(OH). radical produced initiates and also sustains the degradation of the dye	A14
Titanium dioxide	Emerald Green	Degradation rate constant depends on pH	A15
ZnO and TiO$_2$	Rhodamine B Methylene Blue Acridine Orange	ZnO dissolves as Zn (OH)$_2$ and hence shows lower activity as compared to TiO$_2$	A16
TiO$_2$ (UV/Solar/pH)	Procion Yellow	TiO$_2$ in presence of solar irradiation is better	A17
TiO$_2$	Reactive Red 2	Degradation in presence of $H2O_2$ and persulphate ion.	A18
Thermally activated ZnO	Congo Red	Pseudo second order Kinetics was observed	A19
Sol-gel TiO$_2$ films	Lissamine Green B	The film prepared in presence of Polyethylene glycol is better	A20
ZnO	Methylene Blue	Decoloured of actual industrial waste water	A21
Ag-TiO$_2$ core shell particle	Reactive Blue 220	the core shell system was better catalyst under solar light	A22
Anatase Nano-TiO$_2$	Reactive Blue 4 (anthraquinone dye	In presence of H_2O_2 the dye degradation increased	A23
TiO$_2$/ZnO Photo catalyst	Methylene Blue	ZnO appeared to be better than Pure TiO$_2$	A24

P160 TiO_2	Basic Yellow – 28	Better degradation in weak acidic conditions, carbonate ion increased degradation activity	A25
Ferrihydrite modified Diatomite with TiO_2 /UV	Vat Green 03	A composite catalyst with P-25 with co-adsorbent removed colour over 98%	A26
Orthorhombic WO_3	AO7 dye	Phenol, humic acid and EDTA inhibited decolouring but oxalic acid increased	A27
$Fe^{3+}/C/S/-TiO_2$	Mono and Di-azo dyes	Mono azo dye is better than diazo dyes. Decolurization under visible light	A28
Ni doped TiO_2	Malachite Green	Hydroxyl ion as the oxidizing species	A29
TiO_2	Solo phenyl Red 3BL	Concentration of OH^* and O^* radical determines the rate	A30
TiO_2	Mono Azo Orange 7 (AO&) Reactive Green 19 (RG19)	Mono azo dye (AO7) than the binary azo dye (RG19) under solar light	A31
TiO_2	Azo dye and disperse dye	A modelling exercise on governing parameters	A32
TiO_2	Methyl Orange Methylene Blue	Degradation under UV irradiation	A33
TiO_2 Photo-catalyst	Indigo Carmine dye	UV irradiation optimum conditions pH=4 and dye concentration 25 ppm 98% colour removal	A34
ZnO photo-catalyst	Methylene Blue	Basic solution is better.	A35
TiO_2 Photo-catalyst	Methylene Blue	Basic medium is better	A36
Carbon doped TiO_2	Amido Black-10B	Active oxygenated species is responsible for decolourization.	A37

ZnO photocatalyst	Direct Red-31 (DR-31) dye	Effect of annealing temperature (500-800C)- UV irradiation	A38
Sol-gel TiO_2 films	Methyl orange, Congo Red	TiO_2 films with dip coating with Polyethylene glycol (better) 254 UV is better than UV 365 nm	A39
Undoped and Fe doped CeO_2	Methyl Orange	1.5 % doping of Fe^{3+} was optimal	A40
Immobilized TiO_2	Methylene Blue	Deposition of Photosensitive hydroxides decreased the activity	A41
Ni/$MgFe_2O_4$	Malachite Green	Visible light active	A42
TiO_2	Methyl Orange	Superoxide anion radicalPolytetrafluoroethyle-A1 based triboelectric nanogenerator (TENG) assisted the process	A43
Crosslinked Chitosan/nano CdS	Congo Red	Acidic Medium is better, Presence of No_3^- accelerated Br^-, Cl^-, SO_4^{2-}, inhibit decolourization	A44
TiO_2/UV	Methylene Blue	Mineralization of carbon, nitrogen and Sulphur into CO_2, NH_4^+,SO_3^{2-}	A45
Cu impregnated P-25	Azo dye Orange II	Cu Impregnated TiO_2 is better than H_2O_2/UV homogeneous reaction.	A46
Ag-Ni/TiO_2 synthesized by gamma irradiation	Methyl Red	Bimetallic co-doped is better than bare TiO_2	A47
Cr doped TiO_2	Methylene Blue Congo Red	Cr doped promoted Anatase to Rutile phase transition	A48
ZnS Quantum dots doped with Au and Ag	Methylene Blue	Metal loading favours degradation; accounted in terms of increased life time of charge carriers, Opto-electronic characteristics and	A49

		isoelectric point need to be considered in proposing photo-catalyst	
Mesoporous CeO_2	Rhodamine B	Hydroxyl radicals are the active species	A50
ZnS	Rose Bengal	Hydroxyl radicals are shown as the active species	A51
C-TiO_2 films	Azorubine	Photo-degradation and adsorption effects are the reason for better decolourization	A52
La-Y/TiO_2	Methylene Blue	Optimum dose 4 g/L	A53
Ag-TiO_2	Direct Red 23	Optimum dose 3 g/L	A53
ZnO	Remazol Brilliant Blue dye (RBB)	The degradation follows first order kinetics	A54
TiO_2 Degussa P-25	2,4-dimethylphenol, 2,4-dichlorophenol, 2-chlorophenol and phenol	pH 5 was found suitable	A55
ZnO	Crystal Violet	high specific surface area (56.8 m^2/g), high crystallinity and better optical property are responsible for the better activity of ZnO nano nails.	A56
In/ZnO nano particles	Methylene Blue	In is well dispersed on ZnO	A57
TiO2 Degussa P25 and ZnO	Methylene Blue	Visible light is better and ZnO better than TiO_2	A 58
TiO_2 nano particles	Methylene Blue	Basic medium is better	A59
ZnO	Reactive Blue	Reactor design and optimum time	A60
Magnetite+H_2O_2 +UV	Methylene Blue	Process parameter optimization	A61
$Bi_{24}O_{31}Cl_{10}$	Rhodamine B	compatible energy levels and high electronic mobility	A62

BiOI	Rhodamine B anionic reactive blue KN-R	h^+ is the dominant specie for the degradation of dyes.	A63
TiO_2	Alizarin yellow	of Cl^-, SO_4^{2-} inhibit dye removal, depends on TiO_2 source	A64
TiO_2, ZnO	Polycyclic aromatic hydrocarbons (AH)	Surface to volume ratio appears to be relevant	A65
ZnS doped with Mn	Malachite green	UV/ZnS, UV/ZnS/H2O2, UV/doped ZnS systems studied	A66
TiO_2 and Cu-doped TiO_2	reactive blue 4, reactive orange 30, reactive red 120and reactive black 5	Cu-doped TiO2 nanoparticles are very effective in degrading the dye pollutants	A67
Mn_3O_4 nano particles	amido black 10B	peroxomonosulfate (PMS), peroxodisulfate (PDS) and hydrogen peroxide (HP) enhanced degradation	A68
Photo-Fenton system	Reactive orange M2R dye	Acidic pH favours, reaction mechanism is proposed	A69
TiO2 catalyst with a very low level of Pt	Phenol	Eosin Y sensitized TiO_2	A70
TiO_2	Methylene Blue	p-n junction heterostructure CuO-TiO2 enhance photoactivity	A71
TiO_2 coated Cotton fabric	amaranth dye	prepared fabric showed enhanced dye degradation capabilities	A72
titanium dioxide TiO2 and zinc phthalo cyanine (ZnPc)	4-Nitrophenol	Efficiently degrade nitrophenol	A73

Silver phosphate	Methylene Blue	visible-light-driven photodegradation of dye pollutants	A74
$CeCrO_3$	Fast Green dye	First order kinetics,	A75
ZnO	Acid Green 25	Both acidic and basic medium	A76
Anatase TiO_2	Methylene Blue Phenol	pH = 6.4 is optimum	A77
CeO_2-ZnO	Methylene Blue 4’-(1-methyl-benzimidazoyl-2)-phenylazo-2” -(8”-amino-1”-hydroxy-3”,6”-disulphonic)-naphthalene acid	50-80 nm with large defects	A78
Al_2O_3-TiO_2 and ZrO_2-TiO_2 Nanocomposites	Methylene Blue Rhodamine B Methyl Orange	both the composites degrade methylene blue and rhodamine B effectively under UV-A light the photodegradation of methyl orange is slow	A79
MgO	Methylene Blue	Over 90% degradation	A80
TiO_2	Acid Orange 67	light source is UV is better in comparison to Visible.	A81
TiO_2 on Polyethylene film	Crystal Violet Methylene Blue Basic Fuchsine	Sun light degradation Undergraduate experiment	A82
Mo doped TiO_2	Toluidine blue-o	degradation of the dye follows pseudo-first order kinetics	*A83*
Copper Ferrite	Methylene blue	In Glycerol it is not effective H_2O_2 is better	A84
TiO_2 as photo-catalyst	Tatrazine (azo dye)	Influence of addition of other salts studied	A85
$Ni_{0.6}Co_{0.4}Fe_2O_4$	Congo Red	Photo-catalytic degradation maximum at pH 3	A86
Zn-TiO_2	Direct Blue 71 dye	Zn Doped system is better than bare TiO_2	A87

Ag modified ZnO	Reactive Orange *16*	Ag modified system was better than pure ZnO	A88
TiO_2	Reactive Orange 16 Dye (RO16)	Effect of the amount of TiO_2 studied	A89
ZnO-CuO	Reactive black5 (RB5)	This system is suitable technique for degradation of dyes and environmental pollution from effluents.	A90
TiO_2 on polyethylene glycol	Methyl Orange Congo Red	Under UV irradiation higher efficiency observed	A91
g-C3N4 thermally Modified with Calcium Chloride	Rhodamine B	The photo-generated hole and the superoxide radical are the main active species in the degradation process. 50 times more active than unmodified system	A92
CdO/TiO_2 coupled semiconductor	Reactive Orange 4 (RO 4)	best photocatalytic activity in the degradation of RO 4 compared with bare TiO_2	A93
ZnO	Remazol Brilliant Blue R, Remazol Black B, Reactive Blue 221 and Reactive Blue 222	A synergistic effect in the coupled TiO2-ZnO system was not observed	A94
CdS/SL $g-C_3N_4$) SL= Single Layer)	Rhodamine B	visible-light-responsive and environmentally friendly photo-catalyst for the degradation of dye	A95
BiOCl	Rhodamine B and other dyes	Visible light degradation may be complicated. The use of multitude of dyes is necessary	A96

		to assess the degradation activity	
Cr doped ZnS	Methyl Orange	Visible light is better than UV	A97
Nano TiO_2(C-Fe doped)	C.I. Basic blue 9, C.I. Acid orange 52	Real waste water treatment	A98
CeO_2-SnO_2	Direct Black 38	Activity is comparable with TiO_2-P25	A99
Z-scheme SnO_{2-x}/g-C_3N_4 composite	Rhodamine B	Z-scheme mechanism to enhance photo-degradation activity	A100
BiOCl-Au-CdS	Methyl Red Rhodamine B	Z-scheme BiOCl-Au-CdS exhibited excellent sunlight-driven photocatalytic activity toward the degradations of organic dyes and antibiotics	A101
TiO_2-ZnO	RB 21 dye	UV photoreactor and TiO_2 is the best	A102
CaO	indigo carmine dye	pH 9 was suitable	A103
g-C_3N_4/oxygen vacancy-rich zinc oxide	Methyl Orange	deactivated after five cycles of methyl orange degradation	A104
$CoFe_2O_4$/C_3N_4 hybrid	Rhodamine B	Typical Z-scheme system in environmental remediation	A105
α-$Bi_4V_2O_{11}$; γ-$Bi_4V_2O_{11}$	Rhodamine B Methylene Blue	Surface to Volume ratio is responsible	A106
BiVO4-rGO	Rhodamine B	Better than pure BiVO4 and P-25	A107
Flower like N-doped MoS_2	Rhodamine B	27 times better than bare MoS_2 and 7 times better than P-25	A108
$H_3PW_{12}O_{40}$/SiO_2	Rhodamine B	under simulated natural light irradiation	A109
$SrTiO_3$	Methylene Blue Rhodamine Methyl Orange	Non-selective process	A110

$CuO/Ag_3AsO_4/GO$	Phenol	Photo-stability and reusability	A111
TiO_2/diatomite	Rhodamine B, Methyl orange, Methylene blue	wastewater treatment -good photocatalytic property and reusability.	A112
Cr (VI) using Ag/TiO2	4-chlorophenol	stability and reusability of catalysts	A113
$PbCrO_4$/TiO2	Rhodamine B	good visible light-sensitive photocatalyst for removing Rh B	A114
$WO_3/SnNb_2O_6$	Rhodamine B	Z-scheme charge transfer mechanism was proposed for the elimination of organic contaminants under irradiation of visible light.	A115
ZnO	Acid Red 27	H_2O_2, $K_2S_2O_8$, $KBrO_3$ due to concentration increases the rate	A116
CuS	methylene blue, rhodamine B, eosin Y and congo red	photodegradation rates of dyes usually follow pseudo-first-order kinetics for degradation	A117
Cobalt Hexacyanoferrate (II)	Neutral Red dye	Degradation under UV light and photo-catalyst	A118
N-doped ZnO	Azure A	N-doped zinc oxide has been used as an effective catalyst for carrying out number of chemical reactions	A119
Al_2O_3-TiO_2, ZrO_2-TiO_2	methylene blue, rhodamine B	Methylene blue degradation is slow Visible light degradation of rhodamine B	A120

The percentage degradation of dyes in waste water improved with increasing intensity of exposed light. With high intensity irradiation, the recombination may not be significant, but when the intensity is low the recombination of the electron hole formed predominates. The photocatalytic activity depends on the thermal history of the semiconductor and the chemical nature of the semiconductor. The choice of the semiconducting systems is based on parameters like physical form of the semiconductor, their stability under the reaction conditions. Environmentally acceptable, cost effectiveness, less toxicity and in all these counts titanium dioxide appears to be the best choice. Comparing various systems for use of actual waste water treatment the following order has been proposed Degusa P-25 > TiO2 (Anatase) > TiO2 (Rutile). However, the amount of catalyst employed depends on the chemical nature of the semiconductor.

The photocatalytic activity can be altered with modification of the semiconductor. The modification can be with various aims like shifting the irradiation wavelength to the visible region and also coupling semiconductors for effective use of the excited electron-hole pair. Recently g-carbon nitride (g-C_3N_4) has been modified with calcium chloride and the mechanism of degradation of Rhodamine B dye itself is modified. The proposed schematic diagram is shown in Fig.3.

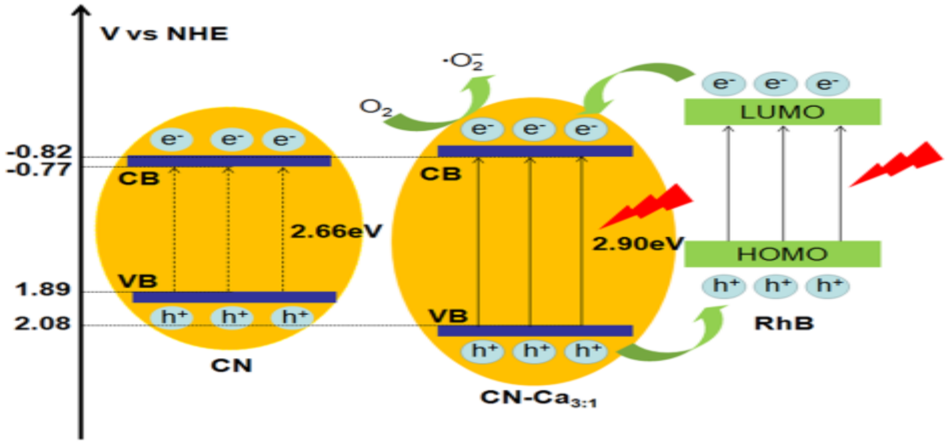


Fig.3. Energy level diagram of CN and CN modified with $CaCl_2$ and how the degradation activity of Rhodamine B is enhanced with modification of CN [reproduced from ref. A92].

The valence band level in modified system is shifted to more positive value and thus enhances the oxidation ability. Simultaneously the dye is also photoexcited and transfers the electrons to the conduction band of the modified g-C_3N_4. This route predominates when visible light is employed.

Apart from these inherent modifications to the semiconductors, (so called doping), coupling of semiconductors have also been tried for shifting the wavelength to the visible region and this is also called Z-scheme in some cases.

Mechanism of Photo-catalytic Degradation of Dyes

It has been stated that radical species generated during photoexcitation of the semiconductor is responsible for the degradation of dyes. The essential steps involved can be visualized as the following steps [34-36].

Semiconductor + photons (hv) → e^- (CB) + h^+(VB) (1)

$h^+ + H_2O \rightarrow H^+ + OH^-$ (2)

$h^+ + OH^- \rightarrow OH\bullet$ (3)

$e^- + O_2 \rightarrow O_2\bullet$ (4)

$2e^- + O_2 + H_2O \rightarrow H_2O_2$ (5)

$e- + H_2O_2 \rightarrow OH\bullet + OH^-$ (6)

Organic pollutant + $OH\bullet + O_2 \rightarrow CO_2 + H_2O$ + other degradation products (7)

The pictorial representation of this process is shown in Fig.2. The excited electron and hole in the semiconductor are responsible for the degradation of the dye. Variety of semiconductors have been employed and most of them are employed in the nano-state due to increased surface area and also due to favourable quantum size effect [37-40].

TiO_2 in various forms with metal and non-metal doping have been employed for the degradation of a variety of dyes owing to its stability, degradation capability, and also non-toxic nature [41,42]. However, the possible experimental variables including the wavelength of the light to be used and separation technology of the solid in treatment process restricts the employment of TiO_2 for commercial dye degradation process. More advanced level research is at present required to find suitable alternative to TiO_2 for this application. Other than TiO_2 the other system that is mostly employed is ZnO and other semiconducting oxides as stated above.

Experimental Variables Studied:

In addition to the chemical nature of the semiconductor employed, the wave length of irradiation employed based on the band gap of the semiconductor, the effect on the degradation of dyes on a number of other experimental variables have been studied. Typical semiconductors studied and the band gap values of each of them are assembled in Table.2.

Table.2. Typical Semiconductors [Refer to Table 1] used for Photo-catalytic Degradation of Dyes and the Band gap (eV) Values of these Materials.

Semiconductors studied for photodegradation of dyes	Band gap values (eV) (wavelength [nm] of irradiation)
TiO_2(Anatase form)	3.2(387)
TiO_2 (Rutile form)	3.0 (415)
TiO_2 (Brookite form)	3.14(395)
ZnO	3.36(370)
WO_3	2.76(450)
CdS	2.42(515)
CuO	1.2 (1035)
Cu_2O	2.2 (565)
MgO	5.90
Mn_3O_4	3.28(380)
ZnS	3.6(345)
CeO_2	3.19(390)
Fe_2O_3	2.3(540)
Fe_3O_4	2.25(550)
ZrO_2	3.87(320)
g-C_3N_4	2.66(465)
Ag_2O	1.4(885)
$SrTiO_3$	3.25(380)
Bi_2WO_6	3.13(395)
$BaTiO_3$	3.30
Bi_2O_3	2.80
CdO	2.20
CoO	2.01
Cr_2O_3	3.50
HgO	1.90
In_2O_3	2.80
MnO	3.60
Nb_2O_5	3.40
NiO	3.50
PbO	2.80
PdO	1.00
Sb_2O_3	3.00
SnO	4.20
SnO_2	3.50
V_2O_5	2.80

Effect of pH on the Photo-catalytic Degradation of Dyes

As seen from Table 2, each of the degradation studies is efficient at a particular pH. The reason for this observation is the change in the value of the oxidation potential (approximately 59 mV per pH) of the species involved in the experimental system studied. Since the oxidation potential of hole and reduction power of the electron generated due to irradiation are dependent on the positions of the top of the valence band and bottom of the conduction band and these are critical for the degradation of dyes on semiconducting systems employed.

The Issues on Hand

Most of the published literature covers as variables, the light source, its intensity, pH of the medium, the amount of the catalyst employed. The initial concentration of the dye taken for study, the irradiation time and the other species like oxygen present in the reaction medium. Almost all the publications have been following these variables invariably. It is recognized that the study of these variables is important for assessing the utility of this method for pollutant removal (textile dye industry) from waste water stream. The purpose of this presentation is to examine on what other aspects of these parameters can be intrinsically examined.

Kinetics of photodegradation of Dyes

Generally, the kinetics of photocatalytic degradation of organic pollutants and dyes by semiconductors have most often been treated as first order kinetics. This is most common in literature and as an example one of the recent references [15] is provided. The purpose is to analyze some of the consequences of treating the kinetic data on the removal of pollutants and other organic species especially under photo-catalytic conditions generally under first order kinetic equation. The first order kinetic equation generally employed in such circumstances [41] can be written as $- \ln (C/C_0) = kt$; where C is the concentration at any time t seconds and C_0 is the value of concentration of the species that is undergoing degradation at zero time (initial concentration taken) and k is the value of the rate constant, this may be a lumped parameter including the value of the intrinsic rate constant, adsorption equilibrium constant and so on. Typical kinetic data analyzed according to first order kinetic equation of the photo catalytic decomposition of Rhodamine B from ref 15 is given as an example.

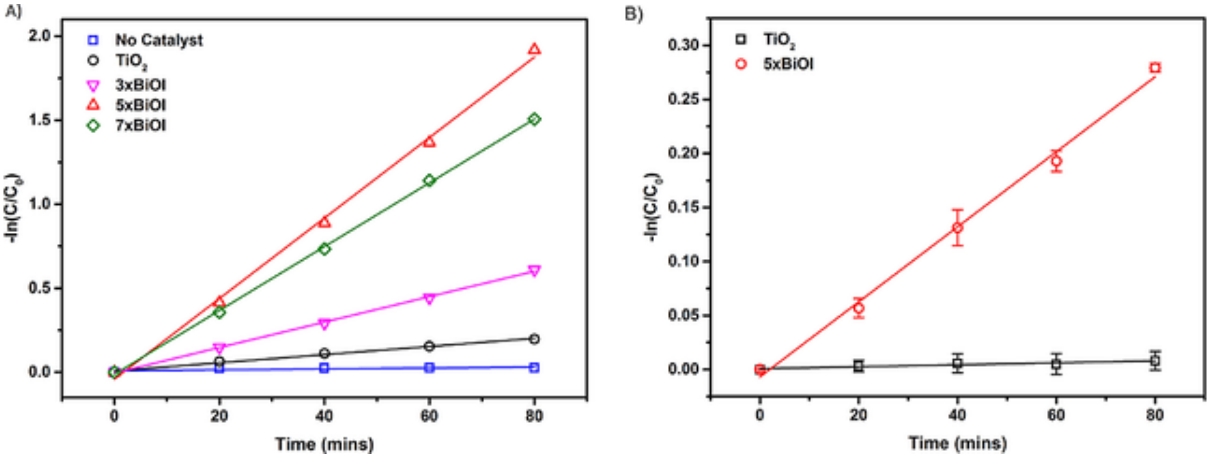


Fig 1 Photocatalytic degradation kinetics of Rhodamine B on various photo-catalysts treated according to first order kinetic equation [data reproduced from ref.15. There are any number of this kind of analysis reported in literature on photocatalytic decomposition of dyes and they are referred to in this article at other places.

The main conclusion of this study is that the inherent rate consists of the photo-catalytic and also photo-induced self-degradation of the dye follows first order kinetics. If this argument were to be accepted then the treatment of kinetic data according to first order is only grossly approximate and the apparent rate constant in the equation is only a lumped parameter consisting of mostly the value of the intrinsic rate constant and the rates of other parallel reactions that would have taken place on the surface of the catalyst and many other accompanying non-elucidated rates of degradation. Possibly, the value of the apparent rate constant cannot be taken as a measure of the activity of the catalyst for comparison since the process taking place on the two or more catalysts are not identical or not even similar. This will have serious misconceptions for comparison purposes.

In the example given, the authors report the apparent rate constant on the most active catalyst as 23.9 min^{-1} while the value of the apparent rate constant for the degradation of chlorophenol (where the photon induced degradation is assumed to be nearly negligible) is 3.47 min^{-1} which can be assumed in this case as the value of the intrinsic rate constant. May be caution has to be exercised while comparing two or more catalytic systems on the basis of the rate constant values of the kinetic data treated as first order since on all catalyst systems the reaction may not follow the same kinetics though the treatment according to first order kinetics may apparently satisfy the first order kinetics. The statements given may be applicable to all general reactions which can involve multiple steps like preceding or succeeding surface reactions which are more often treated with first order kinetics. However, it is not our intention to make a general treatment.

Dye degradation can have many preconditions, one of them is the adsorption of the dye on the catalyst surface and this equilibrium constant should be reflected in the value of the rate constant evaluated from the data. The values of the equilibrium constants of adsorption on various catalyst surfaces can give same or different order of reactivity of adsorbents and this has to be considered while choosing the material for wastewater treatment.

The catalyst loading

Another observation invariably recorded in literature is that the rate increases with catalyst loading till certain weight and above this the rate of degradation of the dye decreases with increase in weight. This is not an unusual result since the exposed surface area of the catalyst will not be directly proportional to the amount of catalyst loaded in solution phase reactions. Since dye degradation is proportional to the amount that is adsorbed on the surface of the solid, there can be a saturation point beyond which the solid amount may not have a direct relationship to the degradation extent. In most of the studies reported the maximum amount of the solid loaded for maximum activity is 3-4 mg per liter [3] of the dye solution. This weight of the solid probably indicates the saturation limit of adsorption of the dye and possibly limits the concentration of the dye solution that can be employed for degradation and thus the industries polluting waterways must restrict their pollution limits to this level. This may be a mark for pollution control authorities to note and it must restrict pollution to this level.

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CHAPTER 8

Semiconductors for water splitting: Material design principles

Sustainable energy through catalysis

The field of catalysis has important roles to play in many energy- conversion processes like decomposition of water to generate hydrogen fuel, conversion of carbon dioxide to useful fuels and in the conversion of molecules into value added products. In this, the selection of suitable and efficient materials has been one of the important tasks. Traditionally this exercise has been based on trial and error method of trying some materials and generating experimental data. These data have been subsequently used to formulate empirical rules for selection of materials for a particular application. For example, in the photo decomposition of water to generate hydrogen, one of the postulates is that the cation of the semiconductor should have d^0, d^5, and d^{10} configurations. Based on such empirical rules, new formulations are proposed and tested but the success seems to be limited in these cases. These exercises have been manly to guide experimental efforts for screening candidate materials and also to build or promote the chosen material.

However, all materials proposed in this process are based on empirical basis. They have some experimental evidences as basis but their predictive capacity is not beyond doubt. When using them to make predictions, one can only say something new in regimes where the proposed model is not explicitly fitted to experimental observations. In these cases, the confidence level of the predictions is questionable. To use such empirical models as predictive tool one has to exercise caution and care.

In order to overcome this problem, most often theoretical methods are preferred but the time and accuracy of the methods are trade off. One such example is shown in the figure 1 for some quantum chemical methods that are commonly employed in these days.

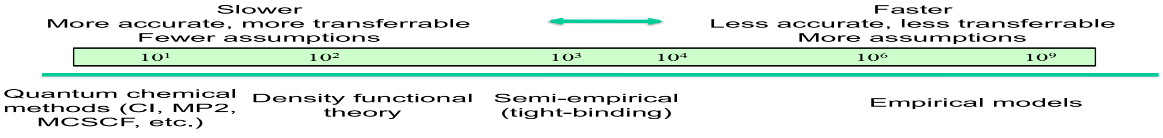

Figure 1 the relationship between time and accuracy of the empical, semiempiral and quantum chemical methods

It is seen from figure 1 that more accurate results require fewer assumptions and also most often the results are transferable.

Now turning our attention to selection of material for photo-electrochemical decomposition of water, the material of choice should have some characteristics. These include that the material chosen should be stable under the experimental conditions employed, the band gap of the semiconductor material suitable for water decomposition, the band positions should be such that hydrogen and oxygen evolution reactions take place spontaneously and the charge carrier should have suitable mobility to reach and react at the interface instead of undergoing recombination. In addition to all these, the sites on the semiconductor surface should favour hydrogen and oxygen evolution reactions efficiently. In figure 2 the band positions of oxide semiconductors and the hydrogen and oxygen evolution potentials are shown and one can deduct from this figure which semiconductor is capable of evolving hydrogen and oxygen by the decomposition of water. A similar scheme is shown for sulphide semiconductors in Figure 3.

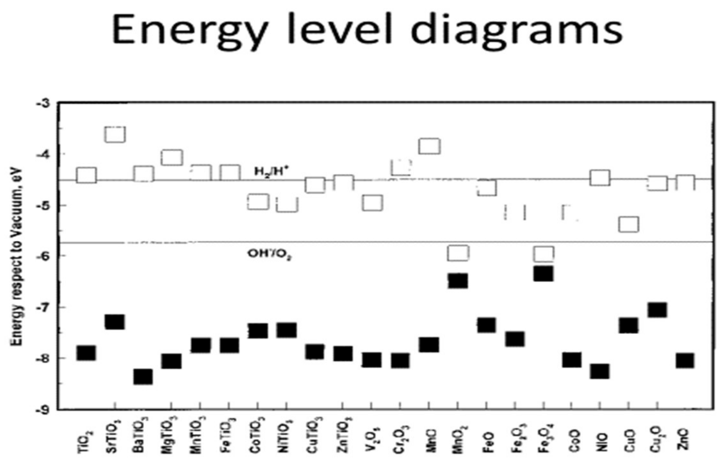

Figure 2 the position of the conduction band (open squares) and the position of the valence band (filled squares) for oxide semiconductors are shown> The hydrogen and oxygen evolution potentials are also shown.

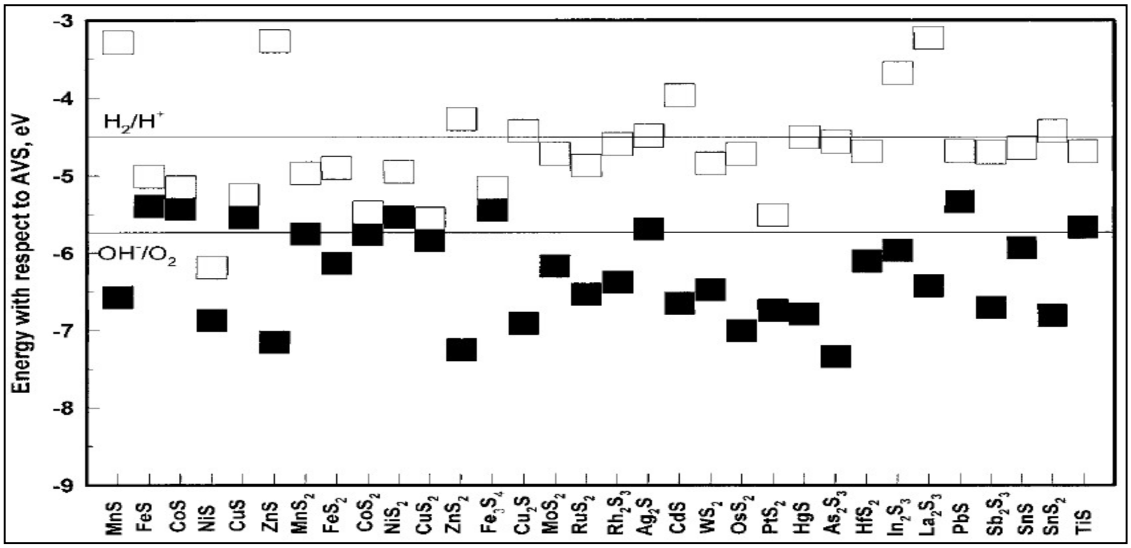

Figure 3. The position of the conduction band (open squares) and the position of the valence band (filled squares) for sulphide semiconductors are shown. The hydrogen and oxygen evolution potentials are also shown.

The positions of the conduction band minimum and valence band maximum can be deduced in a number of ways. These methods are based on the electronegativity values of the species concerned. The Mulliken electronegativity scale which is the average of the electron affinity and ionization energy has been used in these calculations. The Butler Ginley scheme makes use of the following two equations namely

$E_{VB} = -X_{GM} – E_g/2$

$E_{CB} = X_{Gm} + Eg/2$

Where X_{GM} is the geometric mean of the electronegativity values and E_g is the band gap value.

Let us illustrate these calculations with a typical example of TiO_2, ZnO and $SrTiO_3$.

The electronegativity values of Ti, O, Zn and Sr are 3.45, 7.43, 4.45 and 2.0 respectively. The band gaps of TiO_2, ZnO and $SrTiO_3$ are 3.2, 3.2 and 3.4 respectively. If one were to use these values one gets for the conduction band minimum and valence band maximum for these three semiconductors as follows

- TiO_2 : VB -7.4 eV; CB -4.2 eV
- ZnO: VB -7.38; CB -4.18

$SrTiO_3$ is left out as an exercise.

Similarly, one can calculate for sulphide semiconductors and a compilation is given Table 9.1.

An alternate method of calculating the band edge positions is available in the following reference Gritsenko *et al.*, *Phys. Rev. A* **51**, 1944 (1995).

Table.9. 1 Data of Band edges and band gaps of common sulphide semiconductors

Material	Electronegativity	Band gap (eV)	Conduction band	Valence band
Ag_2S	4.96	0.92	-4.50	-5.42
As_2S_3	5.83	2.50	-4.58	-7.08
CdS	5.18	2.40	-3.98	-6.38
$CuFeS_2$	5.15	0.35	-4.87	-5.32
FeS	5.02	0.10	-4.97	-5.07
FeS_2	5.39	0.95	-4.92	-5.87
In_2S_3	4.70	2.00	-3.70	5.70
MnS	4.81	3.00	-3.31	-6.31
MnS_2	5.24	0.50	-4.99	-5.49
MoS_2	5.32	1.17	-4.73	-5.90
NiS	5.23	0.40	-5.03	-5.43
NiS_2	5.54	0.30	-5.39	-5.69
PbS	4.92	0.37	-4.74	-5.11
$PbCuSbS_3$	5.22	1.23	-4.61	-6.11
PtS_2	6.00	0.95	-5.53	-6.48
Rh_2S_3	5.36	1.50	-4.61	-6.11
RuS_2	5.58	1.38	-4.89	-6.27
Sb_2S_3	5.63	1.72	-4.72	-6.44
SnS	5.17	1.01	-4.66	-5.67
SnS_2	5.49	2.10	-4.44	6.54
TiS_2	5.11	0.70	-4.76	-5.46
WS_2	5.54	1.35	-4.86	-6.21
ZnS	5.25	3.60	-3.46	-7.06
ZnS_2	5.56	2.70	-4.21	-6.91
$Zn_3In_2S_6$	5.00	2.81	-3.59	-6.40
ZrS_2	5.20	1.82	-4.29	6.11

The values are calculated using the two following equations:

$E_{CB} = -A = -X+0.5\ E_g$

$E_{VB} = -I = -X+ 0.5E_g$

X is the electronegativity, E_g is the value of the band gap, A is the electron affinity and I is the ionization potential

It is necessary to compare these computed band gap values with the experimental values and one such test is shown in Figure 3

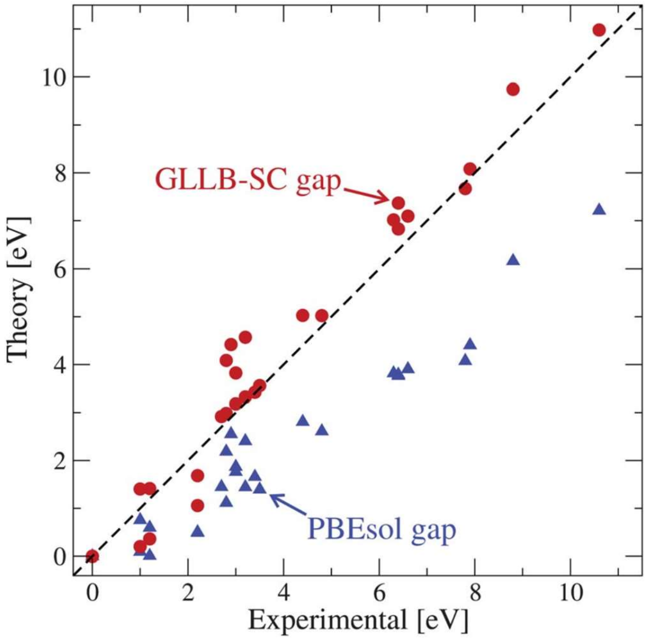

Fig. 3 DFT calculated bandgaps of selected oxides. Comparison between the theoretical and experimental bandgap of non-magnetic metal oxides in their most stable structure. The gaps are calculated using both the standard PBEsol (blue triangles) and the GLLB-SC functional (red circles). The dashed line represents the perfect matching between experiments and theory. (Details of the calculations with a list of the calculated oxides can be found in Table 1 of the ESI†). Plot of computed band gap values against the experimental values.[Reproduced from Ivano E. Castelli, Thomas Olsen, Soumendu Datta, David D. Landis, Søren Dahl, Kristian S. Thygesen and Karsten W. Jacobsen, Energy Environment Sci., 5,5814 (2012).]

One can assume the agreement is good enough and the values of band gap estimated by using these two equations can be good estimates for all practical purposes.

The next issue to be considered is the stability of the semiconductors in relation to the band gap values.

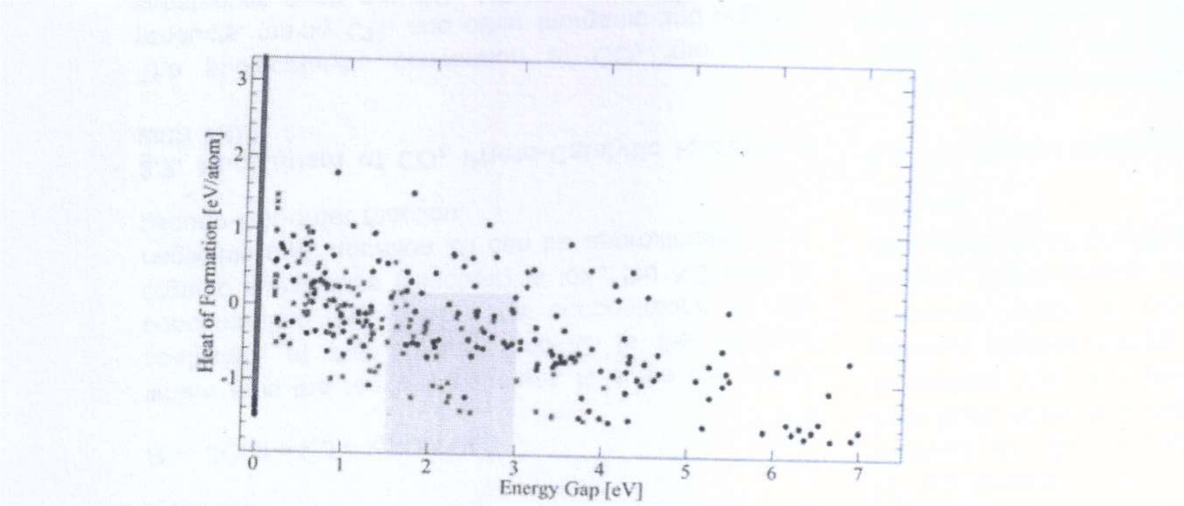

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Fig. 3 Correlation between the heat of formation per atom and the bandgap for the oxide (black circles) and oxynitride (red squares) compounds. The region for candidates for solar light harvesting corresponds to the orange area. [reproduced from I.E.Castelli et al., Energy Environment Sci., 5,5814 (2012)].

The possible candidates for this reaction are shown in Fig.4.

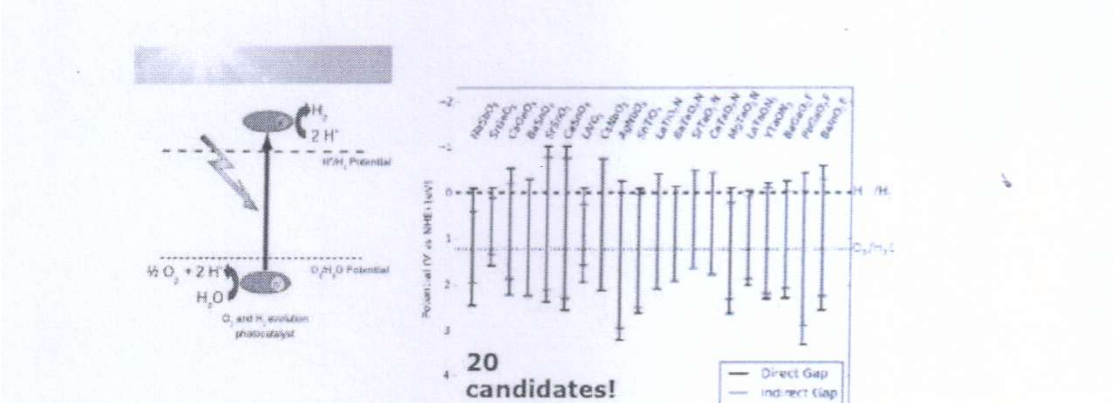

Fig. 4 The identified oxides and oxynitrides in the cubic perovskite structure with potential for splitting water in visible light. The figure shows the calculated band edges for both the direct (red) and indirect (black) gaps. The levels for hydrogen and oxygen evolution are also indicated. Among these the known and successful materials are $AbNbO_3$, $LaTiO_2N$, $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$ and $LaTaON_2$.

The essential steps involved in electrolytic water splitting reaction is listed below

$H_2O(l0 + * \rightarrow OH* + H^+ + e$

$OH* \rightarrow O* + H^+{}_+ e$

$O* + H\ {}_2O(l) \rightarrow OOH* + H^+ + e$

$OOH* \rightarrow * + O_2(g) + H^+ + e$

$*+ 2H^+{}_+ 2e \rightarrow H* + H^+ + e$

$H* + H^+ + e \rightarrow * + H_2(g)$

It is essential that one takes into account the elementary steps indicated for selecting suitable semiconductor for water decomposition by photoelectrolysis or photocatalytically.

CHAPTER 9

Semiconductors for water splitting: Material design principles

Sustainable energy through catalysis

The field of catalysis has important roles to play in many energy- conversion processes like decomposition of water to generate hydrogen fuel, conversion of carbon dioxide to useful fuels and in the conversion of molecules into value added products. In this, the selection of suitable and efficient materials has been one of the important tasks. Traditionally this exercise has been based on trial and error method of trying some materials and generating experimental data. These data have been subsequently used to formulate empirical rules for selection of materials for a particular application. For example, in the photo decomposition of water to generate hydrogen, one of the postulates is that the cation of the semiconductor should have d^0, d^5, and d^{10} configurations. Based on such empirical rules, new formulations are proposed and tested but the success seems to be limited in these cases. These exercises have been manly to guide experimental efforts for screening candidate materials and also to build or promote the chosen material.

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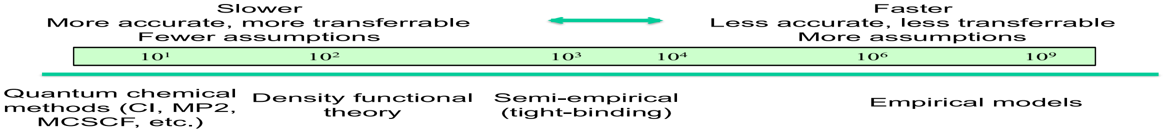

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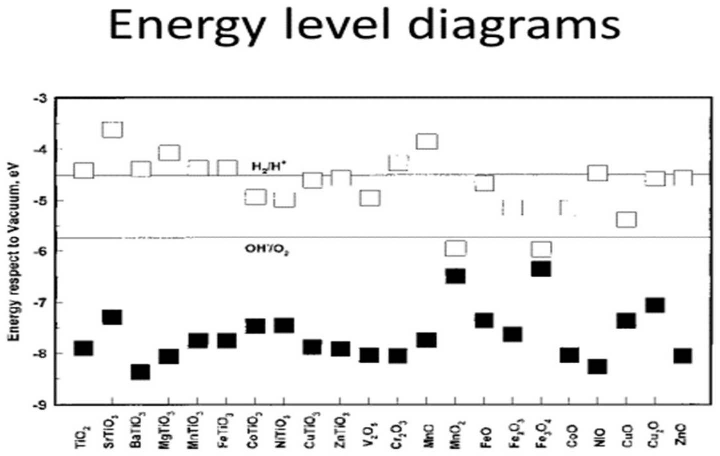

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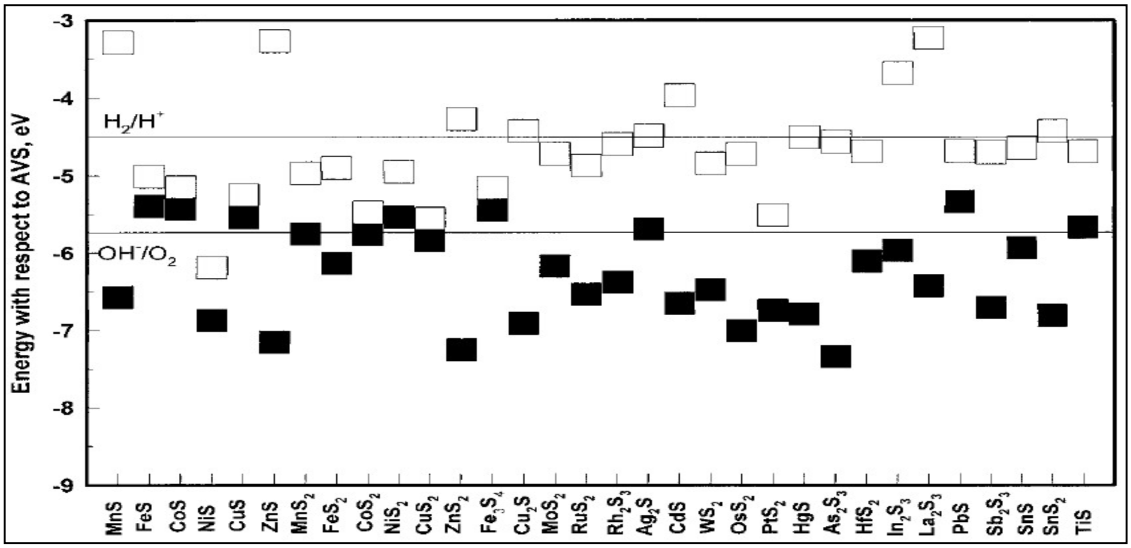

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It is necessary to compare these computed band gap values with the experimental values and one such test is shown in Figure 3

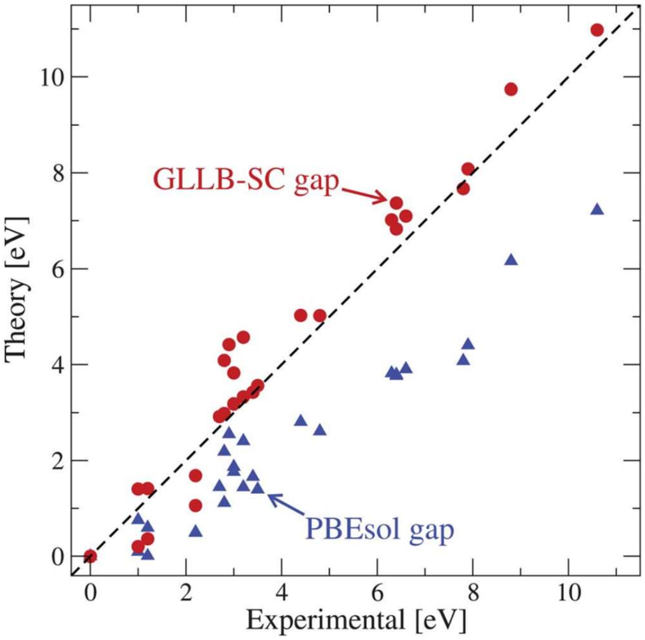
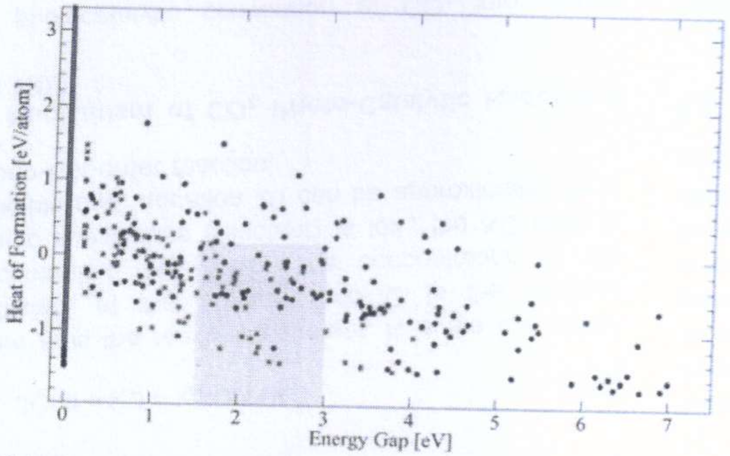


Fig. 3 DFT calculated bandgaps of selected oxides. Comparison between the theoretical and experimental bandgap of non-magnetic metal oxides in their most stable structure. The gaps are calculated using both the standard PBEsol (blue triangles) and the GLLB-SC functional (red circles). The dashed line represents the perfect matching between experiments and theory. (Details of the calculations with a list of the calculated oxides can be found in Table 1 of the ESI†). Plot of computed band gap values against the experimental values.[Reproduced from Ivano E. Castelli, Thomas Olsen, Soumendu Datta, David D. Landis, Søren Dahl, Kristian S. Thygesen and Karsten W. Jacobsen, Energy Environment Sci., 5,5814 (2012).]

One can assume the agreement is good enough and the values of band gap estimated by using these two equations can be good estimates for all practical purposes.

The next issue to be considered is the stability of the semiconductors in relation to the band gap values.



I.E. Castelli, T. Olsen, S. Datta, D.D. Landis, S. Dahl, K.S. Thygesen, and K.W. Jacobsen, Energ Environ Sci **5**, 5814 (2012).

Fig. 3 Correlation between the heat of formation per atom and the bandgap for the oxide (black circles) and oxynitride (red squares) compounds. The region for candidates for solar light harvesting corresponds to the orange area. [reproduced from I.E.Castelli et al., Energy Environment Sci., 5,5814 (2012)].

The possible candidates for this reaction are shown in Fig.4.

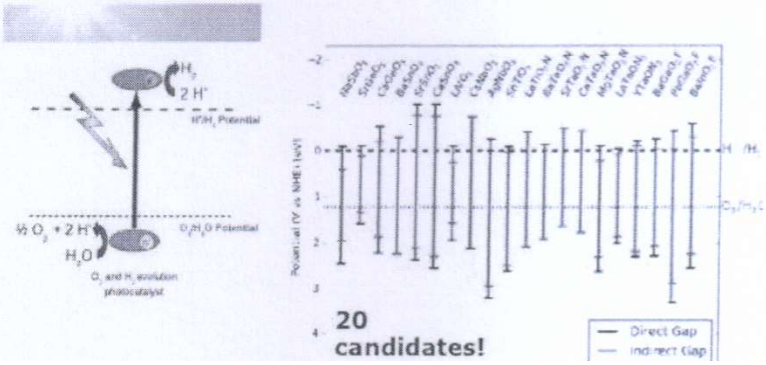


Fig. 4 The identified oxides and oxynitrides in the cubic perovskite structure with potential for splitting water in visible light. The figure shows the calculated band edges for both the direct (red) and indirect (black) gaps. The levels for hydrogen and oxygen evolution are also indicated. Among these the known and successful materials are $AbNbO_3$, $LaTiO_2N$, $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$ and $LaTaON_2$.

The essential steps involved in electrolytic water splitting reaction is listed below

H_2O(l0 + * $\rightarrow$OH* + H^+ + e

OH* $\rightarrow$ O* + $H^+$$_+$ e

O* + H $_2$O(l) $\rightarrow$ OOH* + H^+ + e

OOH* $\rightarrow$ * + O_2 (g) + H^+ + e

+ 2$H^+$$_+$ 2e $\rightarrow$ H + H^+ + e

H* + H^+ + e $\rightarrow$ * + H_2(g)

It is essential that one takes into account the elementary steps indicated for selecting suitable semiconductor for water decomposition by photoelectrolysis or photocatalytically.

CHAPTER 10

One approach for the design of semiconductor materials for photo-electrochemical applications

Today, it appears that the feasibility of photo-electro-chemical splitting of water is hampered by the correct choice of the semiconductor material that can be employed as photo-anode even though as many as 400 semiconductors have been examined with a variety of variations in each of them. This situation has arisen probably due to the fact that the system chosen has to perform both surface catalytic function for two important reactions namely hydrogen and oxygen evolution reaction and at same time should be capable of interacting with the photon field without undergoing degradation, yet possess the band edges so as to be thermodynamically capable of decomposing water yet possess reasonable value of the band gap (certainly greater than 1.23 eV (decomposition potential of water) preferably in the visible range(to be able to utilize most part of the solar radiation) yet possessing high absorption coefficient for photons. In addition, the system has to perform in an electrochemical cell mode, the electrode material should be able to withstand the inherent electrical field at the electrode/electrolyte interface and also may have to couple with both the photon and surface field necessary for the reaction. In the case of oxide semiconductors, the valence band is mostly contributed by the 2p orbitals of oxygen and hence the top of the valence band in most of the oxide systems are more or less at the same level and that is between -7.5 and -8.0 eV from the vacuum level. This level may be favourable thermodynamically for the oxygen evolution reaction from the decomposition of water. However, the substitution at the anionic sites will alter the position of the valence band and according to the nature of the substitution like Nitrogen, sulphur and other heteroatoms, the net free energy [1] for oxygen evolution reaction will be altered and possibly the oxygen evolution rate also. Similarly, the substitution at the cationic position will have effect on the bottom of the conduction band and hence on the capacity to reduce H+ ions and evolve hydrogen. When these two states that is the top of valence band and bottom of the conduction band is shifted either way, the value of the band gap is automatically altered and this has been vigorously attempted and it is called the band gap engineering of materials. Since band edge positions have to be known, the empirical method adopted in Butler Ginley scheme is usually employed and the values are compiled at various sources [2]. Among the available semiconductors, the ones based on oxides and sulphides have been examined extensively and however none of them have yielded the desired efficiency for the water splitting. A recent screening study [3] considered nearly 19000 materials generated with 53 different elements, different anions like O, N, S, F, Cl and different crystal classes like perovskites, rutile and spinels. The essence of their results is given in Fig.1. It is seen from this figure that systems which have band gap value

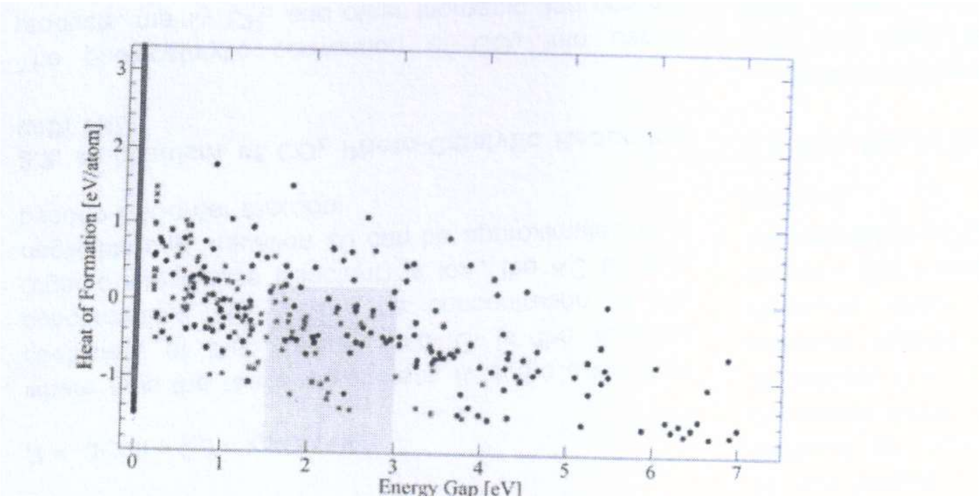


Figure 1: Stability of various semiconductors versus band gap value - Reproduced from I.E. Castelli, T. Olsen, S. Datta, D.D. Landis, S. Dahl, K.S. Thygesen, and K.W. Jacobsen, Energ Environ Sci 5, 5814 (2012).

greater than 1.23 (thermodynamic reversible value for water splitting) and 3 eV are the systems of concern for water splitting application. Among the 20 candidates shown in Fig.2, the possible successful candidates are AgNbO3, $LaTiO_2N$, $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $LaTaON_2$ Another function of the photoelectrochemical material is the catalytic effect for both hydrogen and oxygen evolution. The essential steps in the oxygen evolution reaction can be written as follows:

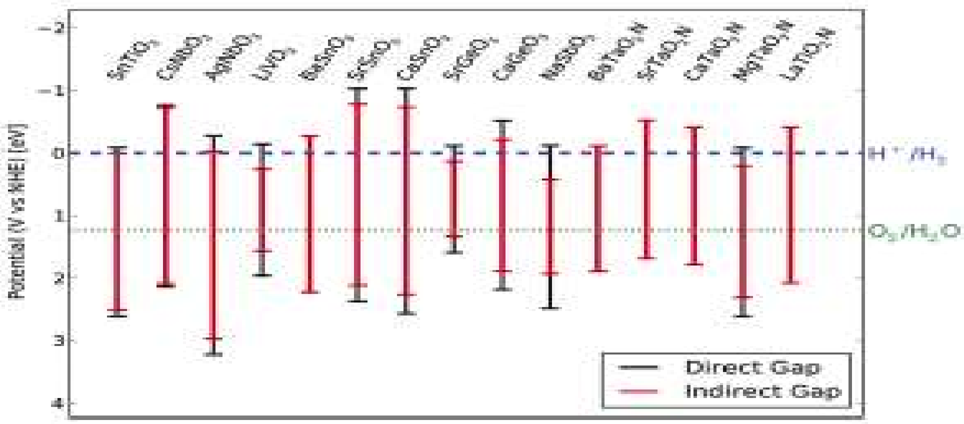


Figure 2: Some of the possible successful candidate materials; Black line direct band gap and red line indirect band gap the materials left to right are: $NaSbO_3$, $SrGeO_3$, $CaGeO_3$, $BaSnO_3$, $SrSnO_3$, $CaSnO_3$, $LiVO_3$, $CsNbO_3$, $AgNbO_3$, $SrTiO_3$, $LaTaO_2N$, $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $MgTaO_2N$, $LaTaON_2$, $YTaON_2$, $BaGaO_2F$, $PbGaO_2F$, $BaInO_2F$

H2O + * → OH* + H+ + e

OH* → O* + H+ + e

O* + H2O → *OOH + H+ + e

OOH → * + O2 + H+ + e

In this reaction sequence, the step three appears to have considerable overpotential and possibly limiting this reaction. This aspect has been discussed in the paper by Noreskov et al []. The reaction sequence for hydrogen evolution involves the following steps: +

2H+ +2e → H* + H++ e

H* + H+ + e → * + H2 (g)

The projection for suitable material for this reaction has also been considered in literature and have been published by Noreskov et al []. Another possibility considered in literature for selection of materials for Photo-electrochemical cells and the concept is pictorially represented in Fig.3. There have been predictions in literature for the search of materials for PEC applications. One such prediction is shown pictorially in Fig.4. There are some predictions on the possible candidates for tandem cells they are basically either perovskite oxides or oxynitrides. However there are some limitations on the choice of materials, these include, high band gap materials and the valence band level must lie in such position so that it promotes oxygen evolution and the holes formed must be mobile enough to effect this reaction. In this presentation we have restricted to some of the predictions in literature for obvious reasons. The interested readers can look to the original literature references given.

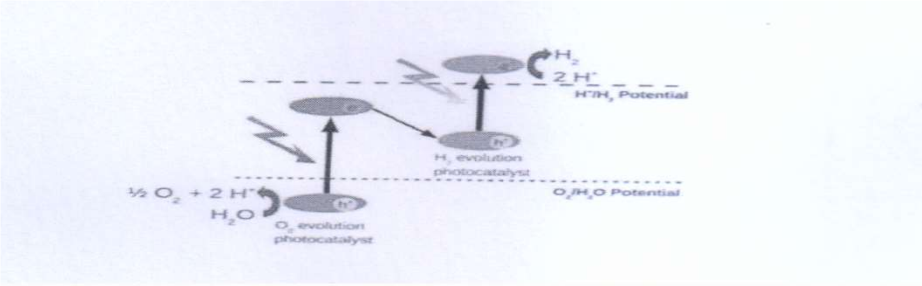


Figure 3: Pictorial representation of a tandem cell for photoelectrochemical applications

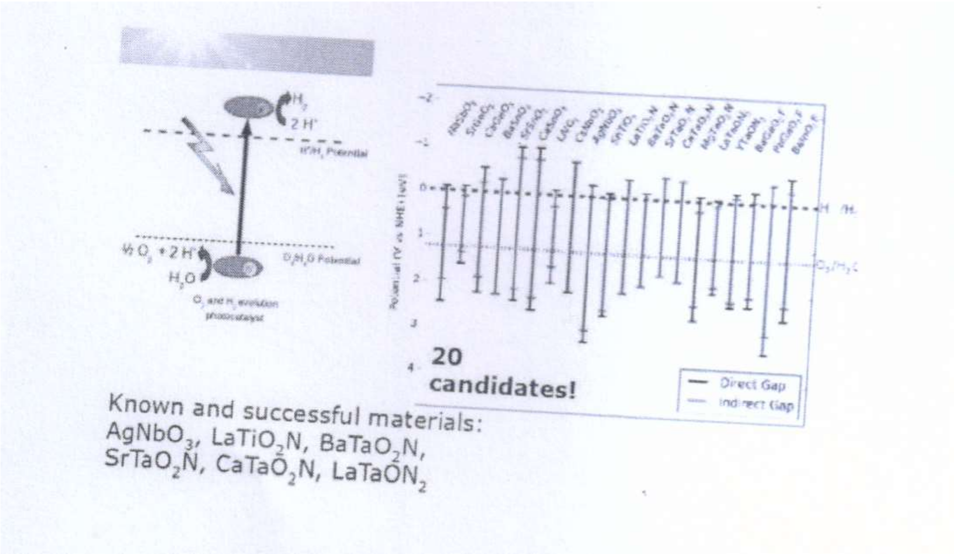


Figure 4: Pictorial representation for the selection of materials on the basis of H_2 and O_2 evolution.

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CHAPTER 11

Photo-assisted catalytic properties of semiconductors without and with modification

1 Introduction

The catalytic reactions assisted by the absorption and utilization of photons by the catalyst and not by the substrate are generally termed as photo-catalytic process. This broad definition was given in 1990s. Bard [1,2] and Nozik [3] have proposed a classification of photo-chemical processes assisted by illumination of the solid catalyst. According to them, photo-catalytic processes are those in which the reactions are driven in the spontaneous direction (Δ G is less than 0) and the light energy is used only to surmount the activation barrier of the reaction. Photo-synthetic processes are those in which photons are used to drive the reaction in the non-spontaneous direction (—Δ G is greater than 0) so that the light energy is stored in the form of chemical energy. This differentiation seems to have been losing ground, since heterogeneous photo-chemical processes i. e. whether Δ G is less than 0 or greater than 0 are generally termed as photo-catalytic processes. However, for puritans one can classify the second set of reactions as catalytic photosynthesis. The initial enthusiasm that was prevalent in the late 70s and 80s in exploiting these processes for solar energy conversion seems to slow down, probably because of the frustrations and the unusual low quantum yields that are obtainable in these processes. Scientific groups active in this area throughout the world were awaiting some break-through in the materials that could be exploited, but they seem to realize now that their choice appears to be limited from various considerations like absorption of photons in the visible or near UV region, the long term stability of the material under photolysis conditions, the redox chemistry of the systems that could be successfully handled as well as the life times of the excitons produced by the absorption of photons. This presentation therefore aims at:

1. Deducing the rationale of the choice of typical photo-active semiconductors
2. Examining the ways and means of increasing the efficiency and selectivity of redox reactions

3. Understanding the ways and means of the effect of additives especially metal deposits and pre-treatment agents in the photo-catalytic properties of the semiconductors

4. Postulating active photo-catalysts for hydrogen evolving reactions using model substrates like alcohols and other organic substrates, polyols, (carbohydrates) carboxylic acids, esters (fats) and amino-acids) related to biomass species.

5. Evaluating photo-catalytic degradation processes for organic and inorganic pollutants.

It should also be kept in mind that no claim is made to the exhaustiveness and comprehensiveness of these points as it is neither possible nor desirable in view of the various other presentations already available in literature [4]. This presentation is mainly aimed at examining critically the current state of knowledge on these five points.

1 Rationale for the Choice of Photo-active Semiconductors

There is parallelism existing between photo-catalytic properties of semiconductors and photo-redox reactions taking place at the semiconductor/electrolyte interface. In both processes the electron-hole pair produced by the photon absorption is utilized for the oxidation reduction reaction in the substrate used. If the electrolyte present in the solution is a couple with redox potentials located within the band gap energy of the semiconductor, then the oxidation of the reduced species by the photo-holes at one of the electrodes will be compensated by the reduction of the oxidized species at the other electrode. In order to store the radiant energy as chemical energy the overall cell reaction has to be driven in the non-spontaneous direction (Δ G is greater than 0). This means that the cathodic redox couple must have more negative potential than the anodic redox couple. In this mode of operation, which is termed as photosynthetic cell, the energy stored corresponds to the energy difference between the two redox systems in the cell. However, when the cathodic redox couple has a less negative potential compared to the anodic couple, the reaction proceeds in the spontaneous direction and this mode of operation is called photo-electro-catalytic cell wherein the photon energy is used only to overcome the activation barrier of the redox reaction. These principles of photo-electrochemical cells can be extended to photo-catalytic properties of the semiconductor particles in various forms including colloids and nano state as well. Since in a given semiconductor particle, both anode and cathode (oxidation and reduction sites) are or can be present on the same particle, this can be considered as a short circuited photoelectrochemical cell. The absence of an external electrical circuit means that one can produce only chemicals in whatever mode of operation, namely in photo-synthesis or photo-catalytic mode of operation. However, it is clear that the effective use of the electrons and holes obtained by photon absorption can be achieved only when these charge carriers can be separated and utilized in the redox reaction within the life time of these charge carriers. Since recombination is one of the predominant routes by which the excitation energy will be dissipated, this pathway should be suppressed as far as possible in relation to induced chemical redox reaction. This is achieved in semiconductor photocatalysts by incorporating suitable electron and hole sinks like the deposition of metals or RuO_2 respectively. This aspect will be considered separately in the section on the modification of the semiconductors. The principles of parallelism between photo-electro-chemical cells (PEC) and photo-catalytic micro-cells (PCM) are illustrated in Fig.1. From these postulates, it is clear that the relative positions of the conduction band and valence band edges of the semiconductor and the redox potentials of the reduction and oxidation couples are deciding factors for selecting a particular

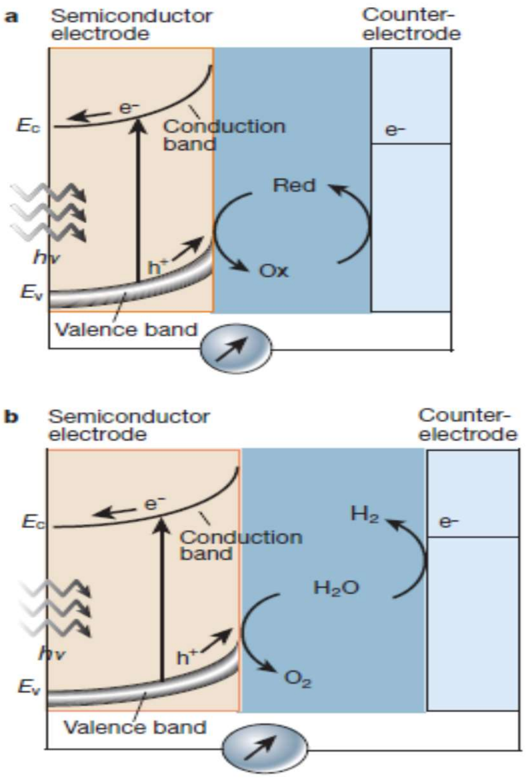

Figure 1: Schematic representation of two photo-electrochemical cells with n-type semi-conductor as photo-anode (a) photo-electro-synthetic cell: (b) photo-catalytic cell.

semiconductor for a chosen photo-catalytic function. This is the basic criterion to be used for the selection of materials for photo-catalysis. However, the photo-catalytic efficiency will be governed by other competing processes like the recombination rate and the photo-corrosion processes. In Fig 2, the positions of band edges of a few semi-conductors exploited in PEC operation are given together with redox potentials of a few couples of interests to demonstrate how the choice of semiconductor is made with respect to the redox reaction on hand. The nature of wave functions of the energy states of valence and conduction bands also has an important implication in the selection of materials. In the case of oxides like ZnO and TiO_2 the holes generated in the valence band have mainly ’2p’ orbital character of oxygen anion sublattice, while reducible oxides like Fe_2O_3 and Co_3O_4, the excited state wave functions are mostly contributed by the ’d’ states of the cations and the cation reduction pair because of variable valency and the energy states are mostly lying in the band gap of the semiconductor [5]. The symmetry of the wavefunctions and the absolute energy values of these states are responsible for their inactiveness or suppressed activity in promoting the desired redox reaction. Extending

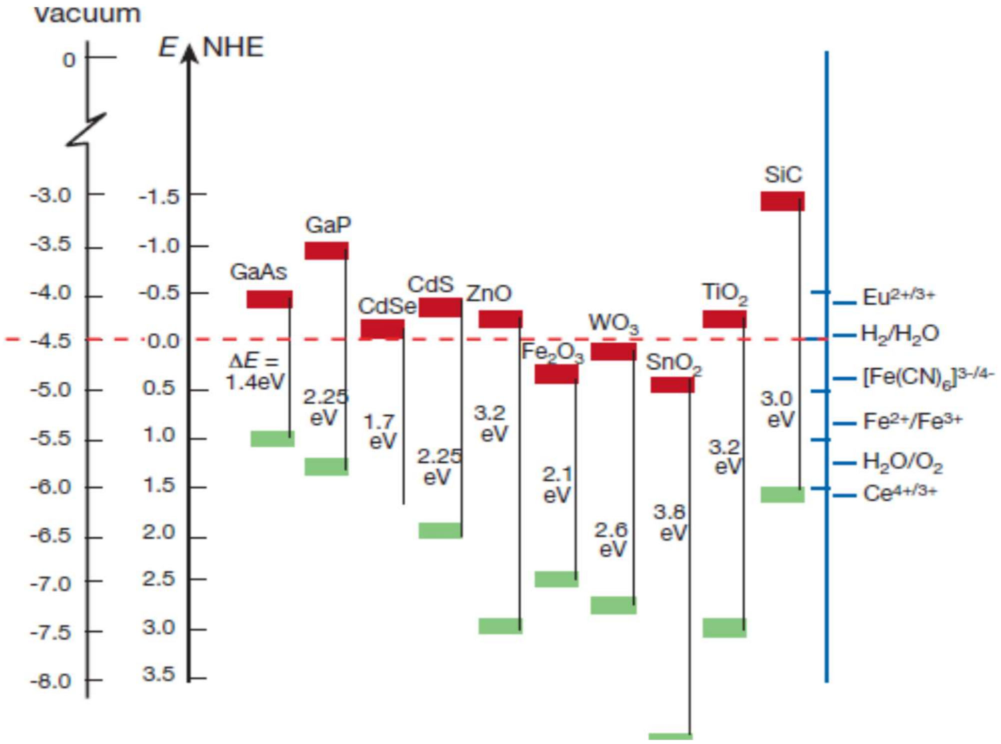

Figure 2: Relative energy values of some common semiconductor electrode materials and redox systems in acid solution

this postulate, one can argue that the photo-activity of the systems will be inhibited by species which are capable of affecting the concentration of O– species by one electron transfer acts at the surface. In some other systems like Fe_2TiO_5, the recombination rate may be higher due to the decreased mobility of electrons. The type of reasoning leads to the conclusion that oxides which form valence band from pure '2p' states of oxygen ions with itinerant O–- type electronic arrangement alone would be effective in PEC and PMC operations. This means that the choice of available for selection of materials appears to be grossly limited. These arguments could not hamper the enthusiasm for using chalgogenides [6] especially CdS, CdSe, CdTe and other hybrid systems as photo-electrochemical and photo-catalytic materials for the photo-splitting of substrates like water and hydrogen sulphide. The major difficulty encountered in these systems which have such lower band gaps than the corresponding oxides thus enabling harvesting of a larger fraction of the solar radiation, is the anodic dissolution process which necessitated the use of modified instead of the naked systems [7]. Another exotic material that has been tried is the heteropoly compounds because they possess multiple reduction sites and could promote hydrogen generating reactions [8]. The interest in these compounds stems from the fact that many reducing equivalents could be stored at a single site and the redox behaviour

Table 1: Characteristics of Semiconductor Electrode Materials; EA Electron affinity; E_C: conduction band energy relative to vacuum level; E_g: band gap; E_V : valence band energy relative to vacuum level.

Material	Electron affinity E_A (eV)	Conduction band E_C (eV)	Band gap E_g (eV)	Valence Band E_V (eV)
ZnTe	3.50	-3.5	3.2	-5.8
Si		-4.0	1.1	-5.1
GaAs	4.07	-4.1	1.4	-5.5
ZnSe	4.09	-4.1	2,7	-6.8
ZnS	4.09	-4.1	3.6	-7.7
$SrTiO_3$		-4.3	3.2	-7.5
GaP	4.30	-4.3	2.3	-6.6
$KTiO_3$		-4.4	3.4	-7.8
InP	4.38	-4.4	1,3	-5.7
CdS	4.50	-4.5	2.4	-6.9
TiO_2		-4.6	3.2	-7.8
$MnTiO_3$		-4.7	3.1	-7.8

PbO	4.95	-4.9	2.8	-7.7
$FeTiO_3$		-4.9	2.8	-7.7
$BaTiO_3$		-4.9	3.3	-8.2
CdSe		-5.0	1.7	-6.7
WO_3		-5.0	2.7	-7.7
SnO_2		-5.0	3.5	-8.5
Fe_2O_3		-5.1	2.2	-7.3
Bi_2O_3		-5.1	2.8	-7.9
MoS_2		-4.53	1.75	-6.28
SiC		-3.04	3.0	-6.04

of these sites has already been probed by appropriate electro-chemical and ESR techniques. It is regarded that the normal limitations that are present for the selection of materials for PEC applications may also hold good for catalytic photo-assisted processes, however a variety of materials can be examined for the later process though could not be effectively utilized in PEC applications. In Table 1 the characteristics of the conventional semiconducting materials used in PEC applications are given.

2. **Ways and Means of Increasing the Efficiency and Selectivity of Redox Reactions in Photo-assisted Catalytic Processes on Semiconductors**

2.1 Metallization It was seen in the previous section that most of the semiconducting materials show poor activity when used alone [9]. But the presence of a metal on a semiconductor increases its efficiency and hence semiconductor powders coated with metals are finding extensive application in the field of photo-assisted catalytic processes [10]. Schematically the electron-hole separation on an illuminated metallized semiconductor particle (M/SC) can be represented as shown in Fig.3. Irradiation of metallized semiconductor with light energy

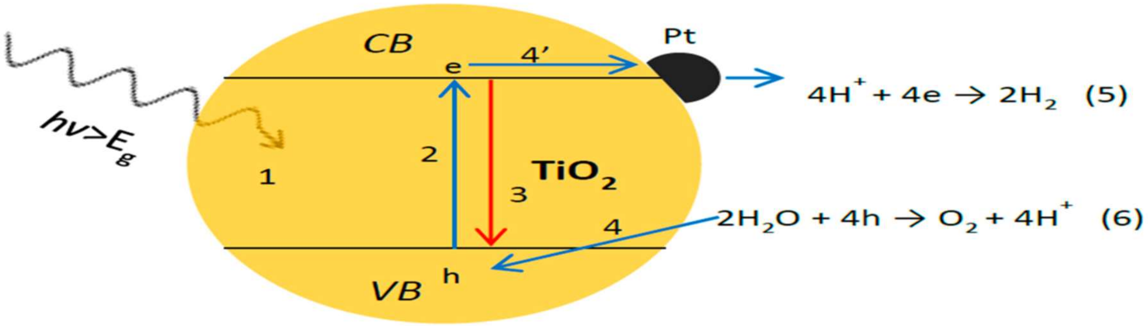

Figure 3: Photon Induced electron-hole separation on a Metallized Semiconductor Particle (SC/M)

greater than the band gap ($E > E_g$) results in the formation of electrons and holes and the presence of metals with high electron affinity effectively traps the photo-excited electrons and uses it to perform the subsequent reduction reaction. The utilization of electron in the reduction reaction at the metal site implies that the hole can be made to perform the oxidation reaction unidirectionally thereby increasing the overall efficiency of the process. One can also use materials like RuO_2 which can act as sinks for holes or employ both metals and hole sinks for achieving higher efficiencies. Even though, in principle one can have sinks for both electrons and holes, the effect of metallization of semiconductors which act as sinks for photoexcited electrons alone has been extensively studied. In this case, according to the photochemical diode model the oxidation should take place on the semiconductor surface for an n-type SC/M system.

Table 2: Electron Affinities and Oxidation Potentials of various metal ion/metal redox couples of noble metals

Reactions	E^0 (V)	Electron affinity of the metal
$Pt \rightarrow Pt^{2+} + 2e$	-1.118	2.128
$Pd \rightarrow Pd^{2+} + 2e$	-0.951	0.557
$Rh \rightarrow Rh^{3+} + 3e$	-0.758	1.137
$Ru \rightarrow Ru^{3+} + 3e$	-0.455	1.05

2.2 Nature of the Metal Loaded

The choice of the metal is determined by the value of the electron affinity of the metal to be loaded. In addition to electron affinity being high, the metal should have low hydrogen overvoltage, if the reaction involves hydrogen evolution. The metal should have suitable work function to make a favourable contact and should show negligible tendency for oxidation. The electron affinity and oxidation potential of various couples of noble metals which are normally used are given in Table 2.

2.3 Method of Metal Deposition

Ever since Bard [11] demonstrated photo-deposition of Pt, Pd, Cu and Ag using reducing agents, this method assumed importance, for the in situ preparation of metal loaded semiconductors [12]. In addition, conventional methods like impregnation

[13], in situ reduction of metal salts [14], exchange impregnation and sputtering methods [15] have also been used to prepare metallized semiconductors.

2.3.1 Use of Sacrificial Agents

Another approach used by Gratzel and his coworkers [16] is to use photoinduced reduction of a relay species (methyl viologen, NN'dimethylpyridine dication MV^{2+} by a sensitizer $[Ru(bipy)_3]^{2+}$ for the cleavage of water in presence of two redox catalysts on a colloidal semiconductor system. This scheme is shown in Fig.4. These studies have been favourably extended to niobium pentoxide substituted anatase (because of the favourable flat band potential, more cathodic to the extent of 300 mV than that of rutile) Pt-RuI_2 system for effecting visible light induced dissociation of water.

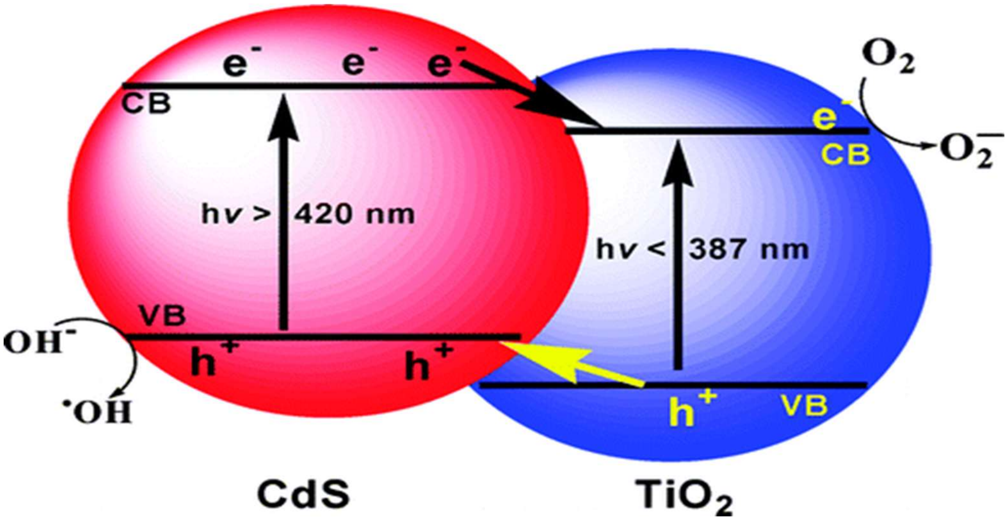

Figure 4: Scheme for photo-redox process in presence of two redox catalysts

2.4 Pretreatments

Another method of increasing the photo-assisted catalytic activity of metal loaded semiconductors is to use various pretreatments. This procedure has been successfully employed for the photo-assisted catalytic dehydrogenation of methanol on metallized TiO_2 system [17]. Typical data generated given in Table 3 for Pd/TIO_2 and Ru/TiO_2 show that the activity is increased in the case of Pd/TiO_2 as also Pt/TiO_2 when it is subjected to oxygen followed by hydrogen treatment at 673 K while in the case of Ru/TiO_2 the favourable treatment is direct hydrogen treatment. Similar data have also been collected on Ru/TiO_2 system and they are given in Table 4. Table 5 shows the surface metal concentration data after various pretreatments and sputtering for the various metallized titania systems studied by XPS. Pt and Pd loaded systems showed an enrichment whereas Rh and Ru loaded systems exhibited an impoverishment of the metal on the surface after oxygen treatment compared to the untreated catalyst. This could be due to the migration of the metal species based on the surface energy values of the metal oxide and that of titania. These postulates agree well with the results

Table 3: Photocatalytic data on Pd/TiO_2 system; 20 ml of methanol was irradiated in presence of 100 mg of the catalyst for 1 hour at 308 K (a) HCHO formed is given in brackets (b) oxygen/hydrogen treatment in oxygen followed in hydrogen at 873 K for 12 h, (c) Nitrogen/hydrogen treatment in nitrogen and then in hydrogen at 678 K for 12h and (d) hydrogen treatment at 678 K for 12 h

Wt % of Pd in Pd/TiO_2	Hydrogen (HCHO)^a in micromoles per hour		
	OH^b	NH^c	H^d
0.38	60(50)	39 (55)	8 (6)
1.50	79(64)	38 (37)	9 (9)
2.40	53 (45)	38 (37)	9 (9)

Table 4: Photocatalytic data on Ru/TiO2 system; for other details see the previous table

Wt % of Ru in Ru/TiO_2	Hydrogen (HCHO)^a in micromoles per hour		
	OH^b	NH^c	H^d
0.04	15 (13)	49 (45)	53 (47)
0.08	15 (14)	60 (51)	62 (58)
0.22	15 (14)	56 (51)	56 (54)
0.38	19 (18)	49 (42)	53 (51)
0.69	19 (18)	45 (36)	53 (50)
1.46	19 (18)	45 (36)	51 (50)

Table 5: Surface metal amount after various pretreatments and sputtering for various M/TiO_2 system determined by XPS: OO oxygen treatment followed by oxygen treatment in situ thus the underlined letters denote the treatment in the preparation chamber of the spectrometer

Metal (M)	nM/nTi Treated /untreated				nM/nT after/before sputtering	
	O$\underline{\text{O}}$	O$\underline{\text{OH}}$	OH$\underline{\text{H}}$	H$\underline{\text{H}}$	OH$\underline{\text{H}}$	H$\underline{\text{H}}$

Pt	1	82	34	18	68	38
Pd	141	97		6		65
Rh	72	66	74	12	30	60
Ru	14	16	6	56	120	40

of sputtering studies which indicate increased concentration of these metals in the bulk of the semiconductor.

3.Physics of Noble Metal - semiconductor Interface as well as before pretreatment

Pt supported titania is used for many catalytic processes because Pt is one of the catalysts for recombination and dissociation of H_2 and H_2O. Moreover, the electron affinity and hydrogen over voltage of Pt seem to be adequate for the catalytic effect. Depending on the nature of the metal and the surface characteristics of the semiconductor a metal-semiconductor contact may give rise to a Schottky barrier or an ohmic contact. The energy level scheme for these two types of contacts is given in Figs 6 and 7. As Schottky barrier will impede the flow of electrons to the metal and if metal deposits were to act as reduction centres the contact should be an Ohmic one. Aspnes and Heller [16] have measured the properties of electrical contacts between catalytically active metals with different work functions (Pt, Rh and Ru) and semiconductors like n-TiO_2, n-CdS, n-$SrTiO_3$ and P-InP. All air exposed contacts formed Schottky junctions with barrier heights ranging from 0.1 eV for N-TiO_2/Ru to 1.84 eV for CdS/Pt. But the exposure to a dry hydrogen atmosphere reversibly converted all the n-$SrTiO_3$ contacts to near Ohmic behaviour. The ambient gas induced barrier height changes observed by the authors are attributed to the formation of low resistance, ohmic junction by the dissolution of hydrogen in metal. Hope and Bard [19] have reported that thermal treatment of contact could lead to the inter diffusion of Pt and rutile. In the case of Pt/TiO_2, the work function of Pt is 5.2 eV while the electron affinity of TiO_2 is 4 eV, thus favouring a schottky barrier which will prevent electron flow to metal centres which are to act as electron sinks. However, the inter

Table 6: Heats of formation of oxides, heats of sublimation and heats of vapourization of metals

Metal oxide	ΔH_f (kJ/mol)	ΔH^0_{sub} of oxide (kJ/mol)	ΔH^0_{vap} of metal (kJ/mol)
PdO	-42.8	91	376

PtO		565	512
Rh_2O_3	-47.9	556	497
RuO_2	-55.0		570

diffusion could create an interfacial region in which there is a high density of surface states, thus the junction approaches an ohmic one. The interface region as deduced from AES depth profiling is approximately 10 nm with less defined boundaries, showing considerable intergrowth of the metal and the semiconductor. The pretreatments employed should create species which will facilitate this inter diffusion of the metal and semiconductor species thus leading to a true ohmic contact. This interdiffusion is facilitated by a number of factors, important among them being pretreatment. Pretreatment could give rise to species whose surface free energy values will be favourable for diffusion into the bulk of the semiconductor. The effect of pretreatment can also be explained based on the standard heats of formation or standard heats of vapourization of metals. These data for typical noble metals are given in Table 6. This was proposed by Wanke et al [20] for the changes in the dispersion of group VIII metals on alumina after high temperature treatments in various atmospheres. The order of surface metal concentration after OHH treatment (refer to data in Table 5) is Rh> Pt> Ru. This is because RuO_2 which has higher standard heat of formation compared to other oxides would sinter more and thereby stability is less because of the exothermicity of the reaction. Block et al [21] have reported that the oxides of Ru (RuO_2 and RuO_3) are mobile. However, after HH treatment (refer to table 5) the order of surface metal concentration is Ru >Pt> Rh> Pd which can be accounted for in terms of heats of sublimation or heats of vapourisation of the oxides. As the value of heat quantities increases the oxides will be stable and sintering will be less. The extent of sintering of metal particles in various atmospheres is also one of the causes of the difference in surface metal concentration after various pre-treatments. The exposed surface area from the metal is decreased when sintering is high and as a result surface metal concentration is also decreased.

Table 7: Rate of hydrogen evolution in micro moles/10h from neutral water and carbohydrates, amino acids, fatty acids, or various types of biomasses using TiO2-Pt catalyst (Data compiled from ref [22]

Reactants	Hydrogen evolution rate
Carbohydrates	
Glucose	1130

Sugar	920
Starch	240
Cellulose	40
Proteins (amino acids)	
Glycine	220
Glutamic acid	7126
Proline	10
Fatty acids	
Stearic acid	88
Pyruvic acid	323
Natural Products	
Ethanol	5080
Lignin	12
Food Materials	
Potato	39
Green algae and other sea weeds	
Chlorella	73
Seaweed	74

4. Active Catalysts for hydrogen evolving Reactions

The photo-catalytic reaction of importance for biomass conversion is the reaction of glucose, sugars, starch and cellulose with water to produce carbon dioxide and hydrogen. In combination with photo-synthetic reaction, the overall reaction will appear to be water splitting. The reaction sequence for glucose as substrate can be written as

$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2 \; \Delta G^0 = 2870$ KJ/mol

$C_6H_{12}O_6 \longrightarrow 6CO_2 + 12H_2 \; \Delta G^0 = -32$ KJ/mol

$12H_2O \longrightarrow 12H_2 + 6O_2 \; \Delta G^0 = 2838$ KJ/mol

The schematic representation of the photo-catalytic hydrogen evolution from various organic substrates is shown in Fig.8. In Table 7 typical data on the rate of hydrogen production from amino acids, proteins, fats and various biomasses in aqueous solution are given. Another reaction of interest is

Table 8: Brief summary of the data on the photo-catalytic reduction of nitrogen in presence of photo-electrolysis of water

Photocatalyst	Band gap (eV)	Yield of ammonia In micromoles	Weight of the catalyst
TiO_2	2.9-3.2	1.75	0.2
TiO_2/0.2 Fe_2O_3	2.9-3.2	6.0	0.2
Fe/TiO_2	2.9-3.2	6.4	0.2
Co/TiO_2	2.9-3.2	3.8	0.2
Mo/TiO_2	2.9-3.2	4.0	0.2
Pt/TuO_2		2.8	0.3
ZnO	3.2	2.1	0.3
Pt/ZnO	3.2	0.8	0.3
$SrTiO_3$	3.2	1.9	0.3
Pt/$SrTiO_3$		2.4	0.3
CdS	2.4	4.9	0.3
Pt/CdS	2.4	4.9	0.3
GaP		4.6	0.3
Pt/GaP		7.5	0.3
TiO_2-SiC		3.0	0.5
NiO-$SrTiO_3$	3.2	0.9	0.5
RuO_2/$SrTiO_3$	3.2	0.75	0.5
RuO_2-NiO-$SrTiO_3$	3.2	2.5	0.5
RuO_2-NiO-$BaTiO_3$		2.6	0.5
CdS/Pt/RuO_2	2.4	2.4	0.5

e photo-assisted catalytic reduction of dinitrogen in presence of photo-electrolysis of water. This is similar to the natural nitrogen fixation. Various attempts have been made to effect direct reduction of nitrogen in presence of photo-splitting of water. The available data are summarized in Table 8. The ammonia yields obtained were quite small since the energetics of the dinitrogen activation on the semiconductor used has not been properly elucidated so as to formulate a suitable modified photo-active catalyst system which can simultaneously promote dinitrogen activation as well as the successive reduction of atomic nitrogen. Another reaction of interest in relation to the nature cycle is photo-methanation of carbon dioxide [24] this reaction has been found to be promoted selectively by dispersed Ru/TiO_2.

5.Catalysts for Photo-assisted degradation of Pollutants

5.1. Photo-assisted catalytic decomposition of hydrogen sulphide on metallised CdS

The photocatalytic hydrogen evolution from aqueous sulphide solution was measured under various experimental conditions and the initial rate data are presented in Table 9. The metal ions as metal chlorides did not show any activity. Among the metallized CdS the observed activity order is Rh> Ru > P>t Pd. XPS studies showed that the metallized CdS contain metal oxides formed by aerial oxidation. Though RuO_2 and Rh_2O_3 could function as hole trapping agents PtO and PdO are not useful as hole transferring agents and hence these two systems showed lower activity as compared to the other two metals. In the case of in situ metallization the activity order is Rh > Pt >Pd >Ru=Ir >Co >Ni=Fe Even though the intrinsic activity of Pt for hydrogen evolution is more than those of the other metals, considering the combined effect of metal and metal oxide or metal and metal sulphide systems containing Rh is the most active one. In aqueous solutions, photocatalytic oxidation of many organic compounds is efficient. Typical photocatalytic oxidation of carboxylic acids, alcohols, aromatics and lactams have been reported in literature and typical reactions studied are given in Table 10. These studies show that there is potentiality for using heterogeneous photocatalysis as a means of decontaminating water and several studies have already been taken up in this direction [28]. It should therefore be of interest to extend these studies for some non-biodegradable pollutants. This is one direction in which photo-assisted catalytic process will be utilized in the near future.

Table 9. Initial rate data for the photo-catalytic hydrogen evolution from aqueous sulphide solution. Reactant 0.25 M sodium sulphide aqueous solution; weight of the catalyst 100 mg; light source 1000 W tungsten halogen lamp and noble metal content is 1.37 percent in each case as metal or metal ion

Photo-catalyst	Initial Hydrogen evolution rate in ml/h/g
CdS (naked)	0.31
Pt/CdS	2.08
CdS +Pt^{4+} as H_2PTCl_6	2.89
CdS + Ir^{3+} as $IrCl_3$	0.96
Ru/CdS	2.39
CdS + Ru^{3+} as $RuCl_3$	0.97
RuO_2 + CdS (thermal oxidation)	0.97
RuO_2 + CdS (Physical Mixture)	1.37
Ru/CdS + Chloride ions	2.38
Rh/CdS	2.53
Rh_2S_3 + CdS	2.83

CdS+Rh as $RhCl_3$	4.15
Pd/CdS	0.94
CdS + Pd^{2+} as $PdCl_2$	2.55
CdS + Ni^{2+} as $NiCl_2$	0.53
NiS/CdS	0.51
CdS + Co^{2+} as $CoCl_2$	0.58
CdS + Fe^{3+} as $FeCl_3$	0.52

Table 10 Examples of photo-catalytic reactions of organic molecules on TiO_2 powder

Reaction
Acetic acid →Methane + CO_2 + Hydrogen + ethane
Propionic acid →CO_2 + ethane +ethylene + hydrogen
n-butyric acid →CO_2 +Propane + hydrogen
n-valeric acid →CO_2 + isobutane + hydrogen +isobutylene
Toluene + oxygen →benzaldehyde + water
Methanol →formaldehyde + hydrogen
Ethanol →acetaldehyde + Hydrogen

6. Conclusion

Photo-assisted catalytic processes appear to have promising future especially in view of the prospects of solar energy conversion. Instead of aiming at evolving more efficient catalytic materials based on naked semiconductors, the research in the near future will be directed towards utilizing the available materials for new reactions which have relevance for energy conversion as well as pollution control. The direction of activity in photo-assisted catalysis would begin with the modification of the available semiconductors so as to increase the efficiency of processes especially in hydrogen evolving reactions and use of biomasses for chemical storage of energy.

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