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 ($-\Delta$ 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
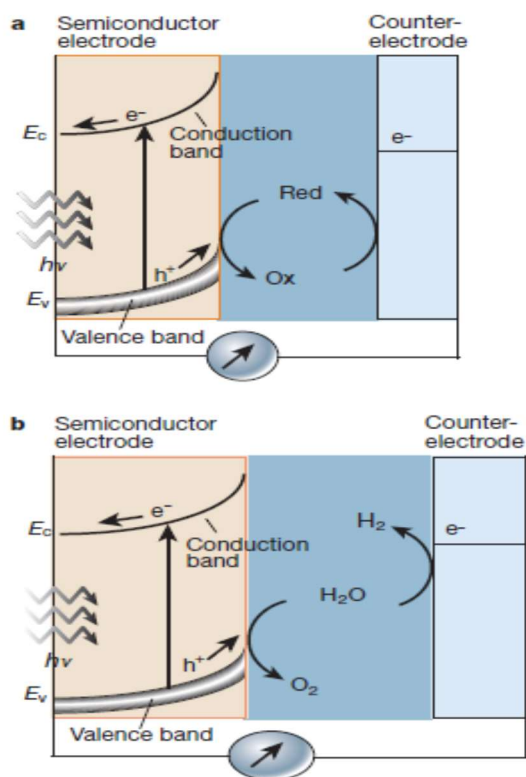

Figure 1: Schematic representation of two photo-electrochemical cells with n-type semi-conductor as photo-anode (a) photo-electro-synthetic cell: (b) photo-catalytic cell.

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

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
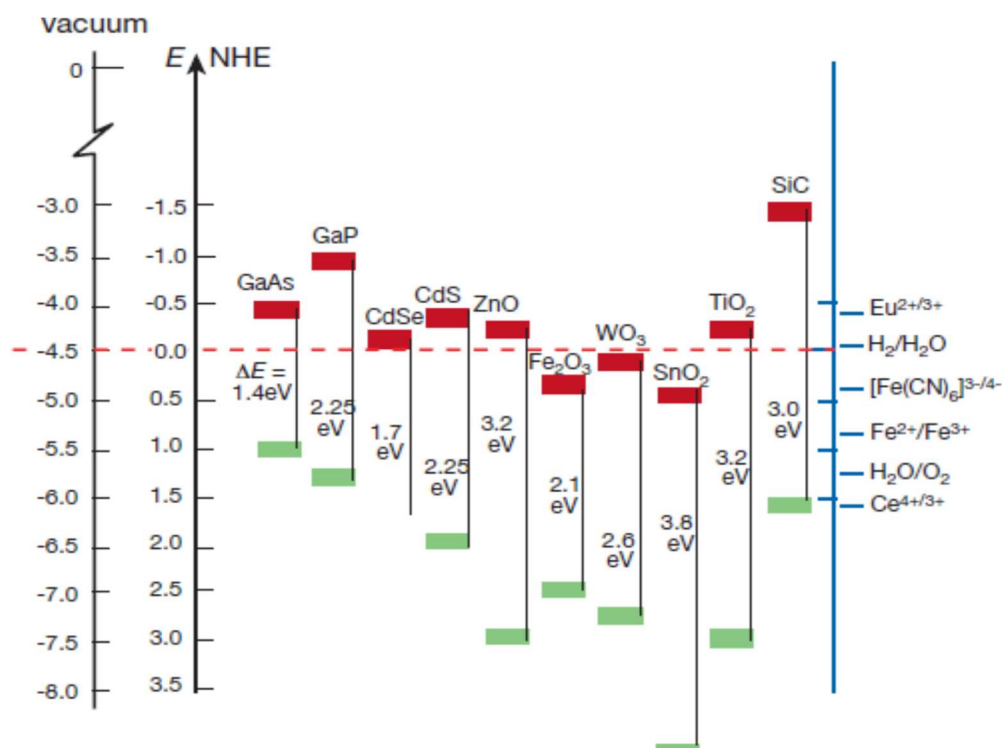

Figure 2: Relative energy values of some common semiconductor electrode materials and redox systems in acid solution

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

		-4.9	2.8	-7.7
PbO		-4.9	2.8	-7.7
FeTiO$_3$		-4.9	2.8	-7.7
BaTiO$_3$		-4.9	3.3	-8.2
CdSe	4.95	-5.0	1.7	-6.7
WO$_3$		-5.0	2.7	-7.7
SnO$_2$		-5.0	3.5	-8.5
Fe$_2$O$_3$		-5.1	2.2	-7.3
Bi$_2$O$_3$		-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

$$4H^+ + 4e \rightarrow 2H_2 \quad (5)$$

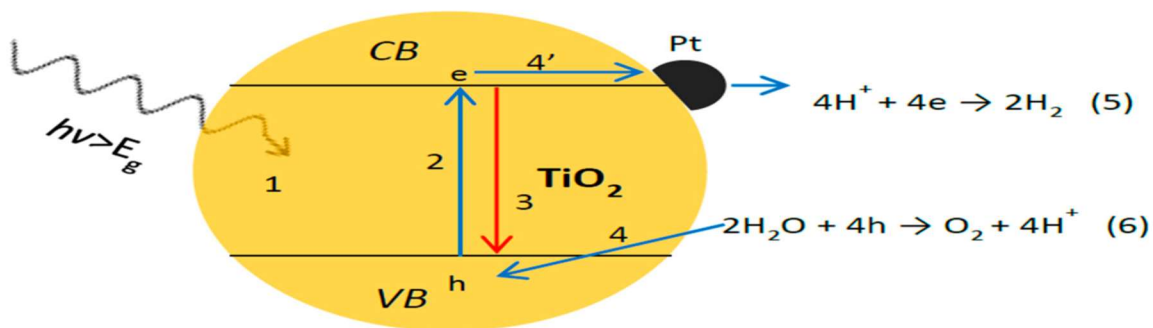$$2H_2O + 4h \rightarrow O_2 + 4H^+ \quad (6)$$

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

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

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.

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.
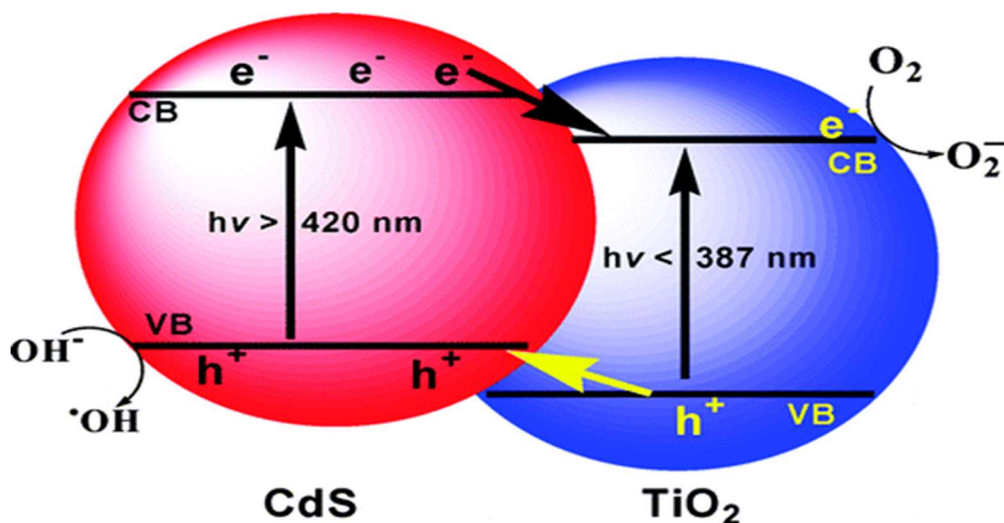

Figure 4: Scheme for photo-redox process in presence of two redox catalysts

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 sputtering	after/before
	O<u>O</u>	O<u>OH</u>	O<u>HH</u>	H<u>H</u>	O<u>HH</u>	H<u>H</u>

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

		565	512
PtO			
Rh$_2$O$_3$	-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.
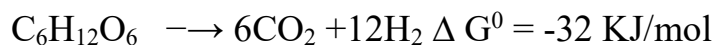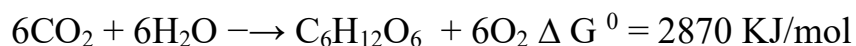
Table 7: Rate of hydrogen evolution in micro moles/10h from neutral water and carbohydrates, amino acids, fatty acids, or various types of biomasses using TiO2-Pt catalyst (Data compiled from ref [22]

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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