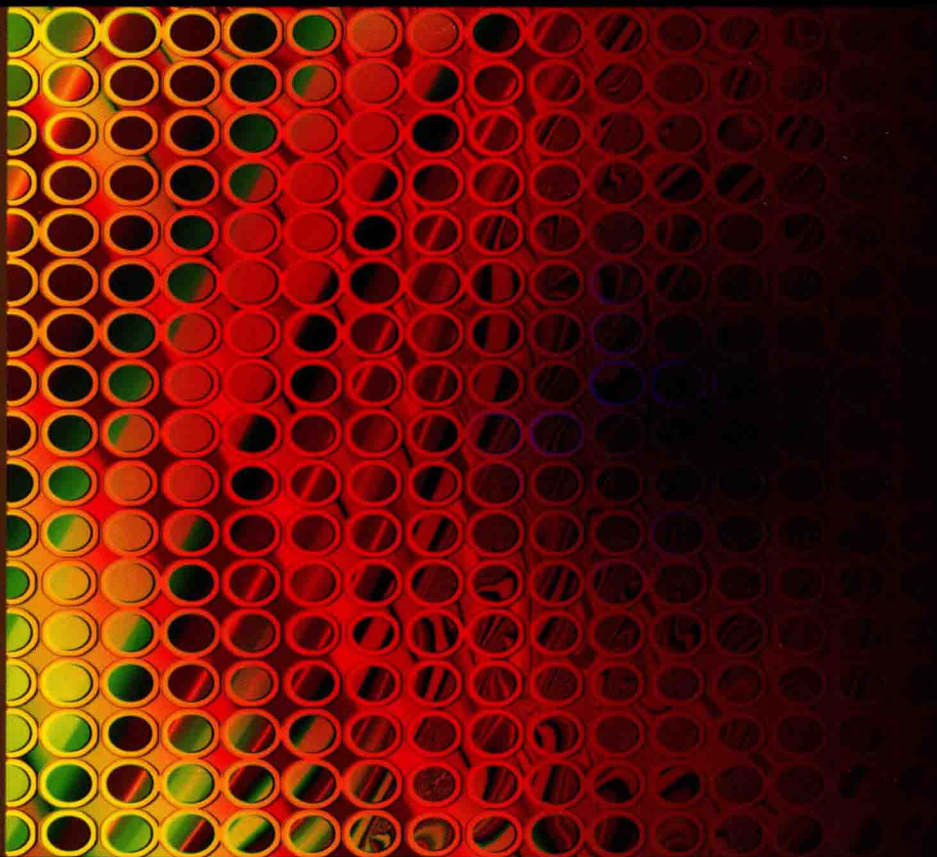


Photoelectrochemistry

PRINCIPLES AND PRACTICES



B. Viswanathan
M. Aulice Scibioh

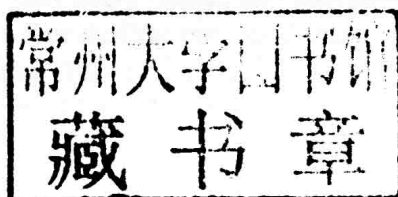


Alpha Science

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B. Viswanathan
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B. Viswanathan

M. Aulice Scibioh

National Centre for Catalysis Research
Indian Institute of Technology Madras
Chennai

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Photoelectrochemistry

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Preface

Over the last four or five decades, the subject of photo-electro-chemistry and photo-catalysis has been receiving considerable attention both academically and also for scientific research and practice. Research in this area is exploding in terms of number of publications. This subject has also been realized as essential for development of effective energy conversion devices and sustainability of life on earth. The authors have been considering formulating a monograph on this subject for a number of years since young researchers who are initiating research in this field find it hard to assimilate all the available knowledge and information in a short period. It has also been reflected and realized during the various special courses that the National Centre for Catalysis Research (NCCR) at Indian Institute of Technology, Madras has conducted on this topic. However, the hesitation to bring out a monograph lingered on due to the fact that every week, the literature in this field is expanding. Hence there was a fear that the coverage may look outdated when the monograph appears in print. This fear being fully present even now, the authors took the bold step of providing a level of knowledge with the fear that the coverage can not be comprehensive nor will be most upto date.

Having felt the need from various points of view, the authors considered the contents of the monograph and decided to restrict to some specific aspects on this branch of science for obvious reasons like affordability, available time for assimilating the knowledge and other related issues. Hence it should not be considered that this is a comprehensive monograph on this subject but has the bias of the authors and also other considerations mentioned above. It is also gratifying to note that many authoritative reviews are appearing on various aspects of this subject from time to time on regular basis and there are other authoritative sources of information on this subject and the readers should peruse these reviews for their knowledge assimilation. At most this monograph can be an introduction to this wealth of knowledge made available on this subject from time to time.

The authors felt that research in this field will have far reaching consequences for life sustainability on earth and hence introduction of these

subjects in the educational curriculum may become possible only when a suitable and appropriately tailored document is available as a reading source material. NCCR has introduced one such course in their Master's curriculum and attempted to experiment with the contents of this proposed monograph as a viable text. It is hoped that this compilation will also serve the purpose of an available text book and the educational curricula of the various institutions may introduce this subject at appropriate levels. It is fully realized that this compilation does not cover all aspects of this branch of science and it is hoped that it will kindle interest in the minds of the readers to dwell deep in this subject and experience the thrill of being in frontier in Science.

In a subject like this, there can be many gaps and limitations and the authors will be grateful if these aspects are brought to their attention so that these left out aspects can be included in subsequent attempts if there were to be some.

The authors wish to thank their learned colleagues and research scholars who have consistently contributed to the formulation and production this monograph. The inquisitive academic atmosphere provided by them especially the colleagues at NCCR has been one of the motivating factors and it is our duty to thank them for the same. We do hope that these colleagues will experiment introducing this course. One of the authors experimented this material in a course on Photo-catalysis for M Tech students in Indian Institute of Technology, Madras. They also wish to thank the *Department of Science and Technology*, Government of India for not only supporting the National Centre for Catalysis Research but also encouraged conducting these short term courses at NCCR.

Finally, the authors will be grateful for pointing out any shortcomings in this compilation.

B. Viswanathan
M. Aulice Scibioh

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1

History 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 [1] in the 70s. Photo-catalysis which is a phenomenon where in 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 [2]. Rev. Sister Markham followed this with a publication in chemical education [3] wherein she reported the photo-catalytic properties of oxides. In fact, Sister Markham had a number of subsequent publications on the photo-catalytic transformations on irradiated zinc oxide [4]. Photo-catalysis deals with the absorption of photons by the solid which generate 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 TiO_2 and Photons). Langford has written a concise article on photo-catalysis as introduction to a special issue of catalysts dealing with this hybrid area of catalysis [5].

Photo-chemistry 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 in the previous paragraph 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 [6]. The effect of particle size on phase stability and phase transformation during growth of nanocrystalline aggregates and the mixed phases transform to brookite and/or rutile before brookite transforms to rutile have been reported by Zhang and Banfield [7]. 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 1.1.

Table 1.1 *Statistical distribution of scientific publications dealing with nano-materials for PEC/Photo-catalysis hydrogen production [8].*

<i>Materials</i>	<i>Percentage of Study</i>
TiO_2	36.2
Non- TiO_2 Oxides	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 photo-catalytic activity comparison, contains both anatase (about 80 per cent) and rutile (about 20 per cent).

It is in general impossible to completely trace the history of Photo-catalysis. Even Fujishima and his coworkers [9] 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 [10]. In 1924, Baur and Perret [11] probably were the first to report the photo-decomposition of silver salt on ZnO to produce metallic silver. Probably Baur and Neuweiler [12] 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 [13] who reported the photo-catalytic reduction of silver nitrate and gold chloride on TiO_2 . Goodeve and Kitchener [14] 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 [2]. 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 fuel hydrogen. Subsequently Kraeutler and Bard 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 in separate chapters in this monograph. Fujishima et al., [9] have provided a more detailed and authentic write-up on the history of photo-catalysis.

1.2 BASIC PRINCIPLE OF PHOTO-CATALYSIS

According to the glossary of terms used in photo-chemistry [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 state in the normally empty conduction band thus creating a hole 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.

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 certainty 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 in Table 1.2.

Photo-catalytic destruction of organic pollutants in water is based on photo-chemical process involving semiconductors. When a semiconductor is irradiated with UV (usually but it can be any other radiation as well) light of wavelength appropriate for excitation from valence band to the conduction

Table 1.2 *Electro-negativity, [χ], Band gap, (E_g) energy levels of the conduction band bottom (E_{CB}) and energy position of the top of valence band (E_{VB}) [data extracted from Y. Xu and M.A.A. Schoonen, *American Mineralogist*, 85, 543-556 (2000)].*

Substance Oxide	Electro-negativity (χ)	Band Gap (E_g)	Conduction Band, E_{CB}	Valence Band, E_{VB}
BaTiO ₃	5.12	3.30	-4.58	-7.88
Bi ₂ O 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 ₂ O ₃	5.88	2.20	-4.78	-6.98
Ga ₂ O 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 ₂ O ₃	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
TiO ₂	5.81	3.20	-4.21	-7.41
V ₂ O 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 1.3 *Oxidizing power of the common oxidizing agents.*

<i>Oxidant</i>	<i>Oxidation Potential(V)</i>
Hydroxy radical	2.80
Ozone	2.07
Hydrogen Peroxide	1.77
ClO ₂	1.49
Chlorine (Cl ₂)	1.35

band of the chosen semiconductor an exciton is created. The photo-chemical 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. 1.1, a simple representation of these possible processes are 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 photo-excitation and catalysis.

Since it is possible that the organic substrate can be completely degraded to carbon dioxide 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 seen from the data given in Table 1.3. It is clear from the data given in Table 1.3 that the aqueous phase reactions will still be preferred in Photo-catalysis.

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 a 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. 1.2.

Scalafani et al., [16] postulated external mass transfer limitations to interpret their results in a packed bed reactor filled with spheres of semiconductor

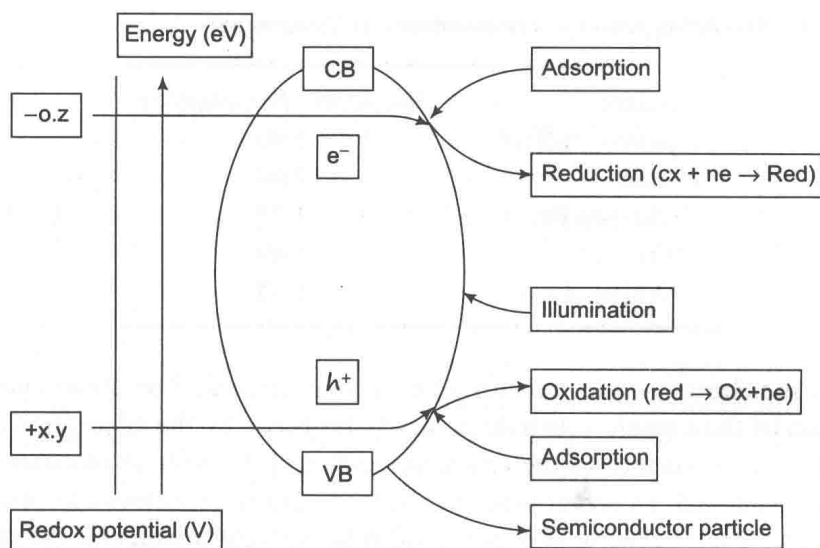


Figure 1.1 Schematic representation of the principle of photocatalysis showing the energy band gap of a semiconductor particle. Typical reactions considered are: $\text{water} \rightarrow \text{hydroxyl radical}$; $\text{organic substrate} + \text{hydroxy radical} \rightarrow \text{carbon dioxide} + \text{water} + \text{mineral acid}$.

catalyst (in this case pure titanium dioxide (ca. 0.12 cm in diameter)). Chen and Ray [17] 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 mass transfer limitations are negligible. 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 [18,19]. and many others (see for example one of the reviews on this topic in Legrini et al., [20]. 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 Table 1.2 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