

Chapter 1

INTRODUCTION

1.1 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 three to four decades is the selection appropriate anode material for the photoelectrochemical cells ¹ especially for the decomposition of water ² and reduction of carbon dioxide ³ and dinitrogen, a few reactions of great relevance in the context of energy carrier or conversion. Even though the governing principles for each of these reactions ⁴ 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 three reactions so as to be economically viable is still eluding ⁵. The primary purpose of this monograph is to address this aspect even though the authors realize 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

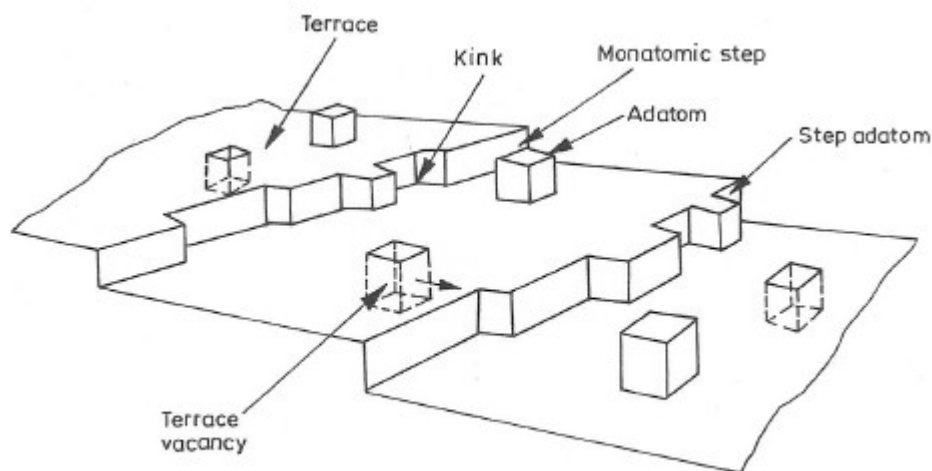


Figure 1.1: Representative model of a one component surface with possible active sites indicated ⁷.

the surface (refer to Fig.1 for a typical conceived defect surface) and this so called **heterogeneity** makes the catalyst selection most often cumbersome.

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.

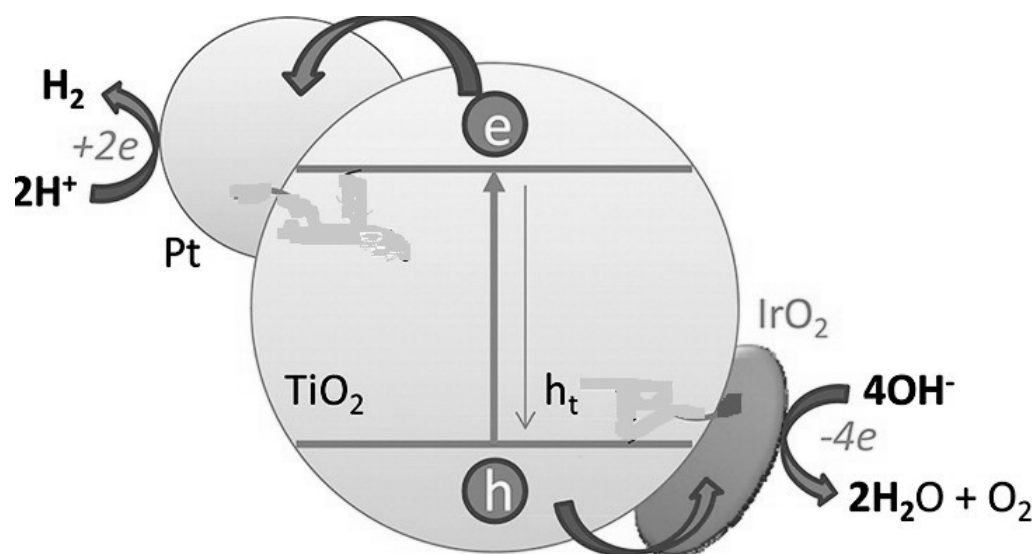


Figure 1.2: Schematic representation of charge transfer across a semiconductor-substrate interface indicating both reduction and oxidation reactions taking place⁸.

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 water⁹ and air, or generation of chemicals by photocatalytic routes¹⁰. A typical general scheme is shown in Fig.3 for the use of photocatalysis for pollutant removal. However, these interesting evolving possibilities will not be considered in this presentation. Heterogeneous photocatalysis 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 catal-

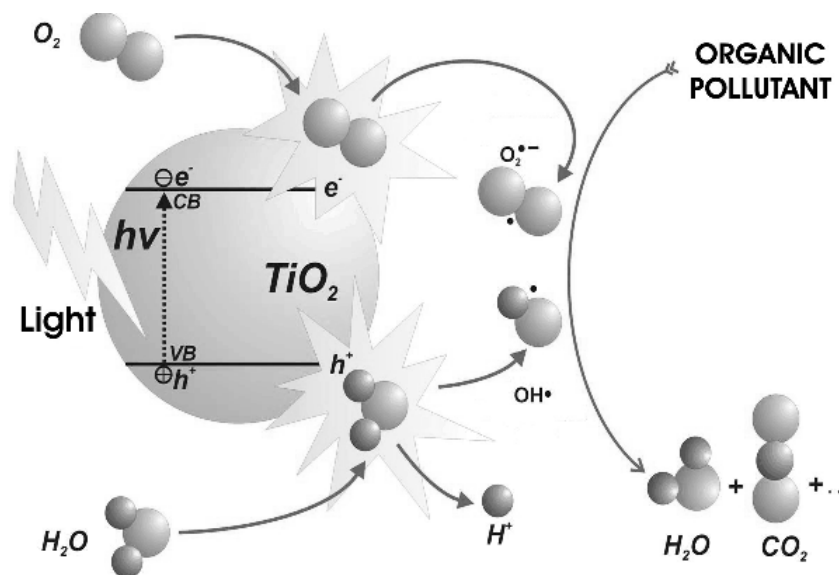


Figure 1.3: A typical representative scheme of pollutant removal by a photocatalysis; reproduced from A.O.Ibhadon and P.Fitzpatrick, *Catalysts*, 3,189 (2013).

ysis like the use of alternate feed stocks for the production of value added chemicals¹¹. The main challenge of this new face of catalysis namely **photocatalysis** is to provide the governing principles for the selection of catalysts. Therefore, the purpose of this presentation is to examine this aspect from theoretical and practical angles.

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**¹². 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 polynary 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 possibly overlooking the necessary physics of semiconductor-electrolyte interface. Interested readers can refer to authoritative documents on this topic elsewhere¹³. There are also other questions relating to this topic which requires 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 semiconductivity (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.

It must be admitted that these aspects are quite relevant, but they are not dealt with in this presentation.

1.3 References

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