

HETEROGENEOUS PHOTOCATALYSIS

2.1 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 four to five decades is the selection appropriate anode material for the photoelectrochemical cells [1] for the following processes:

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

There 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(s) 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 exercise is to address this aspect even though, it is realized that a complete and fully satisfactory solution may not evolve so easily, at least one can formulate a path for 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 on the catalyst surface [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.1.1. for a typical conceived defect surface) and this so-called heterogeneity makes the catalyst selection most often cumbersome.

Among the various manifestations (homogeneous, heterogeneous, bio- and electro-) of catalysis, Photocatalysis has taken a dramatic revolution these days. In simple terms, a catalyst (usually a semiconductor or possibly an insulator) is

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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. But it must be remembered that this is one of the possibilities for the generated electron hole pair. There can be alternate paths where the generated electron hole pair can recombine within the bulk or surface sites of the semiconductor.

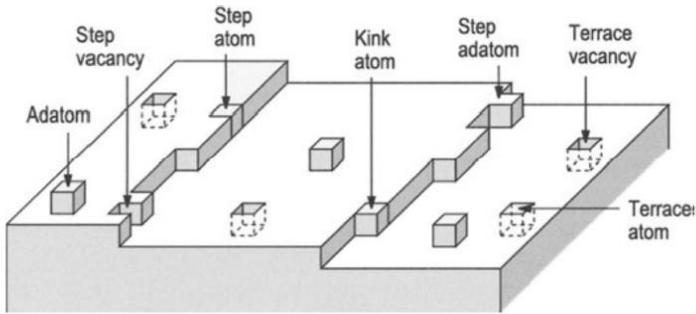


Fig. 2.1: Representative model of a one component surface with possible active sites indicated.

The photon can also be alternatively 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.1.2.

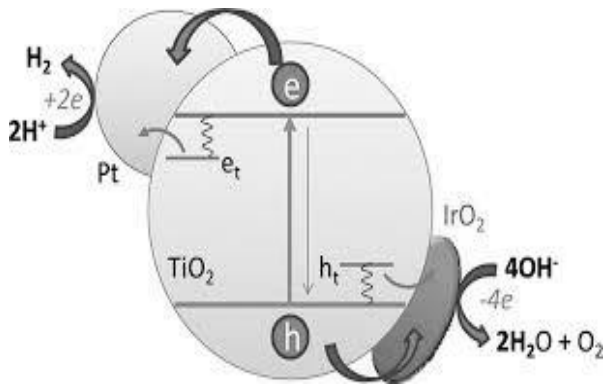


Figure 2.2: Schematic representation of charge transfer across a semiconductor-substrate interface indicating both reduction and oxidation reactions taking place [7]

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 [in conventional sense the reduction and oxidation potentials] 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 photocatalytic routes [9]. A typical general scheme is shown in Fig.1.3 for the use of photocatalysis for pollutant removal.

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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 [since as stated above the photons are utilized and not regenerated we term this process as photon-assisted process instead of 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] and carrying out the chemical processes under available conditions.. The main challenge of this new face of catalysis namely Photocatalysis is to provide the governing principles for the selection of catalysts.

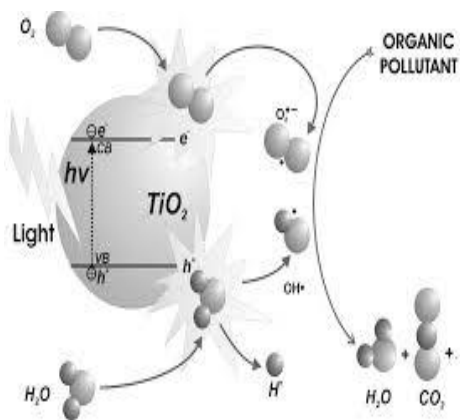


Figure 2.3. A typical representative scheme of pollutant removal by a photocatalyst; Reproduced from A.O. Ibhadon and P. Fitzpatrick, *Catalysts*, 3,189 (2013).

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For some obvious reasons, like the possibility of utilizing solar radiation and the amount of acquired knowledge on the physics of the materials, semiconductors (among them TiO_2 based systems especially) have been the material of choice,

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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 (approximately 40%). Roughly the solar radiation consists of visible and IR radiation and the UV component which is only around 5 %. Details will be taken up subsequently. Even though nearly four to five decades of research has been expanded in search for the suitable and viable semiconductor materials and nearly more than nearly ~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 mainly 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. These require careful examination on the available possibilities. Some of them are:

1. Is it necessary to look for semiconductor 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.

There are still other questions for which suitable and appropriate answers have to be evolved and thus field will flourish.

2.4 SCOPE OF THIS EXERCISE

The study of photon-assisted catalytic reactions requires some fundamental knowledge of solid-state Physics, electrode-electrolyte interface and also some acquaintance on oxidation/reduction reactions in general. In order to effectively

utilize the photons, some knowledge of optics and also to design appropriate reactors, some acquaintance on the fabrication technology is essential.

To define a limited scope for this area, is difficult especially for one reason namely, this field is fast evolving in the last 4 or 5 decades. A simple definition of Photocatalysis is “the acceleration of a photoreaction in the presence of a solid catalyst”. It may be necessary that one has to refine this definition subsequently. Historically, the concept of photocatalysis may be traced back to Edmond Becquerel as early as in 1839, [13] intent research on this topic did not gain mainstream attention until the late 1960s [14], due to efforts by pioneers such as Boddy [15] and Honda and Fujishima [16]. In recent times, the research interest in photocatalysis benefits from the growing awareness of sustainability for the society. One of the applications of photocatalysis is to store solar energy directly in chemicals (generation and conversion) and, hence, the name of solar fuels and artificial photosynthesis. Solar fuels are one of the emerging areas of research including the generation of hydrogen from renewable sources like water. In addition, utilizing carbon dioxide to convert it to useful chemicals is also emerging as an area of research. In fact, photocatalysis is in some sense, is to mimic photosynthesis and configurations of the photocatalytic systems are designed based on the concept of photosynthesis or the so-called Photosystem I and II.

Another important aspect of photocatalysis is environmental protection. Pollutants in water and air can be oxidized by photocatalytic routes and this is another area of exploitation of photocatalysis. Photocatalytic oxidation of dyes and other organic pollutants are evolving areas of studies and these will be considered.

Directly converting light energy into electrical energy is termed as photovoltaics or solar cells. A number of solar cell configurations are evolving to harness solar energy efficiently. This development has also led to development of new materials and these are termed as hybrid perovskites and these also deserve attention.

Plasmonic catalysis is another development on the use of nanometal configurations (especially gold, silver or copper nanometallic states) to harness light energy. This aspect will be considered briefly.

Activation of carbon dioxide and dinitrogen is important for chemical energy conversion. The science of the activation of these two stable small molecules has been experiencing dramatic changes in the presence irradiation. This possibility opens up a new conversion technology for generation of chemical energy sources.

The relationship between photosynthesis and photocatalysis will also be touched upon in order to connect the basis of both these technologies. This will facilitate the growth and understanding of these two technologies.

In general, there are a number of reactions which are potential uphill reactions. Among them there are a few reactions which are important in photon-assisted catalytic processes. The important reactions relevant to photo-assisted catalysis are shown in Fig.1.4

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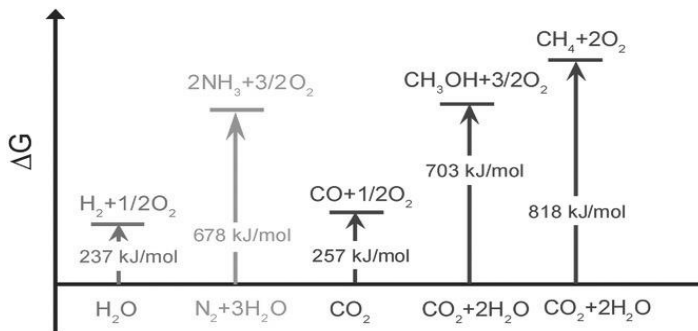


Fig.2.4. Representative potential uphill reactions that are relevant to photo-assisted catalysis

In general, the potential energy profile for this process namely Photo-assisted catalysis is pictorially shown in Fig.1.5. In this figure C and C* are catalyst and excited state of catalyst, R and P represent reactant and Product I, I', are the intermediates.

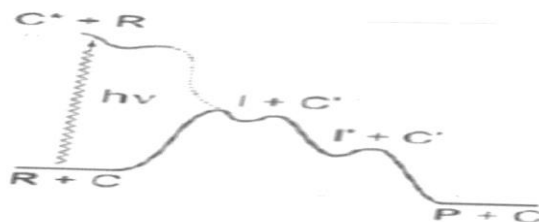


Fig.2.5. Schematic energy profile for photon assisted catalytic process.

It is hoped that this endeavour will be at least to a small extent, beneficial exposure to this new and emerging field of science.

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