

PHOTOELECTROCHEMICAL CELLS

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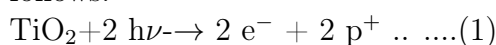
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Chapter 1

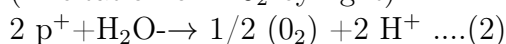
INTRODUCTION

1.1 Opening Remarks

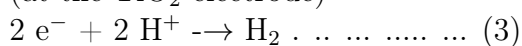
Energy conversion devices have been unique subject for the scientific community. They were fascinated by the possibility of non only converting one form of energy to another, they even used these devices for the production fuels like hydrogen and many other chemicals. This subject turned a leaf in the early 1970 by the introduction of photo-electro-chemical decomposition of water to hydrogen on titanium dioxide surfaces by Fujishima and Honda[1].The design of the cell designed and employed by them is shown in Fig.1.The process taking place on irradiation of light on the TiO₂ electrode was envisaged by them as follows:



(Excitation of TiO₂ by light)




(at the TiO₂ electrode)



(at the platinum electrode)

They further stated that "it is possible that the hydrogen evolution reaction shifts towards more positive



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Figure 1.1: Electro-chemical cell in which the TiO₂ electrode is connected with a platinum electrode . The surface area of Pt electrode was around 30 cm².

potential than normal when suitable p-type semiconductor electrodes are irradiated, in the same way that photosensitized oxygen evolution occurs with n-type semiconductor electrodes. If such a p-type semiconductor electrode is used instead of the platinum electrode, electro-chemical photolysis of water may occur

more effectively." Thus, there appeared at that time that this type of cells can be constructed with a variety of semiconductor materials thus opening up a new branch of science. In the last five decades or so, this branch of science has exploded and many other configurations of cells have been designed with the main aim of increasing the quantum efficiency of the process.

This process essentially takes place at the interface (namely electrode/electrolyte interface) and hence the charge transfer process that take place has to be governed by the electrochemical potential of the charge carriers at both sides. Photo-electrolysis has attained a prominent position. In essence, the basic principle of photo-electrolysis (catalysis) is of generation of electrons in the conduction band (reducing power) and hole in the valence band (oxidizing power) and their use in redox reactions. The values of the redox potentials are usually associated with the position of the top of the valence band and bottom of the conduction band in electro-chemical scale (refer to Fig.2.)

For the two reactions to take place (namely the hydrogen and oxygen evolution from the decomposition of water) the conduction band should be more negative with respect to the hydrogen evolution potential and the top of the valence band should be less positive to the oxygen evolution potential. These situations are shown diagrammatically in Fig.2.



Figure 1.2: Valence band and conduction band positions of TiO_2 and $\text{g-C}_3\text{N}_4$ with respect to vacuum level and also in NHE (Normal Hydrogen Electrode) scale

This criterion has been most often used to scan possible semiconducting materials for water photo-electrochemical decomposition reaction of water. This is reflected in many of the charts showing the conduction band bottom and valence band maximum with respect to hydrogen and oxygen evolution reactions in literature. One such compilation from literature is reproduced in Fig.3.

However, it has to be noted that this selection criterion is not sufficient for photoelectrochemical decomposition of water. This at best can be used at first level for screening the semiconducting systems for this reaction. However, one has to properly understand the band structure and their modifications as a result of the interface.

The semiconducting systems chosen for this reaction should be capable of absorbing the solar radiation. This brings us to understand the solar spectrum and how to optimize the materials so that maximum solar radiation will be absorbed by the material chosen. Typical solar spectrum is shown in Fig.4. The point to note, is that the band gap of the material chosen should have the band gap values so that the system will absorb maximum solar radiation at the same time as stated, the band positions should be such that both hydrogen and oxygen evolution reactions are thermodynamically feasible. This may probably account to the anxiety to use materials with low band gap so that maximum solar radiation can be harnessed. However, though this anxiety is noble, one must realize that even harnessing only a tiny fraction of solar radiation may be sufficient to the human society on earth. It is to be realized that **band gap engineering** should focus on the thermodynamic criterion rather than to satisfy our greedy nature of the people.

1.2 Material Selection

This aspect has received considerable attention in the last few decades. Nearly almost all known semiconductors have been examined for this reaction [2].

1.3 References

- (1) Akira Fujishima and Kenichi Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, *Nature* **volume 238**, pages37–38 (1972)
- (2) Frank E. Osterloh, Inorganic Materials as catalysts for photochemical splitting of water, *Chem. Mater.* 2008, **20**.

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Figure 1.3: The positions of valence band top and conduction band bottom with respect to oxygen and hydrogen evolution reaction of the semiconductors employed for photoelectrochemical decomposition of water

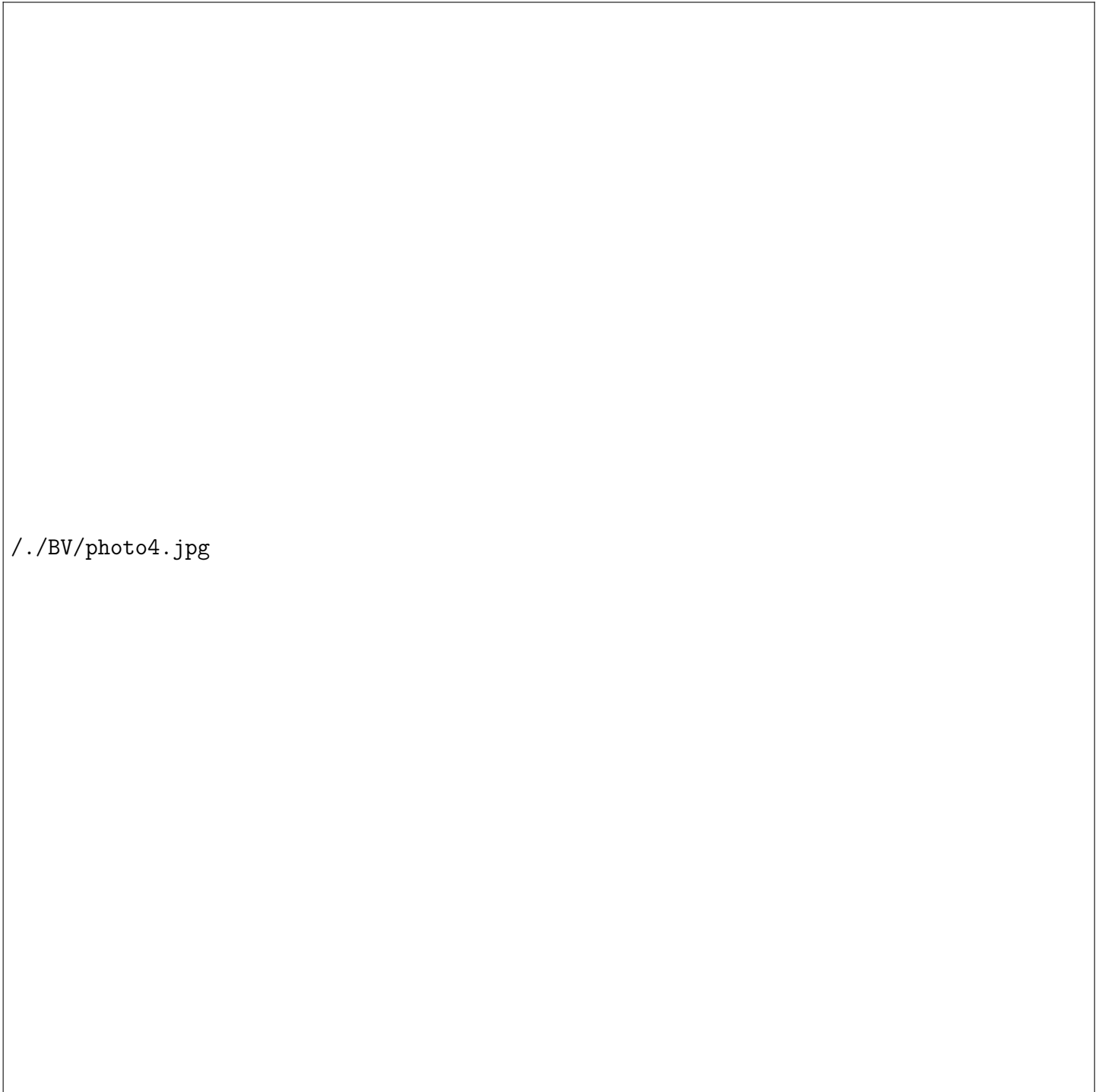


Figure 1.4: Solar spectrum in the wavelength range 250 to 2600 nm and it is seen the UV (about 5-6%), Visible about 40% and the remaining is in the infra red region.