

SOME REFLECTIONS ON PHOTO-ELECTROCHEMICAL AND PHOTOCATALYTIC DECOMPOSITION OF WATER – Part 1

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Photo-electrochemical or photo-catalytic decomposition of water has not seen any remarkable success in the last nearly four decades. The reasons for this slow progress have been analyzed at various levels, yet no condenses has evolved. This situation may be due to the fact that the searches are focused on either various known aspects or on the possible understandable processes where in attempts for improvements were possible. The lesson that we have learnt is that the real reason for the slow progress lies elsewhere other than these known possibilities for improvement. It is possible to list out the possible reasons that have been advocated for the slow progress, namely,

- (i) The active semiconductors employed have low photon absorption cross section.
- (ii) The life times of the excitons formed are low and recombination is the most predominant route.
- (iii) Most of the semiconductors employed undergo other photo-induced processes preferentially like photo-corrosion as compared to the photo-chemical process of interest, namely decomposition of water.
- (iv) It is possible that most of the semiconductors employed, have definite band gap, restricting range of wavelength of the photons that can be absorbed.
- (v) The attempts for increasing the quantum efficiency of the decomposition of water have been centred around a concept of 'chemical bias' wherein instead of attempting to reduced the energy barrier (conventionally termed as over voltage) has only provided means for overcoming the barrier. This necessarily means that ht decomposition voltage (namely 1.23 V) and the conventional over voltages for both cathodic and anodic processes are provided by means of a chemical bias. This chemical bias has been variously termed as 'doping' coupling of semi-conductors' dye sensitization hole or electron traps (either RuO₂ or noble metals). All these processes can also been understood in another terminology, called band gap engineering. This concept of nano state of the materials can also be clubbed into the category of band

gap engineering. It may be necessary to elaborate on the significance of the term chemical bias. Chemical bias is employed in the context of the photo-electrochemical (catalytic) decomposition of water to imply that the chemical potential of the species employed is cumulatively adding to the applied potential so as to surmount the decomposition potential of water. The species employed for augmenting the applied potential can be stationary or decomposable in nature. The concept of doping is an example of stationary chemical bias, while use of sacrificial agents is the available examples for decomposable chemical bias. Dyes and other hybrid configurations also fall under the category of chemical bias where the species act as energy transfer agents without undergoing any chemical change.

The available models of electrode electrolyte interface (for semiconductor/electrolyte in this case) have been adopted from the energetics that are known or evolved for semiconductor/vacuum interface. The adaptation of this interface model to semiconductor/electrolyte interface has incorporated the concept of band bending at the interface due to alterations of the species normally present on the surface (due to adsorption from electrolyte) as well as due to the changes in the potential gradients at the interface. These modifications have been successful in rationalizing the electron injection in conventional electronic devices. The available literature shows this extension to photo-electro-chemical (photo-catalytic) processes is possible. However, in the case of electronic devices the interface is solid/gas while in electrochemical processes this interface in question is solid/electrolyte in nature. Electrolyte does contain other than the depolarizer, other conducting species which are electrochemically not active in the potential range of operation. However, these species can induce changes by adsorption/incorporation (if this were to be possible) on the semiconductor and this causes changes in the surface potential of the semiconductor employed. This can alter considerably the energetics and electron transfer processes at the interface. This will be taken up in the part of this series.

