PHOTOELECTROCHEMIAL DECOMPOSITION OF WATER -IS IT REALIZABLE ECONOMICALLY?

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1 Introduction

For the past five decades or so, photoelectrochemical decomposition of water to generate fuel Hydrogen has been the subject of intensive research. The research area picked up with the publication of Fujishima and Honda who reported the generation of hydrogen from water on semiconductor surfaces by light radiation [1]. Ever since 1972, there have been many attempts to make this process more economically viable, but however, the search is still continuing. In between, there have been many attempts to assess the progress in this field by many eminent scientists as revealed from the publications only limited references are given [2]. The multivarious attempts so far made can come under one or other topics namely, the band gap engineering, sensitization by doping, coupling of semiconductors, sensitization by dyes and other photoactive materials. all these attempts have been aimed to make the process economically viable and to maximize the solar radiation absorption by the semiconductor. All these attempts have been pains taking and considerable progress have been achieved though still the ultimate goal has not yet reached.

It has been considered that Overall, the society could significantly benefit from the implementation of PEC in a sustainable system, contributing to the achievement of self cleaning processes and driving the transformation of the world toward a greener society.[2o]

In between, the debate on hydrogen as the alternate fuel choice has picked up for various reasons and the debate has not yet confirmed if this concept is acceptable or not. From many stand points like cost of production, equi-distribution possibility, safety point view and other issues are brought forth and the conslusion is still to evolve. Thogh it is appropriate at this time scale to discuss this topic, this aspect is not covered in this presentation. Interested readers can look at the recent debates typical reference is given [2].

There are some areas where some clarity has to evolve. Some of them are mentioned

2 Semiconductor Materials

This is one area where a number of publications devoted to introduce new materials for the application of photoelectrochemical decomposition of water. The main objective of this exercise is to utilize the maximum portion of solar radiation and if possible the visible component of solar radiation. This research goes under the title Band gap engineering. However, there are views that even utilizing about 6% UV component of solar radiation is enough to provide enough energy source for this universe. However, the anxiety to introduce low band gap semiconductors has not subsided. The thermodynamic decomposition potential for water is 1.229 V and if one were to add all the over voltage components, then the semiconductors which can be expected to photo-decompose water should have at least a band gap value of 2eV..

. 1.Bandgap and interfacial engineering are deployed to improve light absorption, charge separation and surface reaction for enhanced H_2 evolution. It is essential to develop stable photocatalysts suitable

Figure 1: Various Types of Photocatalystic Materials

Figure 2: A schematic energy illustration for a photoanodes (n-type semiconductor). Several phases of process are displayed, specifically: (i) light-absorption; (ii) charge-transfer; (iii) transportation of charge-induced electron-hole pairs; and (iv) surface reactions.

for visible and infrared light harvesting.

2. Further mechanistic studies should be conducted to reveal the active sites on the catalyst surfaces using advanced techniques.

3. Earth-abundant and environmental-friendly materials are favorable for cost-effective and pollution-free photocatalysts.

There must be clarity on each of these issues normally raised in the photoelectrochemical decompoosition of water for hydrogen generation.

There are other aspects of this reaction, namely using heterojunction systems, carrying out this reaction in combination with decontamination of water and also use of sensitizers and these aspects also require careful attention.

In literature, there are various methodologies employed which can be in general stated sensitization. This includes introducing dopants, employing sensitizers, coupling of semiconductors in various configurations (types and z-scheme) amd so on. The general criterion normally imposed is that the energy of the conduction band bottom should be more negative as compared to the value of hydrogen evolution potential. If one wishes to utilise both the components of exciton then the energy value of the top of the valence band should be such that the oxidation reaction becomes feasible. The schematic diagram of the energetics of this process is shown in Fig.2 [2p]
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The energy positions of the top and bottom of the valence band and conduction band controls the feasibility of the reaction., but still the charge transfer rate is controlled by other inherent properties of the solid surface. The charge transfer has to take place between the lowest unoccupied state of the acceptor state (in this case H^+) and the surface state wave functions of the solid semiconductor.. The energy, symmetry and contour of the surface state wave function should overlap with the wave function of the lowest unoccupied state of the acceptor species. The symmetry and shape of the surface state wave function is dependent on a number of properties of the semiconductor and also its (wave function) alterations caused by the adsorption from the surrounding medium. Additionally, the magnitude of the charge transfer barrier is subject to the band bending that occurs at the semiconductor/electrolyte interface. These effects are in situ generated and is not easily amenable for manipulation. These aspects of photoelectrochemical decomposition of water requires careful consideration.

Material selection appears to be another issue in the photoelectrochemical decomposition of water. As stated. there are various ways of screening materials in terms of band gap, availability, and many other physico-chemical properties of materials, Inherent property based on bonding characteristics have not been taken into condideration [2q. When the percent ionicity in a semiconductor increases, then the band gap also increases so low band gap semiconductors must not be purely ionic and the bonding between the cation and anion should have some covalent character also. However, this concept did not receive attention.

Let us turn our attention to the type semiconductors that have been examined. The main class of materials are pictorially shown in Fig.1.It is not the type of semiconductor that is necessary but their characteristics are important. However, the value of the band gap need not be the sole criterion for choosing a semiconductor for this application but the value of the band gap has to be around 2 eV. The material

selected should not undergo photo-corrosion. Materials ZnO and low band gap materials are susceptible for photo-corrosion and hence are not suitable for this application.

The thermodynamic criterion for the feasibility of the process is controlled by the positions of the bottom and top of the conduction and valence band of the semiconductor respectively. This condition can be ascertained fairly well in the all the semiconductor materials that have been so far examined. But the difficulty is in the overall kinetics of hydrogen and oxygen evolution reactions. As stated, the kinetics of transfer of charge depends on the nature and contour of the wave functions and alterations in this parameter is difficult to realize In the case of hydrogen evolution reaction, bare proton wave function is fixed and this cannot be symmetry modulated, but the wave function of the donor state of the semiconductor has to be altered for facile charge transfer. This means that in order to make this process viable, one has to modify the semiconductor and its electronic energy levels. Conventionally, this has been attempted by the process doping, or inclusion of defects and coupling of semiconductors The answer to this situation is using other substrates where the wave function can be altered but this is not possible since the source for hydrogen is protons and altering its wave function is not an easy task.Therefore, in the present situation, enhancing the kinetics of hydrogen evolution reaction in the photoelectrochemical decomposition of water appears to be not simple. .The use of other substrates has not yielded any progress.

3 Photon Absorption cross section maximization

It is essential to maximize the photons utilization the excitation creation. Recombination centres have to be minimized. Defects are often considered as the adsorption cemtres for the substrate molecules. In addition, defect centres can give rise to surface states which can facilitate the charge transfer reactions in photoelectrochemical process. Therefore, it is necessary to make use of these additional wavefunctions in the forbidden gap of the semiconductor in the photochemical reaction. These addition electron energy state may facilitate the charge transfer in addition to acting as recombination centres. These surface states also facilitate in reducing the photon energy required to create exciton. The maximization of the photon absorption by semiconductors has the following components
The photon absorption cross section of the semiconductor (the percentage of photon absorption) should be maximum, which means the surface scattering of photons should be minimum. This is reflected in the extent of roughness of the surface.
2. The number of excitons undergoing recombination has to be minimized and the recombination centres on the surface (like defect sites and others) should be minimized.
3. There are a variety of other recombination centres not only defect centres and hence, these centres also must be minimized.
4. Other losses like reflection. scattering, which arise due to the morphology of the material should also be minimized.

4 Reactor Design

Various types of reactor have been designed in literature [3]. Transforming a laboratory experiment to industrial scale involves several barrier, since the extrapolation has to be made on parameters are extrapolated outside their obtained operating range. In this process many things may go wrong. Simple linear extrapolation methods may not be always suitable.The design, construction, and scale-up of photocatalytic reacor for large-scale industrial applications is still an open problem. Considering the technologic point of view, intensive efforts of research and development have been invested to help overcome different problems in bulk reactors such as photon transfer limitation, mass transfer limitation, oxygen deficiency, and lack of reaction pathway control. The approaches developed so far are limited. For this reason, it is necessary to explore alternative methodologies for designing novel photocatalytic reactors.
In addition to focus the beam on the semiconductor, but it must be ascertained that all the photons are absorbed and generates excitons

5 Perspectives

Even though the thermodynamic criterion can be managed by proper choice of the semiconductor with the bottom of the conduction band to be more negative to hydrogen evolution potential of water. the kinetic control of the reaction needs to be carefully addressed. This aspect appears to depend on the electric field distribution in the semiconductor, which means we need a proper geometry for the catalyst system chosen. It is now apparent that the three dimensional geometry of the catalyst system so far tried is limiting the kinetics of hydrogen evolution reaction. This could be due to non-uniform distribution of the electric field, which controls the electron emission rate.
When the electric field strength is of the order of 0.1 V /cm then electron emission may set in metals and the field strength can be of this order for smooth transfer of charge. This kind of field distribution is achievable in 1D materials and it means that the semiconducting catalysts used in photo-electro-chemical decomposition of water may have 1D geometry. If this postulate were to be true, then it means that the semiconducting catalysts have to be in one dimensional architecture even if they were to be in nano state. such a field distribution cam ne achieved by the application of a bias voltage or internal field caused by the electrical double layer with addition of electrolyte the so called internal bias. However, it is to be noted that all these require a particular geometry of the semiconducting catalyst. .this geometry should be capable of absorbing the photons also effectively.

The wave function of the conduction band of the semiconductor will be mostly of 's' character and hence it will be effectively overlap with the 1s wave function of hydrogen and hence charge transfer may be feasible.

Another way to increase the charge transfer kinetics is to increase the life time of the exciton. This implies that the wave function where the excited electron occupies should be deep and hence the electron resides there longer time as compared to recombination time. However there are not amenable for alteration and hence the life time of the exciton is mostly dependent on the material characteristics of the semiconductor chosen.

It appears that inherent energy alteration is not the solution to increase the kinetics of water decomposition. The application of bias voltage possibly reduces the potential barrier..

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