**Photo-electrochemical Decomposition of Water – Some Questions to Resolve**

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Photocatalysis is an evolving science with possibilities of overcoming the shortage in fuels and energy conversion processes [ref]. In spite of nearly five decades of intense research, these processes have not reached the desired levels of conversion. These aspects have been outlined a number of times in literature. The main concern is the quantum efficiency of the process which has yet to reach the desired levels. In order to understand the reasons for this situation, various attempts have been made mainly on the mode of activation procedures employed on the semiconductor materials including the band gap engineering [ref]. However, these attempts, which are innumerous reported in literature [ref], have not yet identified the missing element in this search.

Among the various semiconductors that have been examined titanium oxide in its various forms like black TiO2, white TiO2 and others have been widely studied due to various reasons like stability, cost, photo-response to UV/Visible light and flexibility to modify the electronic and geometric property of the semiconducting solid [ref].

After the advent of nano-materials, there is a lingering question in the minds of practicing scientists is that whether dimensionality of the material has any role in the property exhibited by these materials especially in the fuel production from small molecule like water or carbon dioxide. Though it has been already realized in literature that shape and size of nano-materials have profound effect on the property exhibited by nano-materials [ref]. It is already known that electronic property is dimensional dependent and this may be associated with the mobility and life time of the charge carriers. These two properties are also directly involved in fuel production in water oxidation and also carbon dioxide reduction. In three dimensional materials, the recombination of charge carriers is mainly responsible for the low quantum yield of the process and possibly may also account for the low efficiency of the process. This is one aspect where some clarity if required. The reasons for this situation may be due to the difficulties involved in preparing the chosen semiconductor in dimensionally different states, though various morphologies of the same material have been already tested like the activities of various forms of TiO2 namely anatase or rutile or other forms of TiO2 have been tested for the hydrogen evolution in the photo-electrochemical decomposition of water.

Another aspect of photo-catalysis which requires attention is associated with the photon absorption cross section of the material. Instead of this aspect, the studies have been focused on the shift of the region of the electromagnetic spectrum from ultraviolet (~5%) to visible region since the solar radiation has nearly (40%). This band gap engineering studies though improved the efficiency marginally, but have not yet yielded the desired levels of conversion. In spite of these persistent studies, the fact that it did not give the desired results indicate that this method of activation of the semiconductors may not the appropriate route to achieve the suitable material of choice for this process. For shifting photon absorption to visible region, the UV active semiconductors are doped with alter-valent metal cations or any heteroatoms ( especially N,B), and the resultant materials have been shown to absorb in the visible region but still the photon efficiency has not increased considerably so as to make the process a commercially viable one.

The photo-electrochemical decomposition of water is supposed to take place at the semiconductor/liquid interface. The interface science is based on the positions of the valence band edge (oxidizing power) and conduction band edge (reducing power) and these values are considered on the basis of stationary values. The choice of the semiconductor is made if the conduction band edge is more negative to the reduction reaction potential and the valence band edge has to be more positive with respect to the oxidation potential of the half reaction. The values of the band gap determined by physical methods like diffuse reflectance or any other similar techniques have been taken to represent the required photon energy. This alteration in this value at the interface has not yet fully taken into account. The alteration of band edge positions at the interface is supposed to be modified by the band bending concept and hence the redox potential values could be different and hence the equilibrium extent of the interface reaction will be different as compared to other situations. This may mean that the redox potential values are floating in this configuration and this aspect has to be carefully considered, resolved and rationalized.

It is now known that electricity from alternate sources like solar energy and wind turbines are becoming economically competitive, one should device alternate devices from these intermittent sources to convert and store energy. Though electrochemical devices like battery technology, they are not amenable to many activities that are currently supported by fossil fuels, these include transport sector and also transmission of large quantities of energy from one region to another. Synthetic fuels are one of the alternatives for fossil fuels in view of the large energy density among all storage media (see Fig.1).



Figure 1. Volumetric and gravimetric energy densities of different energy storage possibilities. Adopted and Reproduced from J.Kibsgard, P.C.Vesborg, I.Chorkendorff, T.F.Jaramillo, J.K.Norskov, P.G.Moses and J.Sehested, Power to fuels and chemicals innovation challenge, in Accelerating the clean energy revolution perspectives and innovation challenges, DTU I\*nternationa Energy Report (Technical University of Denmark 2018), pp73-80.

It has been realized for some time now that hydrogen is an sustainable energy storage molecule and reaction chemical intermediate that enables a varietyof chemical transformations to energy storage molecules and necessary chemicals. Among the sources for hydrogen water is the possible feedstock for the production of fuel hydrogen. Though the water electrolysis in various forms like alkaline electrolysis, proton exchange membrane (PEM) and solid oxide electrolysis cells (SOEC) is a known, there are challenges especially for the production of hydrogen at scales required for sustainable fuel production in addition to membrane suitability and materials concern.

In circular economy, the conversion of abundant molecules like water, carbon dioxide and dintrogen into fules and chemicals has been effected by renewabes electricity, electrocatalysis, photocatalysis or thermal catalysis. A conveptually feasible sustainable energy system is presented in Fig.2. The key processes are electrochemical and photoelectrochemical water splitting in addition to thermal and electrochemical reduction of carbon dioxide and dintrogen for chemicals.



Figure 2. One of th epossible sustainable energy system. This is reproduced from Z.W.seh, K.Kibsgaard, C.F.Dickens, I.Chorkendorff, J.K.Noreskov and T.F.Jaramillo, combining theory and experiment in electrocatalysis. Insights into materials design, Science, 344 eaad4998 (2017).

The special and prominent position of TiO2 as the archetypical photocatalyst relies on the favourable positions of its valence and conduction band edges with respect to theH+ reduction potential and the oxidation potential of oxygen evolution reaction and the unusual stability under irradiation. In addition, low cost and safety provide additional value for the large-scale commercial exploitation of this material. However, low quantum yield and negligible visible light photo response impose limits on the development of solar photocatalysis. Consequently, there is increased interest in the development of alternative photocatalysts for the different fields of application of this technology.

A number of novel photocatalysts have surpassed the performance of TiO2 for water splitting under different experimental constrains. Thus, the rate of H2 from pure water under UV irradiation over La-doped NaTaO3 is more than fifty times larger than when TiO2 is used. In spite of this plethora of publications, still the process has not reached a stage when a commercial possibility can be realized. This means that certain key questions still remain unanswered in developing a viable process. Let us list some of these important ones

1. How can one predict a suitable semiconducting material for the photo-electrochemical decomposition of water? The basis for this predictive effort has to be identified.
2. The redox chemistry now though well-known in the decomposition of water, how the semiconductor/electrolyte interface adjusts itself to carry out the process in a facile manner? Till now the process is based on the static potential positions of the VB and CB band edges of the semiconductor. It may be possible these positions may be altered at the interface due to charge injection either way.
3. The methodology to determine these alterations has to be evolved. Though the existing methods can be indicative a new precise methodology has to be formulated.
4. Though almost all known semiconductor materials running to few hundreds have been examined and all the possible experimental variables in the preparation process have been attempted, the effect of dimensionality of the chosen material on the photo-electrochemical decomposition of water has to be established. In this case, even the well-known TiO2 seim-conductor in the 1,2 and 3 dimenstional states have not yet been tested for the efficiency of photoelectrochemical decomposition of water.
5. There is some uncertainity regarding the feasibility and facility of the corresponding oxidation reaction (namely oxygen evolution) and its stoichiometric proportion has to be ensured.
6. One has to device the preparation methodology for the resultant semiconductors (namely to chose speicific TiO2 and tatalum based ternary semiconductor as choices for study) from the same chosen precursor but at the same the resultant morphology has to be dimensionally different. Though there may be attempts towards this methodology, no report is yet available on the aspect. This though difficult must be established and examined at the earliest to ascertain if this is the cause for the failure of this process becoming a economically viable process.
7. It is also necessary that these principles should be equally applicable for other photocatalytic process like decontamination and also carbon dioxide reduction for chemicals production. It is at least necessary to establish the applicability or not of these principles to at least decontamination of water by photo-electrochemical decompsotion of the pollutants typically a dye decolourisation as well as establish the product formed instead only monitoring the colour change. The identification of the products formed as a result of decontamination of water will possibly aid in understanding the photo-electrochemical decomposition of water.

These are only some of the questions regarding this process. Even to answer partially these questions, it is necessary that one has to design and plan the experiments appropriately and get the results in order to deduce the correct directions. The possible attempts will be outlined.

The strategy for preparing one semiconductor materials in various dimensioanlities will be attempted to control the hydrolyis rate of the precursor like TiCl4 and growing the TiO2.The control of the hydrolysis rate has to be modulated by conventional varialbles like solvent employed, concentration, temperature, and also ionic strenth of the medium. The prepared semiconductor material will be subjected to various conventional characterization methods and also the semiconductor/solution interface will be probed by conventional diffuse reflectance spectrocopic measurements and also by Electrochemical impedenace spectroscopy.

In addition, DFT calculations will be carried out to monitor the extent of band bending and also the alterations in the density of states in the semiconductor at the interface by selecting suitable model systems incorporating adsorbed electrolyte and also taking into account any solvation that will occur simultanesously. These type of theoretical studies are limited in literature and in this sense this will pave way for treating these complex systems within the framework of DFT calculations.

On the whole, the proposed project aims to answer some of the outstanding questions on the fuel production from water by photo-electrochemistry. In addition, the electrochemical potentials involved under the experimental conditions of photo-electrochemical decomposition of water may be resolved and identified.

The experimental and other work-elements of the proposal

1. Establishing the preparative methodology for 1,2 and 3 dimensional state of the chosen semionconductor TiO2 from the same precursor. This will be attempted by controlling the hydrolysis rate and device the medium for control of the nucleation and growth of the semiconductor material.
2. Evaluting the band positions under experimental conditions and its alteration from the stationary values under experimental condions including irradiation.
3. Measuring the photo-electrochemical hydrogen production from the decomposition of water and showing how to optimize the same.
4. Extending the material for testing the activity for the photodecomposition of pollutants
5. Carrying out DFT calculations on mdel systems with taking into account the solvation of the adsorbed ions (H+ and OH-) from water molecule.
6. Consolidating the results with predictive capability.

