International Journal of Engineering Research and Applications (IJERA) ISSN: 2248-9622
National Conference on Advances in Engineering and Technology
(AET- 29th March 2014)

RESEARCH ARTICLE OPEN ACCESS

A Review on Photoelectrochemical Splitting of Water by Semiconductors

P.K. Farsoiya*, D. Prasad A.*
*(Department of Chemical engineering and Technology, IIT BHU, Varanasi-221005
Email: farsoiya@gmail.com)

ABSTRACT
Hydrogen, if it can be produced using solar energy, stored and transported safely then it has the potential to be a non-fossil fuel. Research and development of an efficient system for solar energy to hydrogen energy is one of the challenging tasks to solve global energy problem. This article will give a short review on photoelectrochemical approaches for water splitting using semiconductor anodes.
Keywords – Hydrogen, Photoelectrochemistry, Photoelectrolysis, Semiconductor, Solar Energy, Water splitting

I INTRODUCTION

One major issue is the need to develop highly efficient photoactive materials capable of harvesting and converting solar energy into stored chemical energy, *i.e.* a clean non-fossil fuel like hydrogen. In the overall reaction of photosynthesis (Eqn. (1)), plants transform water and carbon dioxide in the presence of light into oxygen and carbohydrates. In effect then, H_2O is split into O_2 and H_2, where the hydrogen is not in the gaseous form but bound by carbon.

$$6CO_2 + 6H_2O + \text{Light} \longrightarrow C_6H_{12}O_6 + 6O_2 \quad (1)$$

$$2H_2O + \text{LIGHT} \longrightarrow O_2 + 2H_2 \quad (2)$$

The photo-electrochemical (PEC) path to water splitting involves separating the oxidation and reduction processes into half-cell reactions. In equations (3) and (4) the half-cell reactions with their corresponding standard reduction potential E° with respect to the standard hydrogen electrode (SHE) are shown. Eqn. (5) shows the overall reaction and the corresponding ΔE°. The negative ΔE° indicates that water splitting is not a thermodynamically spontaneous process.

For the reaction to proceed, 1.23 V must be provided externally.

Oxidation:

$$2H_2O + \text{Light} \longrightarrow O_2 + 4H^+ + 4e^-$$

E° = 1.23 V *vs.* SHE (3)

Reduction:

$$2H^+ + 2e^- + \text{Light} \longrightarrow H_2 \quad (4)$$

E° = 0.00 V *vs.* SHE

Overall:

$$2H_2O + \text{Light} \longrightarrow O_2 + 2H_2 \quad (5)$$

ΔE° = −1.23 V

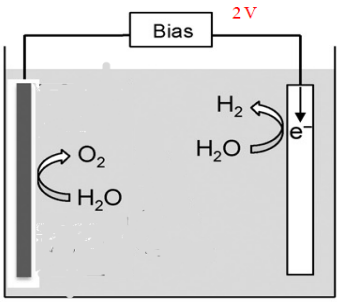
Water splitting reaction is energy intensive and requires external energy to proceed. For this, three fundamental requirements should by the semiconductor:

- The band gap of semiconductor should be more than 1.23eV.
- Appropriate band edges to carry out water oxidation and water reduction reaction.
- It should be chemically stable in the water.

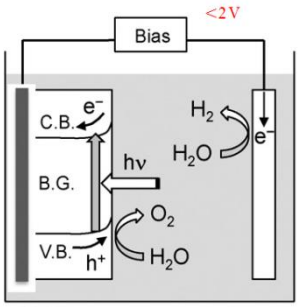
This review focuses on photoelectrochemical approaches for splitting of water using inorganic semiconductors. It covers classical and more recent studies spanning approximately four decades.

II ELECTROLYSIS AND PHOTOELECTROLYSIS

In electrolysis of water, an external voltage of approximately 2.0 V is required which includes 1.23 V thermodynamic energy requirement and polarization losses but in photo assisted electrolysis of water this requirement is reduced but still the external voltage is required called as bias voltage as shown in Fig 1 (a). The semiconductor absorbs the light and produces electrons and holes. Electrons get conducted to cathode and holes oxidize water to produce oxygen and hydrogen ions as shown in Fig 1 (b).



(a) Electrolysis



(b) Photo Assisted Electrolysis

Fig 1: Bias Voltage Requirement for Electrolysis and Photo Assisted Electrolysis

Over 150 materials and derivatives are discovered either to catalyze the overall water splitting or cause water oxidation or reduction in presence of external redox agents. So far, no material capable of catalyzing overall water splitting having quantum efficiency larger than 10% has been found. Here 10% is the limit for commercial applications[1].

Many oxide semiconductors had been found to catalyze water oxidation or reduction reaction at low efficiencies and on irradiation of ultraviolet light like TiO_2 as shown in Fig 2.

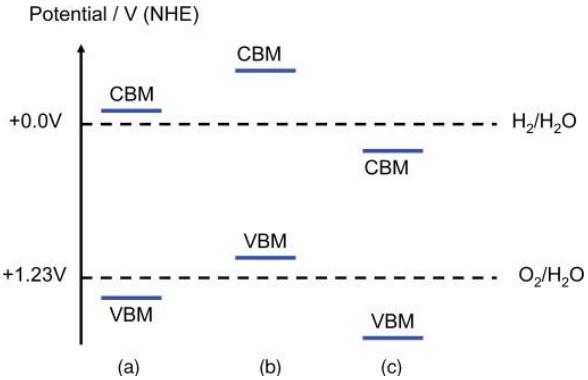


Fig 2: (a) Most desirable band edges position, (b) Only water reduction reaction possible, (c) Only water oxidation possible

However there are also many semiconductors like WO_3 which oxidizes water in visible region but unable to reduce hydrogen ions.

III LITERATURE SURVEY

Fujishima and Honda first discovered the water splitting using UV light and TiO_2 anode and platinum cathode [2]. In [3], authors showed the hydrogen produced by photoelectrolysis using platinized $SrTiO_3$. In [4], authors explored the concept of photochemical diodes and showed the necessity of a bias potential for rutile photoanodes. Early studies on titanium dioxide semiconductors are given in Table 1. Titanium dioxide as a semiconductor has a band gap of 3.2 eV which corresponds to UV region. To narrow its band gap and bringing their responses in visible region doping with non metals were studied which is given in Table 2 and Table 3. In [5], authors studied the composite effects of CdSe with nitrogen TiO_2 and were able to narrow its band gap and brought the response in to the visible region. In [6], authors used Cu_2O layer protected by FTO layer for depositing the thin film of TiO_2 by atomic layer deposition. In [7], authors employed hydrothermal method and used TiO_2 nanoribbons morphology to narrow the band gap.

Table 1: Representative Early Study on Tio_2 Anodes

Title of the study	**Comment**	**Reference**
Electrochemical Photolysis of Water at a Semiconductor Electrode	First demonstration of the feasibility of water splitting	[2]
Photoassisted Electrolysis of Water by Irradiation of a Titanium Dioxide Electrode	The initial claim in Ref. 1 supported along with data on the wavelength response and the correlation of product yield and current	[3]
Improved Solar Energy Conversion Efficiencies for the Photocatalytic Production of Hydrogen via TiO_2 Semiconductor Electrodes	Heat treatment of Ti metal found to influence performance	[8]
Novel Semiconducting Electrodes for the Photosensitized Electrolysis of Water	Appears to be the first study on doping TiO_2 to extend its light response into the visible range of the electromagnetic spectrum.	[9]
An Effect of Heat Treatment on the Activity of Titanium Dioxide Film Electrodes for Photosensitized Oxidation of Water	Heat treatment in argon atmosphere found to improve performance of both anodic and pyrolytically prepared TiO_2 films.	[10]

Table 2: Doping in Titanium Dioxide with Non Metals for Band Gap Narrowing

Title of the study	**Comments**	**Reference**
Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides	Both films and powders considered. Substitutional doping with nitrogen shown to bring about band gap narrowing and also high photocatalytic activity with visible light. Experimental data supported with first-principles calculations.	[11]
Formation of TiO_2-xFx Compounds in Fluorine-Implanted TiO_2	Fluorine substituted for oxygen sites in the oxide by ion implantation.	[12]
Band Gap Narrowing of Titanium Dioxide by Sulfur Doping	Oxidative annealing of TiS_2 used. Ab initio calculations also reveal mixing of S 3p states with the valence bond to bring about band gap narrowing.	[13]
Efficient Photochemical Water Splitting by a Chemically Modified n-TiO_2	Combustion of Ti metal in a natural gas flame done to substitute carbon for some of the lattice oxygen sites. The photocatalysis performance data have been questioned	[14]
Visible Light-Induced Degradation of Methylene Blue on S-doped TiO_2	Oxidative annealing of TiS_2 used	[15]

Table 3: Recent Studies on TiO_2 Composite Electrode and Morphology

Title of the study	**Comments**	**Reference**
Synergistic effect of CdSe quantum dot sensitization and nitrogen doping of TiO_2 nanostructures for photoelectrochemical solar hydrogen generation	Study shows the sensitization of TiO_2	[5]
Highly active oxide photocathode for photoelectrochemical water reduction	Cu_2O atomic layer deposition on FTO substrate	[6]
Synthesis of TiO_2 nanoribbons and its application in photoelectrochemical water splitting for hydrogen production	bring about band gap narrowing and also high photocatalytic activity with visible light.	[7]

IV CONCLUSION

Titanium dioxide is a very stable semiconductor in aqueous conditions and economical but due to its large band gap it does not offers commercial application. But in last few years doping metals and non-metals and using composite electrodes with other semiconductors such as CdS, CdSe and Cu_2O, it is possible to narrow its band gap and solar light can be used to produce hydrogen. Overall efficiency of such anodes currently is not enough for commercial purposes but further research is going on to develop such anodes. With increase in prices of petroleum and coal it is going to be a viable alternative to produce hydrogen from solar light which is also environment friendly. The use of irradiated oxide semiconductor-liquid interfaces for hydrogen generation is now a mature field of research. Indeed, impressive results have been obtained at the laboratory scale over the past three decades and a range of new oxides are being continually discovered. On the other hand, much needs to be done to improve the H_2 generation efficiencies. The photoelectrolysis process must be engineered and scaled up for routine practical use. In this regard, oxide semiconductors appear to be particularly promising, especially from an environmental and process economics perspective.
While interesting chemistry, physics, and materials science discoveries will continue to push this field forward, two types of R&D will be crucial: the use of composite semiconductors for electrodes development and innovations in reactor/process engineering once efficiencies at the laboratory scale have been optimized at a routinely attainable ~10%benchmark. Only then will the long sought after goal of efficiently making H_2 from sunlight and water using this approach be realized.

References

Journal Papers:

[1] J. Nowotny, C.C. Sorrell, T. Bak, L.R., "Sheppard, Solar-hydrogen: Unresolved problems in solid-state science", *Solar Energy, 78(5), 593-602.*

[2] A. Fujishima, K. Honda, "Electrochemical photolysis of water at a semiconductor electrode", *Nature, 238 (5358),* 1972, 37-38

[3] M.S. Wrighton, P.T. Wolczanski, A.B. Ellis, "Photoelectrolysis of water by irradiation of platinized n type semiconducting metal oxides", *Journal of solid state chemistry, 22,* 1977, 17-29.

[4] A.J. Nozik, R. Memming, "Physical chemistry of semiconductor-liquid interfaces", *Journal of physical chemistry, 100(31), 1996, 13061-13078.*

[5] J. Hensel, G. Wang, Y. Li, J.Z. Zhang, "Synergistic Effect of CdSe Quantum Dot Sensitization and Nitrogen Doping of TiO2 Nanostructures for Photoelectrochemical Solar Hydrogen Generation", *Nano letters, 10, 2010, 478-483.*

[6] A. Paracchino, V. Laporte, K. Sivula, M. Gratzel, E. Thimsen, "Highly active oxide photocathode for photoelectrochemical water reduction", *Nature materials,* 10(6), 2011, 456-461

[7] P.K. Dubey, R.S. Tiwari,,O.N. Srivastava, A.S.K. Sinha, "Synthesis of TiO2 nanoribbons and its application in photoelectrochemical water splitting for hydrogen production", *International Journal of Nanoscience, 10, 2011, 723-726.*

[8] J. F. Houlihan , D. P. Madacsi , E. J. Walsh, "Improved Solar Energy Conversion Efficiencies for the Photocatalytic Production of Hydrogen via TiO_2 Semiconductor Electrodes", *Material Research Bulletin, 11 (9), 1976, 1191-1197.*

[9] J. Augustynski , J. Hinden , C. Stalder, "Novel Semiconducting Electrodes for the Photosensitized Electrolysis of Water", *Journal of Electrochemical Society, 124 (7), 1977, 1063-1064.*

[10] Tamura H, Yoneyama H, Iwakawa C, Murai T, "An Effect of Heat Treatment on the Activity of Titanium Dioxide Film Electrodes for Photosensitized Oxidation of Water", *Bulletin of Chemical Society, Japan, 50, 1977, 753.*

[11] R. Asahi , T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, "Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides", *Science 293, 2001, 269-271.*

[12] Yamaki T, Sumita T, Yamamoto S, "Formation of TiO_2-xFx Compounds in Fluorine-Implanted TiO_2, Material *Science Letters 21 (1), 2002, 33-35.*

[13] Umebayashi T, Yamaki T, Itoh H, Asai K, "Band Gap Narrowing of Titanium Dioxide by Sulfur Doping", *Applied Physics Letters, 81: 454, 2002.*

[14] Khan SUM, Al-Shahry M, Ingler Jr WB, "Band Gap Narrowing of Titanium Dioxide by Sulfur Doping", *Science 297, 2002, 2243.*

[15] Umebayashi T, Yamaki T, Tanaka S, Arai K, "Visible Light-Induced Degradation of Methylene Blue on S-doped TiO_2", *Chemistry Letters, 32, 2003, 330.*