



Photoelectrochemical water splitting: An ideal technique for pure hydrogen production

Nitu Singh Parihar and Sushil Kumar Saraswat*

Department of Chemical Engineering, MBM Engineering College, Jai Narain Vyas University, Jodhpur-342 011, Rajasthan, India

E-mail: nitu84.jalore@gmail.com, dr.sushilsaraswat@gmail.com

Manuscript received online 20 March 2020, accepted 12 June 2020

Photoelectrochemical (PEC) water splitting is one of the promising process to generate hydrogen in an easier and sustainable way. Hydrogen production through PEC provides a green and sustainable source of energy and addresses the solar intermittency problem. While considerable efforts have been made over the past several decades but till date, there is no solar water splitting materials that simultaneously fulfills the high efficiency, long-term stability and low cost. In PEC, the semiconductor materials must exhibit sufficient voltage on irradiation to split water, long-term stability against corrosion in the aqueous electrolyte and the band edge potentials at the surfaces. The charge transfer from surface of the semiconductor to the electrolyte must be facile to minimize energy loss due to kinetic overpotential and selective for the oxygen and hydrogen evolution reaction. The photocatalysts such as TiO_2 , WO_3 , CuGaSe_2 , InGaN , Fe_2O_3 , Cu_2O etc. are the most promising semiconductor material due to its suitable band gap and valance band structure. But, the major concern in PEC water splitting is charge separation and transportation. Various strategies such as controlling the morphology, introducing defects, constructing a heterojunction and loading a co-catalyst are used raise the efficiency of PEC process.

Keywords: Hydrogen production, photocatalysts, PEC water splitting.

Introduction

Converting solar energy into hydrogen through the splitting of water by photoelectrochemical (PEC) is a desirable method to store renewable energy. Solar energy to hydrogen production is the most eco-friendly way that can convert solar energy directly to chemical energy with no CO_x emission¹. Semiconductor materials attracted much attention in the past decade owing to their electrical and photocatalytic properties for PEC water splitting process². Hydrogen fuel production through water-splitting provides a green and sustainable source of energy and addresses the solar intermittency problem.

Hydrogen is an energy carrier and can store tremendous amount of energy that can utilized in various sector viz. transportation, power generation and chemical industries. However, the most common method, till date for hydrogen production is from natural gas reforming process. To, overcome the dependency on fossil fuels for hydrogen, various researchers are trying to develop new technology via renewable energy sources. Photovoltaic coupled with electrolysis

(PV-E), photocatalysis (PC), and photoelectrochemical (PEC) water splitting are the popular way to produce hydrogen through solar water splitting process. Compare to PV-E and PC, PEC required less severe process conditions.

In PEC, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) occur at separate electrodes that can be easily separate and provide a viable method for commercial hydrogen production. PEC employs both n-type and p-type semiconductor material for photoelectrode synthesis. If n-type photoelectrode is used, electrons are collected in the photoanode and further transported to the counter electrode to drive the OER. While on the other hand, p-type semiconductor photocathode, HER happens at semiconductor/liquid interface by transmitting electrons toward the electrolyte.

Fujishima and Honda³ reported the phenomena of PEC water splitting to produce hydrogen via TiO_2 photocatalyst in 1972. Since then, numerous n-type (ZnO , TiO_2 , Fe_2O_3 , WO_3) and p-type (NiO , Cu_2O , ZnRh_2O_4) semiconductor material have been reported for PEC water splitting system. Semi-

conductor material such as SrTiO₃, WO₃, BaTiO₃ and SnO₂ are stable in aqueous electrolyte but revealed less photocatalytic activity due to large band gap structure. Whereas, GaAs, CdSe and CuO have small band semiconductor material but corrode rapidly when dipped in electrolyte solution. Similarly, intermediate band gap semiconductor material like Fe₂O₃ revealed low mobility of holes resulted less quantum efficiency. In order to overcome the deficiencies in all types of semiconductor materials various modification methods viz. doping, bilayered system and nano structured formation have been applied to obtain the desired properties.

Substantial efforts have been made over the past several decades to obtain desired properties in semiconductor material that simultaneously fulfills the high efficiency, long-term stability and low-cost requirements for PEC water splitting system⁴. The cause of concern is to design the effective photoelectrode that composed of costly photoabsorbers and low performance for solar to hydrogen conversion. Research is going on in search of new materials and the improvement of existing low cost photoelectrodes. Therefore, a new benchmark photocatalyst is needed for techno-economical process development.

Principle of PEC water splitting:

In a PEC cell, a substrate as a thin film deposited on the photocatalyst to synthesize a photoelectrode that convert solar energy into electrical energy by using semiconductor/electrolyte junction. Fig. 1 showed the process of photocatalytic water splitting achieved in a PEC used for conducting the reaction. The PEC method has principally involved 4 reaction steps:

- (1) Generation of e⁻/h⁺ pairs on photoanode by light irradiation,
- (2) Oxidation of water through e⁻/h⁺ pairs on the photoanode to form O₂ and H⁺,
- (3) Transfer of e⁻ to cathode via an external circuit, and
- (4) Reduction of H⁺ on the cathode surface to produce H₂.

PEC cells typically have the benefit of less severe process, as there is no need for additional film deposition or coating equipment. Further, PEC system is also containing of high surface area photoanode for photocatalytic reaction.

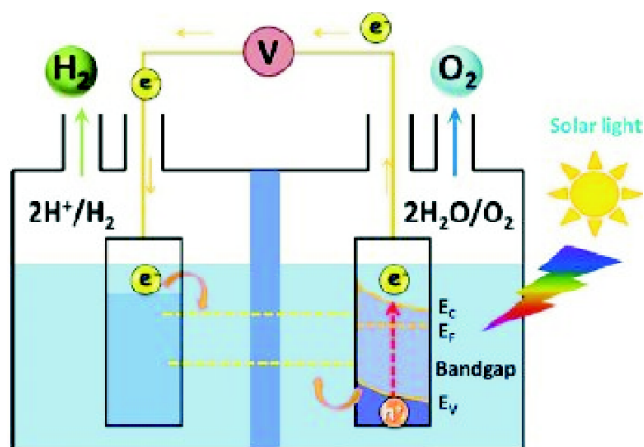


Fig. 1. A schematic diagram of PEC water splitting process⁵.

Apart from this, PEC system has to synthesize different photoanode material which can easily attain an internal bias. This bias promote separation of the e⁻/h⁺ (electron/hole pair) that enhance the photocatalytic activity for PEC process. Additionally, internal, external bias have also needed to further differentiation between the electrodes. Therefore, in a water-splitting system if open circuit potential is less than 1.23 V, an external bias may be required to increase the reduction potential of the electrodes, resulted e⁻ movement faster and complete the process.

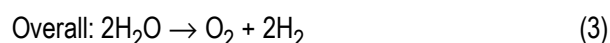
PEC conditions to decompose water in H₂ and O₂, is widely regarded as the dawn of artificial photosynthesis work as per the following reaction mentioned below⁶.



(HER: H₂ evolution reaction)



(OER: O₂ evolution reaction)



(light condition)

$$(\Delta E^\circ = -1.23 \text{ V})$$

$$(\Delta G^\circ = 237.18 \text{ kJ mol}^{-1})$$

The negative value of the standard electrodynamic potential means that the splitting of water is thermodynamically uphill, and the reaction requires additional energy. Relative to HER (which requires 2 electrons and 2 protons), OER is much more complex since 4 electrons and 4 protons are needed.

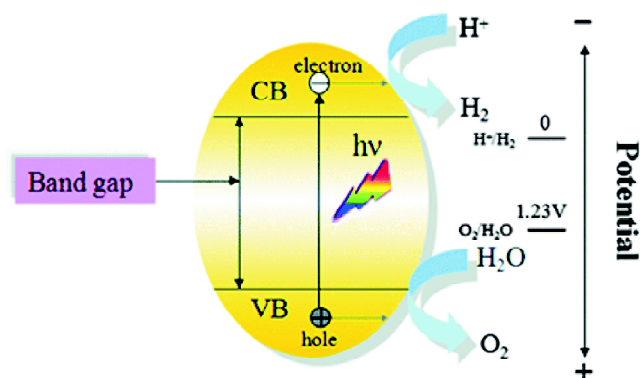


Fig. 2. Schematic description of band gap⁷.

Fundamentals to select a semiconductor material for PEC:

There are various considerations for selecting a semiconductor as a photoelectrode.

Potential requirement:

The water splitting reaction can only take place under standard conditions if the potential difference between the two half reactions exceeds 1.23 eV ($\Delta G^\circ = 237.1 \text{ kJ mol}^{-1}$) i.e. the semiconductor average bandgap should be greater than 1.23 eV. Other energy losses, especially the overpotential loss at the electrodes and the loss of ionic conductivity in the electrolyte must be taken into account. The actual potential requirement in a functional cell usually exceeds 1.6 V.

Suitable band structure:

For water reduction and oxidation reactions, respectively, proper conduction and valence band edge positions should be taken into account aside from a sufficient bandgap. Values obtained from traditional measurements based on the vacuum are often not reliable due to effects such as solvent adsorption. In order to calculate the relative positions of the band edges, experimental measurements are often needed

by instruments such as ultraviolet photoelectron spectroscopy (UPS), which reports on the ionizing energy (effectively the valence band maximum energy, eV).

High crystallization and surface area:

Semiconductors with high crystallinity for charging transport and high surface activity for the OER/HER reactions are required for efficient charging separation and processing.

Stability:

Stability is of paramount importance when applying splitting solar water. The engineered photoelectrode content, often in the extreme acidic or simple regime, should be stable in electrolytes of a certain pH range. The photoelectrodes may need effective protection to prolong their lifetime. A protective layer that is optically transparent and does not compete with the photoelectrode in absorbing light is required for this function.

Low cost:

One of the major critical factor in PEC is the economic cost of system. We need materials composed of earth abundant elements for large-scale implementation. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a suitable example for it.

Over the past years, many semiconductor materials, such as TiO_2 , GaAs, MoS_2 , ZnO, Al_2O_3 , CuO, etc., have been interestingly studied due to their stability, suitable band gap and activity for hydrogen evolution rate (HER) under solar irradiation. The Table 1 depicted the HER for recently used photocatalysts/co-catalysts for PEC water splitting process.

Some photocatalysts are:

Cu_2O :

Cu_2O is one of the well known, p-type semiconductors that has a direct bandgap of 2 eV. It can absorb visible light and has a theoretical 14.7 mA cm^{-2} photocurrent at 1.5 AM irradiation⁸. Owing to its favorable properties, several re-

Table 1. Various hydrogen producing photocatalysts via PEC water splitting

Photocatalysts	Co-catalysts	Light source	HER ($\mu\text{mol/h/g}_{\text{catalyst}}$)	Ref.
$\text{Cu}_2\text{O}/\text{TiO}_2$	MoS_{2+x}	AM 1.5 G	2700	10
$\text{BiVO}_4/\text{Cu}_2\text{O}$	RuO_x	100 mW/cm^2	–	11
TiO_2/Au	–	300 W, Xe	1019	12
MoS_2/CdS	–	300 W, Xe	49800	13
$\text{TiO}_2/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$	Au	AM 1.5 G	–	14
CeO_2	Pt	200 W, W	203	15

search groups have intensively studied Cu_2O as a photocatalyst for hydrogen evolution. In order to obtain effective Cu_2O thin films, specific synthetic paths, electrodeposition, sol-gel and ionic layer deposition method etc. are also investigated.

CuO:

Transition metal oxide semiconductor material, CuO is a p-type material with a narrow bandgap of around 1.2–1.3 eV. CuO is used to create photoelectrodes of heterojunction with other semiconductor materials and are able generate maximum photocurrent of 35 mA cm^{-2} . Compare to Cu_2O , CuO depicted higher photocatalytic activity for PEC process. Cu_2O and CuO possess electrochemical properties that are effective to convert solar energy to electrical energy. CuO also showed high absorption in the visible region which makes it most promising material for photocatalyst.

BiVO_4 :

BiVO_4 is one of the propitious materials for photocatalyst synthesis for PEC owing to its small band gap (2.4 eV) and high aqueous stability. Due to small band, even visible light can easily excite an e^- from valence band to conduction band resulted e^-/h^+ generation. However, the study suggested that the behavior of photo-induced charge is primarily dependent on BiVO_4 crystalline phases⁹. On the other hand, BiVO_4 suffers from poor carrier mobility and extreme recombination of holes in the bulk of the BiVO_4 surface.

Ta_3N_5 :

Ta_3N_5 has a small bandgap (2.1 eV), and this dark red compound can absorb visible light up to 600 nm and capture more than 45% of total energy from the solar spectrum. Like other semiconductor materials, its conductive banding and valence banding straddle the HER and OER reaction potential. Theoretically, it can reach a maximum photo conversion efficiency of the theoretical solar spectrum of 15.9%. Nonetheless, photoanode based on Ta_3N_5 suffers from instability, which is caused by its holes from oxidation. Once the PEC process starts, tantalum oxide rapidly appears on the surface along with the release of N_2 .

Solar-to-hydrogen conversion efficiency (STH efficiencies):

Efficiency of solar-to-hydrogen (STH) is a measure of the conversion of the generated H_2 from incident solar energy to

the chemical energy. If the photogenerated carriers are involved in the division of energy, and the products are stoichiometric ($\text{H}_2:\text{O}_2 = 2:1$), then

STH efficiencies under one-sun irradiation can be represented as:

$$\text{STH} = \frac{((\text{mmol H}_2 \cdot \text{s}^{-1}) \times (273 \text{ kJ mol}^{-1}))}{(P (\text{mW} \cdot \text{cm}^{-2}) \times \text{Area} (\text{cm}^2))} \quad (4)$$

where, $\text{mmol H}_2/\text{s}$ is the rate of H_2 production and the Gibbs free energy of H_2 is 237 kJ mol^{-1} . H_2 production rate can be found by mass spectrometry or gas chromatography. If we know the current, voltage, and the faradaic efficiency (η_F), eq. (4) may be modified as:

$$\text{STH} = \frac{(|J_{\text{SC}} (\text{mA} \cdot \text{cm}^{-2})| \times 1.23 \text{ V} \times (\eta_F))}{(P (\text{mW} \cdot \text{cm}^{-2}))} \quad (5)$$

The faradaic efficiency for HER and OER is supposed to be 100%. Then, eq. (5) could be represented as:

$$\eta_{\text{STH}} = \frac{1.23 \text{ V} \times J_{\text{SC}}}{P_{\text{IN}}} \quad (6)$$

where J_{SC} is a short circuit current density and P_{IN} is the overall photon energy flux input into the cell (i.e. for simulated solar light AM 1.5 G, 100 mW cm^{-2}). The STH efficiencies can be achieved in a configuration with two electrodes (determination from a test with three electrodes also leads to miscalculations).

Conclusion

There are some difficulties such as the slow surface dynamics, low durability photocorrosion, weak absorption in the visible spectrum, etc. in the PEC water splitting process to produce hydrogen. The extensive research is going on to fulfill the gap. In this paper, the basic concept of PEC, mechanism and the current status of the photoanodes and electrocatalysts are describe in details. Apart from it, the suitable material used for electrode and properties required in the PEC process were also explored.

References

1. L. Pan, Y. Liu, L. Yao, D. Ren, K. Sivula, M. Grätzel and A. Hagfeldt, *Nat. Commun.*, 2020, **11**, 1.
2. A. Tabish, A. M. Varghese, M. A. Wahab and G. N. Karanikolos, *Catalysts*, 2020, **10**, 95 (doi:10.3390/catal10010095).

Parihar *et al.*: Photoelectrochemical water splitting: An ideal technique for pure hydrogen production

3. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37.
4. P. E. A. Salomão, L. R. de S. Barbosa, T. S. Andrade, E. J. da C. Ferreira and M. C. Pereira, *Int. J. Hydrogen Energ.*, 2019, **54**, 28603.
5. M. D. Bhatt and J. S. Lee. *J. Mater. Chem. A*, 2015, **3**, 10632.
6. M. Grätzel, *Acc. Chem. Res.*, 1981, **14**, 376.
7. L. Yang, H. Zhou, T. Fan and D. Zhang, *Physical Chemistry Chemical Physics*, 2020, (doi: 10.1039/C4CP00246F).
8. A. Paracchino, V. Laporte, K. Sivula, M. Gratzel and E. Thimsen, *Nat. Mater.*, 2011, **10**, 456.
9. M. Misra and K. S. Raja, "On Solar Hydrogen and Nanotechnology", 1st ed., Lionel Vayessieres, John Wiley & Sons, Inc. Singapore, 2010, Chap. 10, pp. 267-288.
10. C. G. Morales-Guio, S. D. Tilley, H. Vrubel, M. Grätzel and X. Hu, *Nat. Commun.*, 2014, **5**.
11. P. Borno, F. F. Abdi, S. D. Tilley, B. Dam, R. Van-De Krol and M. Graetzel, *J. Phys. Chem. C*, 2014, **118**, 16959.
12. T. Liu, W. Chen, T. Huang, G. Duan, X. Yang and X. Liu, *J. Mater. Sci.*, 2016, **51**, 6987.
13. X.-L. Yin, L.-L. Li, W.-J. Jiang, Y. Zhang, X. Zhang and L.-J. Wan, *ACS Appl. Mater. Interfaces*, 2016, **8**, 15258.
14. P. Peerakiatkhajohn, T. Butburee, J.-H. Yun, H. Chen, R. M. Richards and L. Wang, *J. Mater. Chem. A*, 2015, **3**, 20127.
15. N. R. Manwar, A. A. Chilkalwar, K. K. Nanda, Y. S. 141Chaudhary, J. Subrt and S. S. Rayalu, *ACS Sustain. Chem. Eng.*, 2016, 2323.