

Review Paper

Hydrogen Production by Photoelectrochemical Water Splitting

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Abstract The basic principle and concept for hydrogen production via water-splitting process are introduced. In particular, recent research activities and their progress in the photoelectrochemical water-splitting process are investigated. The material perspectives of semiconducting photocatalysts are considered from metal oxides, including titanium oxides, to carbon compounds and perovskites. Various structural configurations, from conventional photoanodes with metal cathodes to tandem and nanostructures, are also studied. The pros and cons of each are described in terms of light absorption, charge separation/photoexcited electron-hole pair recombinations and further solar-to-hydrogen efficiency. In this research, we attempt to provide a broad view of up-to-date research and development as well as, possibly, future directions in the photoelectrochemical water-splitting field.

Keywords: Photoelectrochemistry, Water-splitting, Hydrogen production, Photocatalyst, Solar-to-hydrogen efficiency

I. Introduction

Hydrogen, the most abundant element in the Earth and Cosmos, and has the highest energy per mass. The hydrogen has recently proven to be a viable energy source in the fields of transportation, cooling and heating, while accompanying with an advance in compression and storage technologies [1]. Recently, hydrogen-based airport ground support equipment truck at in Tennessee was deployed and the first station selling hydrogen to public was built in California in US [2].

At this moment, the production of hydrogen is mainly based on natural gas reforming, which is the mature process with existing natural gas pipeline infrastructure. The methane in natural gas is thermally processed to produce hydrogen with a steam-methane reformation and oxidation. It means that the production is not renewable and generates green-house gas as a byproduct. But if one notices the fact that hydrogen has water as an oxidation product and ‘hydrogen’ indeed means the water-carrier in the Greek, there must be a genuine way to split water to take off hydrogen.

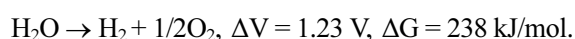
Back in to 1766, Henry Cavendish found the flammable nature of the hydrogen gas which produces water when burned [3]. Jules Verne in his book published at 1874, father of science fiction, proposed the idea that “*water will one day be employed as a fuel, that hydrogen and oxygen that constitute it, used singly or together, will furnish an*

inexhaustible source of heat and light, of an intensity of which coal is not capable. Someday the coal rooms of steamers and the tenders of locomotives will, instead of coal, be stored with these two condensed gases ...” [4]. Surprisingly, French novelist Verne foretold that hydrogen be introduced from water as a renewable energy source to replace the fossil fuel about 150 years ago.

In this article, the current status of water-splitting technology for production of hydrogen, including the recent scientific breakthrough, will be studied. Especially, we will mainly focus on the photoelectrochemical (PEC) water-splitting process, which is the chemical reaction-based methods to produce hydrogen from water using sunlight. Its counterpart can be the thermochemical water-splitting process requiring a high temperature to dissociate water. The PEC water-splitting has a several advantages over thermochemical water-splitting: relatively higher solar-to-hydrogen efficiency, capability of separating hydrogen and oxygen streams, and flexible reactor size enabling for small scale applications [5]. Also note that the thermochemical approach is simpler in terms of the process steps but the requirement for extremely high temperature makes it less cost-competitive and less favorable [6].

II. Water-splitting Process

In the water-splitting reaction, water is separated into oxygen and hydrogen, that energy is generated by a chemical reaction rather than combustion as given,



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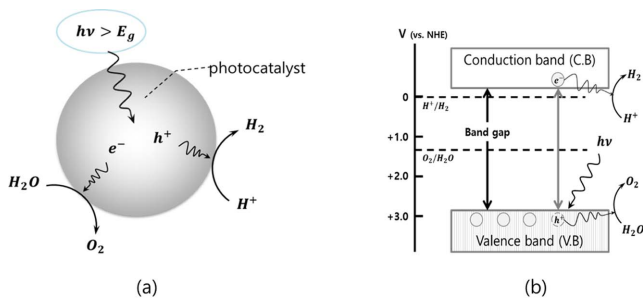


Figure 1. (a) PEC water-splitting process by photocatalyst, (b) Energy band gap and alignment with respect to Oxygen/hydrogen evolution.

There are two major schemes to produce hydrogen in cost-competitive and environmentally friendly ways; thermochemical and photoelectrochemical (PEC) water-splittings.

Thermochemical water-splitting uses a high temperature heating, 500°C- 2000°C, to enable a chain of chemical reaction cycles with [7]. During the production cycle, chemical reagents, like sulfur-iodine or cerium-oxide or copper chloride, are introduced. But the cycle is a closed loop that only produces hydrogen and oxygen. To achieve a high temperature, the concentrated solar power and nuclear reactor are usually used. This solar and nuclear energy-driven thermochemical process produce the hydrogen without green-house gas generation. However, a several issues need to be resolved; an improvement of efficiency, durability and cost.

In PEC water-splitting, the catalyst, usually semiconductor, is used for the conversion of light energy to electrical energy. Here, the light energy $h\nu$ must be bigger than the band gap energy of the catalyst to be absorbed. The PEC catalyst is immersed in a water or water-based electrolyte, where dissociation of water into hydrogen and oxygen are generated electrically [Fig 1(a)]. At this time, energy band level must be aligned accordingly [Fig 1(b)]. Basically the potential of the conduction band (CB) minimum of the catalyst should be more negative than $\text{H}_2\text{O}/\text{H}_2$ level and that of the valence band (VB) maximum be more positive than $\text{O}_2/\text{H}_2\text{O}$

PEC water-splitting has a great potential since it is capable to have a high energy conversion efficiency, benefiting from the recent development of photovoltaic (PV) technologies. So far, the record of solar-to-hydrogen energy conversion efficiency is over 30% in tandem PEC/PV system [8].

III. Photoelectrochemical (PEC) Water-splitting : Material Perspectives

The mechanism includes the absorption of light, charge separations, and dissociation of the water. For the widely studied TiO_2 catalyst case, 1) the light, which energy is bigger than the bandgap of TiO_2 , is absorbed and generate

electron-hole pairs, 2) the photoexcited electrons and holes are separated and migrate to the surface of TiO_2 , 3) adsorbed water is oxidized by holes to produce O_2 and H^+ , 4) the electrons moves to an external circuit, usually Pt, and reduce water to produce H_2 . [Fig 2(a)]

To achieve the highly efficient PEC water-splitting, the semiconductor catalyst needs to be stable (not corrosive) in electrolyte solutions, cost-competitive, and a good crystallinity with a lower defect concentration. Note that defects act as the electron-hole recombination sites and thus reduce the energy conversion efficiency. In this regard, various kinds of materials were introduced and tested.

Metal oxides

Since metal oxide materials are comparably less corrosive in electrochemical solvent, the stable PEC performance with them is expected. Figure 3 presents the band gap energies and their alignment of the metal oxides with respect to the normal hydrogen electrode (NHE) level. As described above, the potential of the CB edge of the catalyst should be more negative than $\text{H}_2\text{O}/\text{H}_2$ level and that of the VB edge be more positive than $\text{O}_2/\text{H}_2\text{O}$ to have both oxygen and hydrogen production, which is fulfilled by a few oxides; TiO_2 , ZnO , TaNO and so on.

But some drawback exists: the band gap energy of TiO_2 and ZnO is large, ≥ 3.1 eV, so that visible light absorption is not efficient, and the photo-corrosion in ZnO by photoexcited holes was reported [9]. In comparison, WO_3 and Fe_2O_3 have been extensively studied due to an ideal band gap energy, 2.6 and 2.1 eV, although CB minimum is less negative than $\text{H}_2\text{O}/\text{H}_2$ [10,11]. They can be easily synthesized and be resilient to photo-corrosion. With an oxygen evolution catalyst, the effective CB can be readjusted to enable for the water reduction [12,13].

Cu_2O , as p-type semiconductor, has an appropriate band gap energy of 2.1 eV as for photocathode but its stability in electrolyte solutions has been an issue. But the improved electrochemical stability with the controlled surface facets was recently reported [14,15]. CuO has also shown a promising property as sensitizer of a composite catalyst [16].

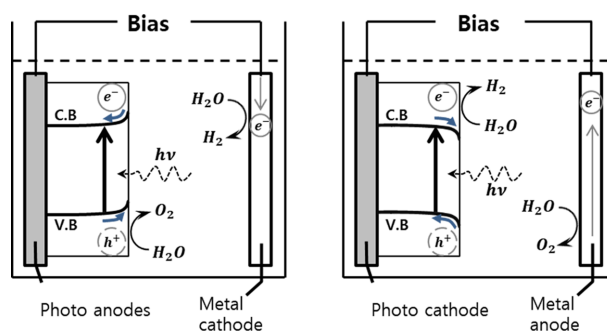


Figure 2. (a) PEC water-splitting process with photoanode with metal cathode, (b) PEC water-splitting with photocathode with metal anode.

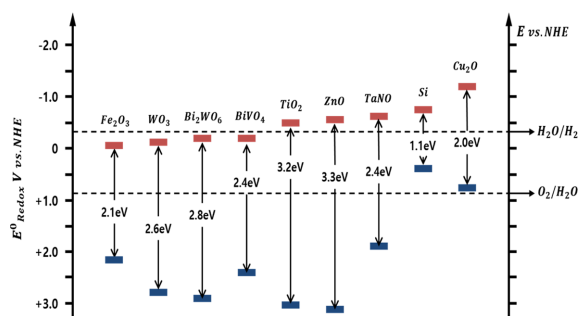


Figure 3. Band gap energy and alignment of metal oxides with respect to NHE level at pH 7.

TiO₂ and the related catalyst

PEC water-splitting with TiO₂ was reported in 1972, where TiO₂ was used for the photo anode while Pt was used for metal cathode [17]. TiO₂ has an obvious merit as catalyst because of its favorable energy band alignment and electrochemical stability. It is also cheap and environmentally friendly. However, the comparably larger energy band gap (3.1~3.2 eV) and rapid recombination of photoexcited electron-hole pairs are the problems to be resolved [18].

Many efforts have been made in this regard. Use of metallic co-catalyst has shown an apparent improvement in reducing the recombination rate of photoexcited electrons-holes. Wu *et al.* confirmed that Pt, Ni, and Pd coated TiO₂ has significantly escalated the production of hydrogen [19]. Besides, TiO₂ with carbon nanotubes and graphene also showed the enhanced light absorption and the lowered recombination rate of photoexcited electrons-holes [20, 21]. The non-metallic doping was also considered in TiO₂ systems. Carbon, nitrogen, and sulfur have been tested to adjust the band gap energy and alignment but found to degrade the structural quality, often resulting in the rapid recombinations [22-24]. Among them, the nitrogen doped TiO₂ have gotten a special attention [25]. Very recently, the improved charge injection efficiency and stability as well as enhanced solar-to-hydrogen conversion efficiency was reported with the progress of structural qualities [26,27].

Carbon-based catalyst

The carbon-based catalysts have their own merits in the sense of energy band structure and chemical stability. The structural modification is also formidable. In particular, g-C₃N₄ has an ideal band alignment but still be with the limit of low photoactivity and high recombination rate [28]. Nitrogen, sulfur, phosphorus doped graphene and reduced graphene oxides have shown the bifunctional catalytic behaviors; both for hydrogen and oxygen evolution, which leads to the enhanced PEC activities [29-32].

Perovskite catalyst

Oxide-based perovskite materials with a configuration of ABO₃ (A: Alkali or rare earth element, B: transition metal)

have been reported as potential materials as PEC water-splitting [33]. Among them, BNiO₃, BiOCl and Bi₄NbO₈Cl have shown adequate PEC characteristics [34,35]. CH₃NH₃PbI₃ with perovskite tandem solar cell with a NiFe layered double hydroxide electrode, the solar-to-hydrogen efficiency of 12.3% was observed [36].

IV. Photoelectrochemical (PEC) Water-splitting : Structural Perspectives

Basic structure: Single PEC cell

For n-type semiconducting catalyst (e.g., photoanode), electrons and holes are generated when a photoanode absorbs light. The photoexcited electrons are transferred to a metal cathode through the outer circuit and then reduce water to hydrogen, while the holes move into the photoanode surface and then oxidize water to oxygen Fig 2(a). In many cases, an external bias is applied between the electrodes for an efficient charge separation. In the case of p-type semiconductor (e.g., photo cathode), water is reduced on the photocathode surface and is oxidized on the counter electrode Fig 2(b). However, there are few photo cathode materials that are stable under hydrogen production.

PEC/PV Tandem Structure

Photovoltaic (PV) cell can be added to provide the bias voltage for the efficient water-splitting. In addition, superposed PEC/ PV materials having a different band gap allow the enhanced absorption of light. At this time, the PV cell should be chosen dependent on the actual current and voltage needs of the PEC to secure the efficient operations [37]. The highest solar-to-hydrogen (STH) energy conversion efficiency is observed in tandem PEC/PV system [8]. In this work, the triple-junction PV cell with III-V materials with two series-connected polymer electrolyte membrane was used to achieve very high STH efficiency.

Nanostructural PEC

In a nanostructure, photoexcited electron-hole can move to the catalyst surface rapidly and react with water. Thus the improved charge separation, or lower recombination rate, is expected. Besides, the quantum size effects lead to the modification of the band structure, allowing tuning of the energy band alignment. Recently, the improved photoactivities and STH efficiencies were revealed in nanostructure-utilized PEC cells with a different materials and configurations [38-41]. Various hybrid, or hetero, nanocomposites of p-n junctions or cocatalyst were also introduced to achieve the enhanced light absorption and charge transfer properties [42-44].

V. Summary

The recent research progress in the photoelectrochemical

water-splitting process were studied. The material perspectives of semiconducting photocatalysts as well as structural configurations of the PEC cells in relation to the light absorption, electron-hole recombinations and STH efficiency was reviewed.

Acknowledgements

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