

Photoelectrochemical Hydrogen Production and Its Storage: From Laboratory to Industry

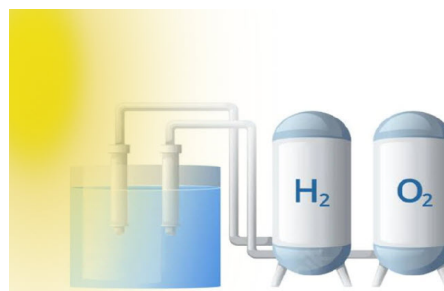
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Abstract: Due to the increase in fuel consumption in the world and the creation of a lot of pollution by fossil fuels, hydrogen has received a lot of attention as a clean fuel, and extensive studies have been conducted on it from small-scale to large-scale production, and also studies have been done on the storage of this gas. Therefore, in this article, various methods of hydrogen production have been investigated on a laboratory and industrial scale, and references have been made to hydrogen storage.



Keywords: Hydrogen production, Hydrogen storage, Industry

1. INTRODUCTION

Due to increasing global energy demand and the non-renewability of fossil fuels and their depleting resources and their incompatibility with the environment, we have to look for renewable, sustainable, and environmentally friendly alternative fuels.¹⁻³

Among all the fuels used in the world, according to Figure 1, solar energy produces the most power, and this energy is fully available, clean, and renewable.⁴ To convert solar energy to chemical energy, one of the most ideal methods is utilizing two abundant terrestrial sources of water and the sun, which can produce hydrogen gas by dividing water into hydrogen and oxygen by sunlight and use it as fuel and other applications.⁵⁻⁷

The produced hydrogen can be used in industrial processes, electricity management, heat, ammonium nitrate production in agriculture, and the production of lower-carbon fuels for air and sea transport (Figure 2).⁸ Currently, about 40-45% of global hydrogen production is from natural gas, about 30% from petroleum materials, about 18% from coal, and 4% through water electrolysis. The three first ways to produce hydrogen are through fossil fuels and cause air pollution. The production of hydrogen gas through water electrolysis also requires electrical energy, which is usually supplied by fossil fuels. Thus, we must look for a way to produce hydrogen that does not cause pollution or harm the environment.^{9,10} Hydrogen generation from low-cost renewables at \$25/MWh with a capacity factor of 50% yields a cost of

underground will cost an additional \$0.30/kg, making the hydrogen \$2/kg. The cost of using this hydrogen to produce electricity ranges from \$100 to \$200/MWh. The cost is \$100/MWh under ideal circumstances (for example, a combined cycle gas turbine (CCGT) at 60% utilization), while simple-cycle turbines at 25% utilization would provide power for \$200/MWh. There are currently a number of power-to-gas systems, which use electrolysis to convert renewable energy sources into gaseous energy carriers, but many are still relatively small, less than 1 MW. Nonetheless, a number of large-scale "renewable hydrogen" projects have been suggested. According to the report, electrolysis costs have decreased by around 60% since 2010 (from between \$10/kg and \$15/kg hydrogen to as low as \$4/kg). By 2030, costs can have decreased another 60%, according to one scenario provided that uses offshore wind-based electrolysis in Germany.¹¹ However, photoelectrochemical hydrogen production, in addition to not using fossil fuel, can reduce the costs even below these values.

Hydrogen production by solar water splitting is done through 3 main categories: photo-biological water splitting, thermochemical water splitting, and photo (electro) chemical water splitting.^{5,12-15} Thermochemical water splitting uses the high temperature of the sun to drive a series of chemical reactions that involve solid reactors to produce hydrogen and oxygen from water (200°C-500°C).^{12,15} The photo-biological water splitting uses microorganisms (cyanobacteria or algae) for splitting water into hydrogen and oxygen. The viability of

microorganisms in the presence of sunlight is the main problem of this method.^{13,14}

The photo (electro) chemical process is performed at ambient temperature with stable photocatalytic semiconductors to split water molecules into hydrogen and oxygen. This method is one of the most promising methods for the production of stable hydrogen.¹⁶⁻²⁰ This Review summarizes the photoelectrochemical hydrogen production methods and photocatalytic materials used in this way from the laboratory to the industry. In the end, this review briefly describes the storage of hydrogen gas as the most significant challenge to practical applications of hydrogen.

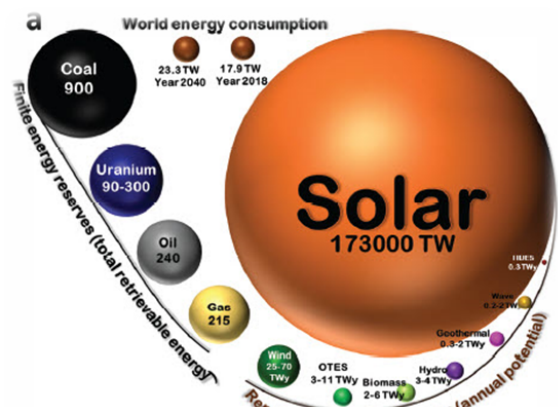


Figure 1. Comparison of solar energy with other energy resources. Reproduced from ref.⁴ with permission from the IEA/SHC Solar Update, copyright 2009.

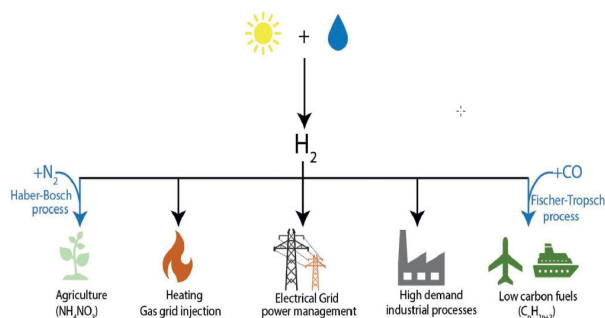


Figure 2. Potential uses of hydrogen produced by solar-powered water splitting, include agriculture (when reacts with N_2 for producing NH_3), heating, power management (as an energy storage medium), industrial processes (such as steel production), and renewable production of fuels for freight (when reacts with CO to produce hydrocarbons). Reproduced from ref.⁸

2. PHOTOELECTROCHEMICAL METHODS OF SOLAR HYDROGEN PRODUCTION

As mentioned in Figure 3, the photoelectrochemical method of hydrogen production can be divided into three main categories: electrolyzer with photovoltaics, single photoelectrochemical systems, and water-dispersed photocatalytic systems.²¹ The single photoelectrochemical

system can be divided into three categories: single photoelectrodes, photoelectrochemical/photovoltaic, and photoanode/photocathode. The photoelectrochemical/photovoltaic system can also be divided into three categories: photoelectrochemical/perovskite solar cells (PEC/PSCs) photoelectrochemical/dye-sensitized solar cells (PEC/DSSCs), and photoelectrochemical/photovoltaic (PEC/PV).^{22,23}

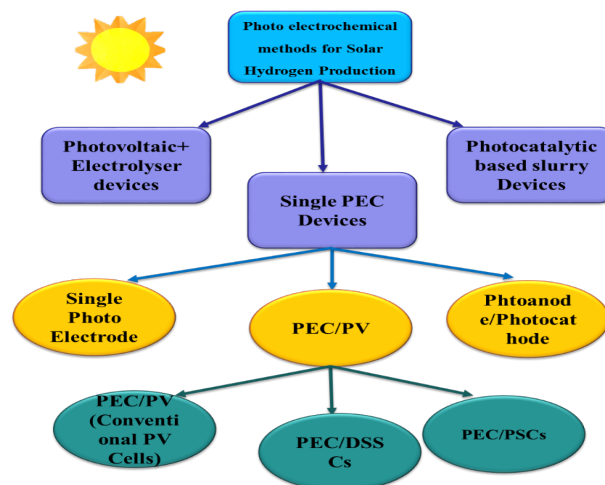


Figure 3. Solar hydrogen production methods using a photoelectrochemical approach. Reproduced from ref.²¹

Figure 4a shows a photochemical system in which semiconductor particles are dispersed and hydrogen gas and oxygen are produced simultaneously. In this method, it is difficult to separate the hydrogen gas, and it may also be an explosive and dangerous process, these two gases are combined.¹

In Figure 4b, the photoelectrochemical system shows a combination of a photoanode and a photocathode. Figure 4c is a photovoltaic electrochemical system that provides the potential needed to electrolyze water from photovoltaic cells.¹

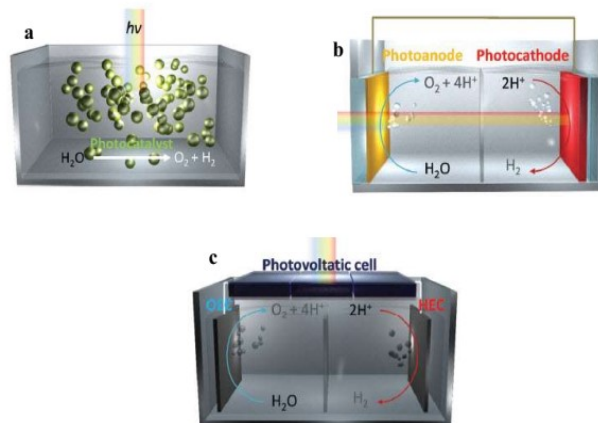


Figure 4. Various photo-driven water splitting systems; (a) PC, (b) PEC and (c) PV-EC systems. Reproduced from ref.¹

For the first time in 1972, Fujishima and Honda²⁴ reported the photoelectrochemical water splitting with a TiO₂ semiconductor under UV radiation, and since then, much attention has been paid to solar hydrogen production through this process.^{25,26}

The basic processes of photoelectrochemical water splitting have been summarized in the Figure 5a, where first the incident light is absorbed by the semiconductor and produces charge carriers, then the charge carriers are separated and finally, the charges are transferred to the surface of the Photocatalyst and the oxidation of water is performed.^{5,27} To perform photoelectrochemical processes, an anode (photoanode or metal anode), cathode (photocathode or metal cathode usually made of platinum), and electrolyte are required. depending on the type of semiconductors, the type of electrolyte, and its pH is variable (Figure 5b).^{5,28}

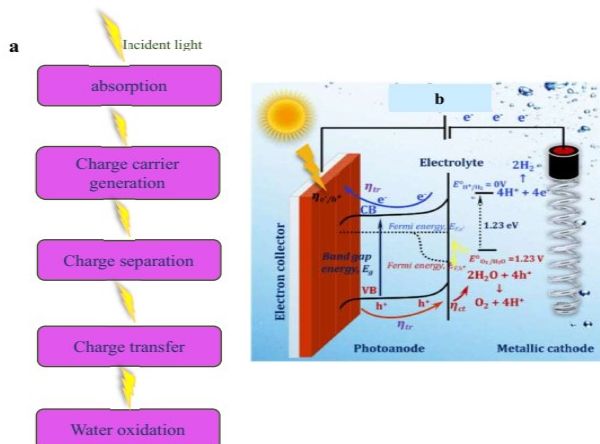


Figure 5. a) The basic processes of photoelectrochemical water splitting involved in water oxidation on photoanode. Reproduced with permission^{5,27} Copyright 2017, PCCP Owner Societies. b) Schematic of the photoelectrochemical water splitting mechanism, Reproduced with permission^{5,28}

To perform photoelectrochemical processes, semiconductors must have features including suitable bandgap, high stability, earth abundance, low cost, non-toxicity, high electrical conductivity, and long hole diffusion length.^{5,29} Finding a single semiconductor to have all these properties together is not possible. Among the materials that have been studied as semiconductors, transition metal oxides are promising materials for this process, among which TiO₂, Fe₂O₃, WO₃, and BiVO₄ have suitable properties to carry out these processes. They are n-type semiconductors that are commonly used as photoanodes. Cu₂O is also a promising material as a p-type semiconductor and can be used as a photocathode.

TiO₂

TiO₂ has been extensively studied as a photocatalyst in the photoelectrochemical water splitting and is currently the only photocatalyst that has expressed large-scale

commercial application with application in self-cleaning windows, tiles and air purifying paints. This material can be synthesized using relatively inexpensive methods and grown as nanostructures.^{8,30-32} However, the application of TiO₂ in the system of photoelectrochemical water splitting is very restricted due to its large bandgap and maximum theoretical efficiency of 1.38%.

Fe₂O₃

The second most popular material studied for water-splitting applications is Fe₂O₃. This terrestrial abundance and low-cost material is very stable in alkaline conditions and has a narrow gap of 2.2 and is, therefore, able to absorb visible sunlight and has a maximum theoretical photocurrent density of relatively high about 12.6%. However, it has many inherent limitations including low photovoltaics, very short hole diffusion lengths, and low electrical conductivity, which limit its photoelectrochemical water-splitting performance.^{8,33-37}

WO₃

WO₃ is another commonly studied material whose applications as a photoanode in photoelectrochemical water splitting have been studied. It has a relatively narrow gap of 2.5-2.8 with a maximum theoretical photocurrent density of 5.9. It is very stable when the applied potential is kept positive in acidic conditions and has a deep and highly oxidizing capacity band to guide the water oxidation reaction. It conducts the reaction with much faster kinetics, and WO₃ has a longer hole diffusion length than many other commonly studied oxides, but the early-onset potential is found in this material. Electron extraction of this material is slow, the faradic efficiency is very low and its performance in terms of photocurrent density is average of TiO₂ and Fe₂O₃.³⁸⁻⁴²

BiVO₄

BiVO₄ is one of the most promising emerging materials for use as a photoanode in photoelectrochemical water-splitting devices. BiVO₄ has a bandgap of 2.4 and its maximum theoretical photocurrent density is 7.4. It is generally found that the monoclinic scheelite structure is the most active phase and is relatively stable at positive potentials at neutral pHs. Although BiVO₄ is sensitive to photocorrosion and this process is kinetically slow, it can be inhibited by using a vanadium-rich electrolyte (which prevents the dissolution of vanadium ions from BiVO₄ in the electrolyte) or suitable co-catalysts. BiVO₄ also has inherently poor electrical conductivity, a weak charge transfer, and therefore high charge recombination. It has been overcome these issues by some modification methods.⁴³⁻⁴⁶

Cu₂O

Cu₂O is a p-type semiconductor and is perhaps the most

widely studied material for applications as a photocathode in photoelectrochemical water splitting. Although Cu_2O has almost ideal band positions for conducting water splitting and a narrow band 2eV with a maximum photocurrent density of 14.7 , it is highly sensitive to light corrosion. This is not only because Cu_2O is unstable but also because the bond positions in Cu_2O have enough energy to reduce the material to copper and oxidize it to CuO . Given these inherent stability issues, the protection of the Cu_2O surface is a critical requirement when developing this material for use in photoelectrochemical water splitting. This typically requires the use of atomic layer deposition techniques that can grow coatings on substrates with thickness control at the atomic scale. However, compared to other methods, this technique is expensive, slow, and has been limited by industry to date.⁴⁷⁻⁵⁰

3. COMMON STRATEGIES TO INCREASE THE PHOTOELECTROCHEMICAL PERFORMANCE OF PHOTOELECTRODES

As mentioned, a semiconductor that has all the appropriate properties for the photoelectrochemical process of water splitting has not been reported so far. To improve the performance of these semiconductors, a series of strategies including controlling the morphology of photoelectrodes, doping, forming heterojunction, and surface modifications are applied.⁵

Doping

Doping is one of the most likely photocatalytic semiconductor modification methods that can reduce the bandgap, increase the electrical conductivity, as well as change the shape, size, and crystallinity of the semiconductor. Dopants can be metallic, non-metallic, or multiple dopants.^{51,52}

Heterojunction formation

The formation of a heterojunction by coupling two different semiconductors with a suitable bandgap creates an internal electric field on the surface that directs electrons and holes in opposite directions and improves charge separation. One of the heterojunctions that have worked well so far is the $\text{BiVO}_4/\text{WO}_3$ heterojunction, where the charge separation is faster and the charge recombination is reduced. The mechanism of the heterojunction is shown in Figure 6.^{53,54}

Surface modifications

The potential to start photoanodes, for example, hematite photoanodes, is mainly surface-dependent and can be adjusted by changing the surface potential. Various strategies have been adopted to reduce the starting voltage

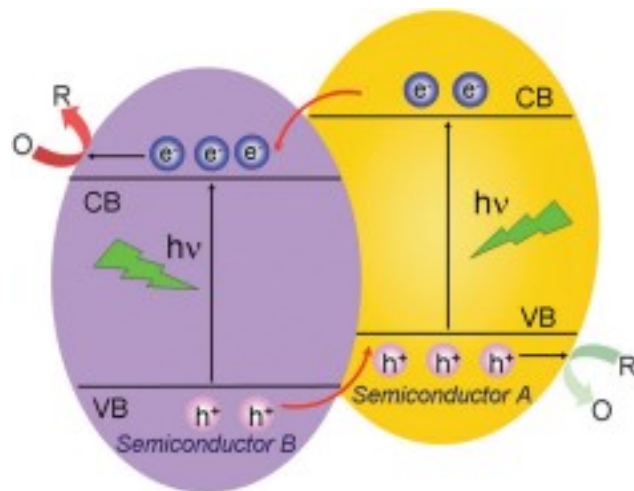


Figure 6. Schematic diagram showing the energy band structure and electron-hole pair separation in the non-p-n heterojunction. Reproduced with permission.⁵⁵

by accelerating the oxidation of water, preventing recombination on the photovoltaic surface as well as the electrode-electrolyte interface, enhancing the oxidizing power of the holes, and managing the surface bond potential.^{5,56,57} These surface modifications can include a coating of the multilayer oxide surface, surface modification by carbon-based materials without metal, inorganic catalysts for oxygen evolution, and molecular co-catalysts for oxygen evolution.⁵

Multilayer Oxide Surface Coating. Fe_2O_3 Photoanode Coating Improves the photoelectrochemical performance. For example, Fe_2O_3 photoelectrode coating by a layer of TiO_2 utilizing the atomic layer deposition method has a great effect on charge separation and also enhances charge transfer throughout the surface solid-liquid interface.⁵⁸

Surface modification with carbon-based materials. Recently, non-metallic carbon-based materials such as quantum dots of carbon, graphene, reduced graphene oxide, and carbon nitride have attracted much attention to change the surface of semiconductors to improve the photoelectrochemical water splitting performance. For example, their high conductivity, light absorption potential, cost-effectiveness, high stability, and surface efficiency make them good conductors of various photoelectrodes as a catalyst as well as surface coating.⁵⁹⁻⁶¹

Inorganic oxygen evolution co-catalysts. One of the major challenges for high photoelectrochemical water splitting performance, is the efficient transfer of surface charge to surface oxidation to prevent charge recombination or energy loss. The most effective way to increase surface charge transfer is to load an oxygen evolution catalyst to enhance the kinetics of the water

oxidation reaction at the interface of the semiconductor and the electrolyte. Popular oxygen evolution catalysts include cobalt phosphate (Co-Pi), IrO_2 , cobalt ions, NiOOH , nickel borate, and more.^{36,62-64}

Oxygen evolution Molecular co-catalysts. Opaque inorganic catalysts at high concentrations reduce light absorption, while too low concentrations do not fully affect the activity of oxygen evolution catalysts for photoelectrodes. Molecular catalysts for the evolution of oxygen, which are chemically bonded to the photoelectrode's surface, offer no resistance to light and have high electrolytic permeability.^{65,66} For example, molecular structures based on ruthenium, iridium, and cobalt are good catalysts for oxygen evolution, two examples are shown in Figure 7.⁶⁷

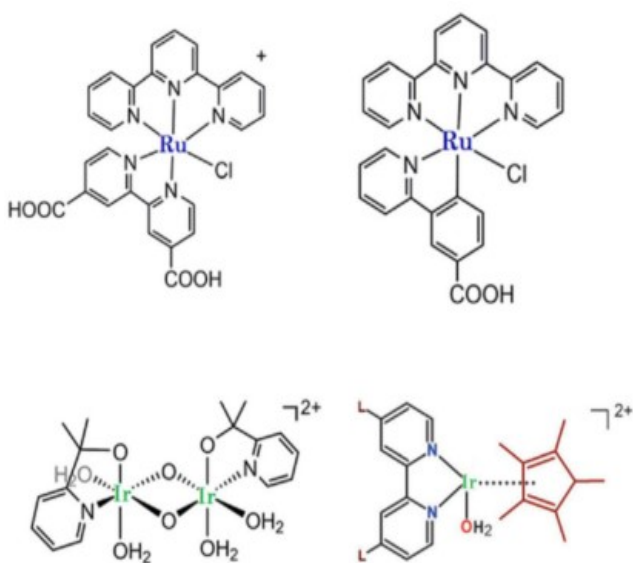


Figure 7. Molecular structures based on organic ligands coordinated to Ru and Ir metals. Reproduced from ref.⁶⁷

4. NEW STRATEGIES TO INCREASE THE PHOTOELECTROCHEMICAL WATER SPLITTING PERFORMANCE OF PHOTOELECTRODES

Heretofore, the common methods of improving the performance of photoelectrodes have been studied. Now, we will review three new strategies including resonance light trapping, surface plasmon resonance, and dual photoelectrodes to improve the PEC performance.

Resonance light trapping

By designing photoelectrodes in various shapes such as V-shaped as shown in Figure 8, more light can be trapped and light loss can be prevented. Thus, the photoelectrochemical performance of water splitting can be improved.^{5,68}

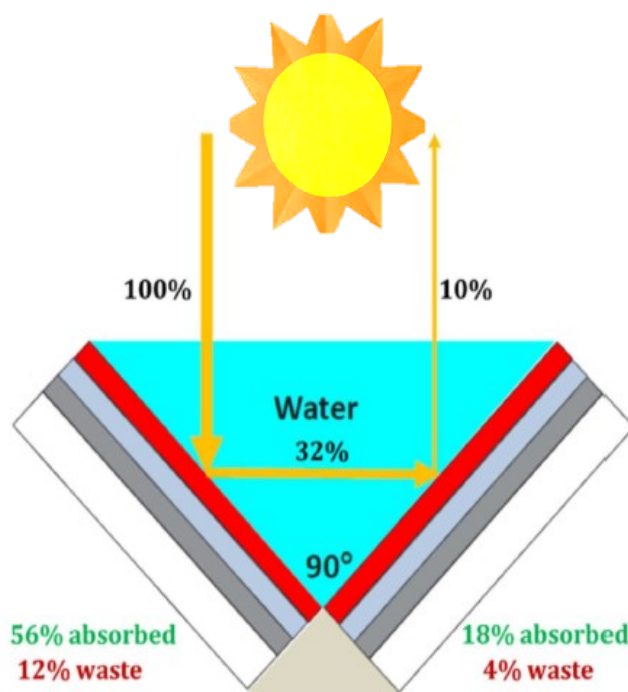


Figure 8. V-shaped cell structure for light re trapping. Reproduced with permission⁶⁸. Copyright 2013, Macmillan Pub. Ltd.

Surface plasmon resonance

One of the research works done in this case is that gold nanoholes and gold nanopillars were grown on the surface of Fe_2O_3 photoanodes. This strategy increases light absorption and reduces charge recombination. In this method, nanoholes or nanopillars act as an efficient hole depletion layer due to surface plasmon resonance, which, by better charge separation, accelerates the photoelectrochemical process of water splitting.^{69,70}

Dual photoelectrodes

As mentioned, it is very difficult to find a single semiconductor that has all the characteristics of good photoelectrochemical water-splitting semiconductors. Therefore, recently, one of the most widely used methods is to combine two photoelectrodes next to each other or in tandem mode, regardless of the matching of their bandgap. In this method, by placing two photoelectrodes in a row, a wider range of light is absorbed and the photoelectrochemical performance of water splitting increases.^{5,71} In this method, it is better to place the photoelectrode with a larger bandgap in front so that absorbs the light with a shorter wavelength (more energy), and the photoelectrode with a narrow bandgap in the backside so that absorbs the light with longer wavelengths (lower energy) which crosses through the first photoelectrode (Figure 9).

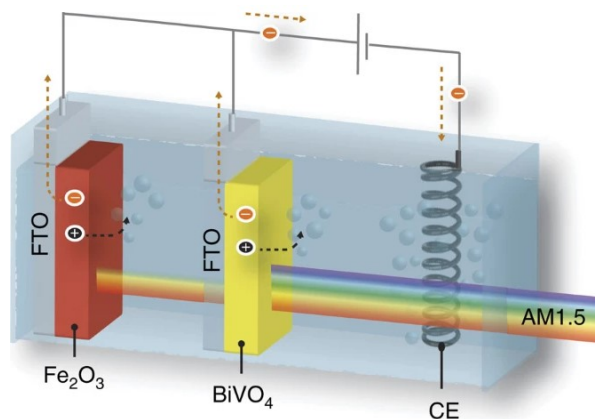


Figure 9. Schematic diagram of the placement of dual photoelectrodes. Reproduced with permission.⁷²

5. LARGE-SCALE PHOTOELECTRO-CHEMICAL WATER SPLITTING

So far, we have studied photoelectrochemical water splitting at the laboratory level and briefly reviewed the methods and materials used to improve the performance of this process. Now, to use this process on a large scale, in addition to using laboratory materials or laboratory methods, we must pay attention to a series of points to expand this method.

For large-scale hydrogen production, the minimum efficiency of converting light to hydrogen produced by semiconductors should be 10%. In addition, not only is crucial to use materials that perform well in the laboratory but also a reasonable price, convenient methods for their synthesis, and earth abundance should be considered. The hydrogen produced in the industry can have different applications, the most important of which are the use in fuel cells, electricity supply, and as fuel for combustion engines of cars. Therefore, the production of hydrogen in large quantities and at a reasonable price can be a very good alternative to fossil fuels without any incompatibility with the environment because its only product is water vapor. In the laboratory, there are different designs of connecting semiconductors to each other for producing hydrogen in the solar water splitting process.^{1,21}

The first design, which is very simple, is the design of single photoelectrodes in which a metal anode is connected to a photocathode, or a photoanode is connected to a metal cathode, or connection is such that a photoanode and a photocathode are connected. This connection can be in two ways: a wired connection (Figure 10a) which is more adjustable and is mostly used for laboratory-level work, or a wireless connection where both photoelectrodes are on a conductive surface without a wire connection. It is considered that the use of this structure is more suitable for large scales (Figure 10b).^{21,73}

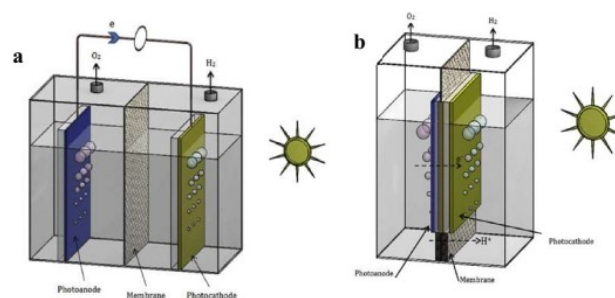


Figure 10. Sketches of dual cell photoelectrodes: a) wired T mode and b) wireless T mode. Reproduced from ref.⁷³

Another method is to use solar cell devices, which can be connected to a photoelectrochemical system with different dye-sensitized solar systems, photovoltaic, and perovskite solar systems (Figure 11). These designs work better because the photoelectrochemical process requires a voltage that can be obtained by solar cells. But each of these designs has its own challenges that limit their development at the industry level. In all these designs, the efficiency is 10% or less, the photovoltaic systems themselves are expensive, and along with different semiconductors and the combination of them, their price increases to a greater extent.^{21,74,75}

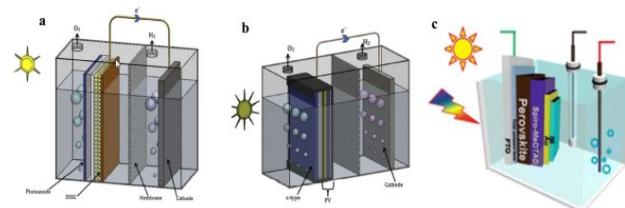


Figure 11. Schematic form of different PEC/Solar cell systems: a) PEC/DSSC system Reproduced from ref.⁷⁶ b) PEC/PV system Reproduced from ref.⁷⁷ c) PEC/Perovskite system reproduced from ref.⁷⁸

Notably, most promising designs for large-scale production of hydrogen is the use of photoelectrochemical/photovoltaic systems (Figure 12), which should be worked on reducing its cost and increasing its light absorption. Also, most of the materials used in the photoelectrochemical process have a reported shelf life of up to 48 hours, and to use these materials on a large scale, we need materials with a lifespan of 5 to 10 years.⁷⁹

Other large-scale methods have been used, for example, Kim *et al.* used a large-scale photochemical method to produce hydrogen, and separated two gases of hydrogen and oxygen with membranes. The maximum efficiency of this method was 5% and the amount of hydrogen produced was not high enough to be economical.¹ Meanwhile, there are refueling stations around the world that are monopolized by private companies and most of them produce hydrogen by the electrolysis-photovoltaic

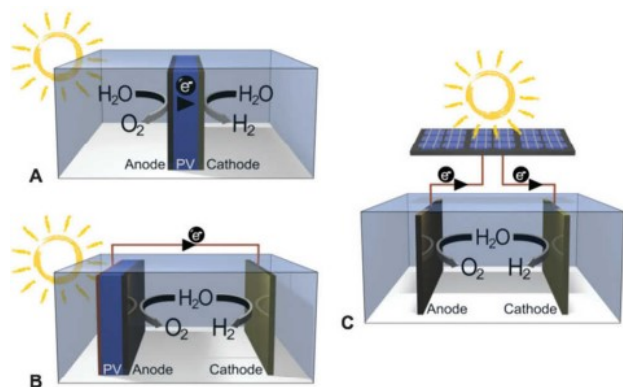


Figure 12. Three approaches for coupling the photovoltaic material and electrolytic water splitting components. (A) integrated PEC device; (B) partially integrated PEC device; (C) non-integrated PEC device. Adapted with permission from reference ⁸⁰. Copyright 2015 Royal Society of Chemistry.

method. This method breaks down water into hydrogen and oxygen using electricity supplied by photovoltaic systems but it is hoped that the photovoltaic/photoelectrochemical method can be used on a large scale to produce hydrogen gas.

Among the works that can be done to increase light absorption and prevent light wastage for large systems are the use of light focusing plates, v-shaped systems, or Fresnel lenses that focus light on semiconductors and it makes better use of light (Figure 13).^{8,79}

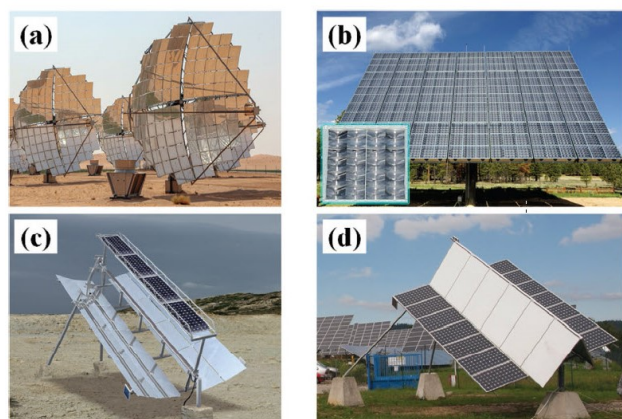


Figure 13. Four kinds of solar concentrators: a) solar dish, b) Fresnel lens, c) pseudo-parabolic concentrator, and d) V-trough. Permissions: (c) and (d) photographs courtesy of V. Poulek. Reproduced from ref. ⁸

Another challenge of large-scale photoelectrodes, especially the bismuth vanadate electrode, is that as the size of the photoelectrode increases, its resistance increases, and its performance decreases. Therefore, instead of a large photoelectrode, it is better to use several small photoelectrodes close together.¹

The researcher's aim is to use this new hydrogen production system in the various applications shown in Figure 14.¹

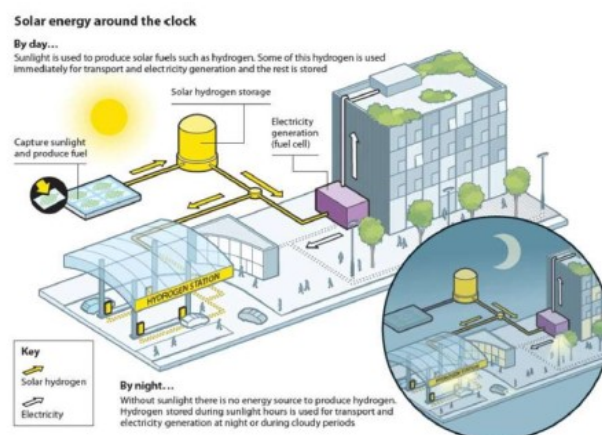


Figure 14. Use of solar energy around the clock. The capture of sunlight to produce fuel, storage, usage as solar fuel from hydrogen stations, and electricity generation. Reproduced from ref.¹

6. STABILITY FACTOR

This issue is different for diverse types of catalysts. For example, in laboratory scales, transient photocurrent and chronoamperometry results have shown that metal oxides such as $\text{WO}_3/\text{BiVO}_4$ were stable after ten cycles of on-off light illumination over 600 s. In this heterojunction structure, the photocurrent density of 1.21 mA/cm^2 was relatively stable over 5000 s under constant illumination.⁸¹ These photocatalysts are economically viable. However, some compounds, such as metal-organic frameworks, were less stable in these conditions. Moreover, in a DSSC-PEC system, a tandem device where the photoanode was composed of $\text{SnO}_2/\text{TiO}_2$ core/shell nanoparticles sensitized by a ruthenium-based chromophore, the current density is reported to be about 0.3 mA/Cm^2 with five cycles on-off irradiation in 600 seconds.⁸² Furthermore, in a PSC-PEC system including $\text{CH}_3\text{NH}_3\text{PbI}_3$ with Ni surface layer tandem cell, the photocurrent of 12 mA/Cm^2 was obtained and after 14 cycles in 500 s, the photocurrent density decreased to about 4 mA/Cm^2 .⁸³ Meanwhile, in a heterodual configuration of $\text{BiVO}_4/\text{Fe}_2\text{O}_3$, the photocurrent density of 7.0 mA/Cm^2 remained almost constant under 8 h constant illumination.⁷²

6. HYDROGEN STORAGE

Hydrogen storage is another issue to be explored. Hydrogen storage methods should be economically viable, have moderate operating temperatures, and bear high hydrogen storage capacity. So far, three main methods of hydrogen storage have been investigated, which are: Hydrogen storage in compressed gas, liquid hydrogen storage, and hydrogen storage on solid substrates.⁷⁹

Compressed gas hydrogen storage

Low temperature or high pressure is required to store

hydrogen gas due to its low density.⁸⁴ One of the most common ways to store hydrogen is to store hydrogen gas under high pressure (700 bar) in special capsules, which causes the volume of storage capsules to increase a little and these capsules are also somewhat heavy. Hydrogen gas has a high vapor pressure and to prevent the capsule from exploding, these capsules must be made with a thick wall, which causes the capsule to be heavy. However, it is still one of the most practical ways to store hydrogen.^{85,86}

Liquid hydrogen storage

Another method of hydrogen storage is to use liquid hydrogen, that is, to cool hydrogen to liquefy it and then use it. However, hydrogen gas has a low boiling point, so to store liquid hydrogen, we need low-temperature tanks with a temperature of about 21 Kelvin. This temperature is close to absolute zero, requires special technology, and is expensive.⁸⁷⁻⁸⁹ If hydrogen is to be stored for a short time, this method is also preferred because there is a risk of continuous boiling due to its low boiling point⁹⁰⁻⁹², but for long-term storage of hydrogen gas, the storage method which is usually preferred is Compressed gas.

Hydrogen storage on solid substrates

The use of porous solids, carbon nanostructures, organic metal frameworks, metal hydrides, and metal borohydrides is another way of storing hydrogen. In the solid-state storage method, large amounts of hydrogen can be stored in a small volume. It is better than other methods because it occupies less volume. In general, the solid-state hydrogen storage method is a system in which hydrogen atoms or molecules are combined with other materials. Solid-state storage is done in two ways: nanostructured materials and hydrides. The efficiency of hydrogen storage in nanostructured materials is low because the storage process is at a low density.⁹³ Nanostructured materials will be able to store more hydrogen with developing nanotechnology.¹⁰

Metal hydrides. Metal hydrides are one of the most promising solid hydrogen storage substrates that can form a chemical bond with hydrogen to form a metal hydride and release it as a molecular gas in a reversible reaction. (figure 15).^{79, 94, 95} This method is safer than others, and storing hydrogen at low pressure and high density is also possible.⁹⁶ The advantage of the metal hydride method is that it is more convenient regarding safety.⁹⁷ The US Department of Energy recommended that metal hydrides have an operating temperature of less than 353 K and a hydrogen storage capacity of 6% by weight.⁹⁸

Metal-organic frameworks (MOFs). Metal-organic frameworks (MOFs) are a class of materials that generally work well for hydrogen storage at temperatures as low as about 77 K. There is a wide variety of MOFs that have been engineered for various applications, including fuel storage,⁹⁹ batteries,^{99,100} supercapacitors,¹⁰¹

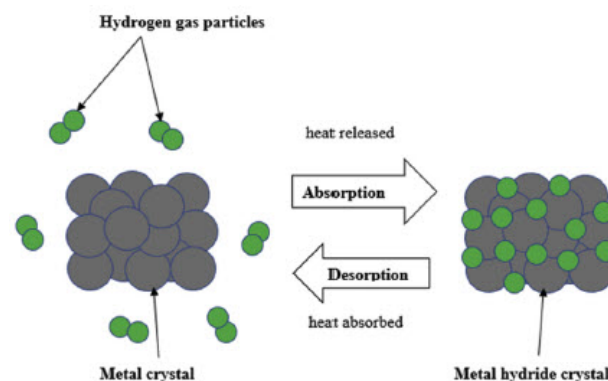


Figure 15. A simplified model of a metal hydride hydrogen storage. Reproduced from ref.⁷⁰

photocatalysis,¹⁰² and phototherapy.¹⁰³ Rosi et al.¹⁰⁴ reported a capacity of 4.5 wt% at 78 K and 1.0 wt% at room temperature and a pressure of 20 bar for MOF-5. MOFs are porous materials composed of crystals¹⁰⁵ and hydrogen must diffuse through those crystals to be stored.¹⁰⁶ The rate of adsorption depends on the rate of hydrogen diffusion in the MOF and also on the size of the crystals.¹⁰⁷ When adsorption and desorption are induced by a temperature change, a thermal management system is required.¹⁰⁸ In designing such systems, many approaches are possible.^{95,109} It is worth noting that the thermal conductivity of MOFs is approximately 0.3 W/(m·K),¹¹⁰ which is very low compared to the thermal conductivity of some materials such as copper with 400 W/(m·K) conductivity. The low conductivity of MOFs is an additional challenge for thermal management in the design of MOF-based storage systems. Adding nanoparticles of precious metals such as platinum and palladium to MOFs can increase their hydrogen storage capacity.⁹⁵ Proch et al.¹¹¹ achieved a storage capacity of 2.5 wt% by adding platinum particles, but it drastically decreased to 0.5 wt% after several cycles. DeSantis et al.¹¹² predicted that 2.5 million kg/year industrial-scale production costs of MOFs for hydrogen storage would fall between \$13/kg and \$36/kg.

For the commercialization of hydrogen, we need materials that have a significant amount of stored hydrogen, are cheap, light, and can easily return the stored hydrogen and be used again.^{79,95}

The goal of all research work is to find ways or materials to store hydrogen so that has lightweight and size for the hydrogen storage tank and can store a significant amount of hydrogen in a small space. If we want to keep hydrogen gas in the tank at normal temperature and pressure, it will not be a significant amount and we need high pressures and low temperatures. However, it is necessary to use alternative methods to store hydrogen. In this regard, it should be synthesized adsorbent materials with a large surface area that can store a large amount of hydrogen using physical adsorption. For example, using

carbon nanofiber capsules (CNC) instead of thick steel capsules can be a suitable solution. Because CNCs are lighter and withstand pressures of 350 to 700 bar, however, the high price of carbon nanofibers remains a challenge to overcome.

4. CONCLUSION

In this review, hydrogen production from a laboratory scale as well as widely used laboratory materials and methods of this process were briefly studied. Then we examined the production of hydrogen on a large scale. It was mentioned that one of the most promising methods for large-scale hydrogen production is the photoelectrochemical/photovoltaic system. For its industrialization, more studies should be done because the life of the materials used should be about 5 to 10 years, they should be cheap and have a conversion efficiency of light to hydrogen above 10%. We also provided a brief overview of hydrogen storage. In this regard, studies are needed to provide a lightweight solid substrate for significant hydrogen storage so that can store and release hydrogen in a reversible reaction. In this context, one of the promising materials is metal hydrides.

CONFLICTS OF INTEREST

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