SEMICONDUCTORS FOR GREEN HYDROGEN PRODUCTION: COMPARATIVE RENEWABLE ENERGY APPLICATIONS

https://doi.org/10.22533/at.ed.804112520034

Data de aceite: 04/04/2025

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ABSTRACT: This chapter book mainly focuses on the recent advancements in the green hydrogen production using environmentally friendly approaches: Photovoltaic (PV) electrolyzers and Photoelectrochemical methods. First, an introduction with the basic topics of the hydrogen production and its applications is presented. Then, a comparison between photovoltaic (PV) cells and photoelectrochemical approach for sustainable H_2 generation using sunlight is discussed. Important eco-friendly and cost-effective semiconductor oxides employed for hydrogen production are summarized. This is followed by an overview of economics evaluations in order to discuss on cost aspects of clean-hydrogen economy. Therefore, this chapter sum-up sunlight-based technologies for green hydrogen generation with an objective to decrease the world's dependence on fossil fuels.

KEYWORDS: Photovoltaic cells, Hydrogen, Sustainability, Semiconductors, Photoelectrochemical.

INTRODUCTION

Why Hydrogen Gas (H_2) is Important?

During last decades, fossil fuels, such as coal, gasoline or natural gas, have been extensively used as important components for human life and social civilization. The growth of the global population, expected to reach 8 billion by 2030, rapid industrialization, and rising income levels have increased the consumption of non-renewable fuels. These excessive consumption of fossil fuels have promoted damage to the environment and negative consequences to population's life, including amplification of global warming, air pollution, acid rains (*Acid Rain Program Results*, 2022; Jørgensen et al., 2022). Therefore, the development of sustainable energy sources is highly needed to meet the global energy demand and also decrease greenhouse gas emissions to the atmosphere (Grimm et al., 2020).

In particular, hydrogen gas (H_2) arises as a promising chemical fuel for sustainable energy applications (Tributsch, 2008). Hydrogen usually does not exist naturally and need to be produced from compounds that contain it (water, biomass, fossil fuels and other sources), except by a very small percentage found in the atmosphere. Hydrogen gas possesses outstanding characteristics, including high storage capacity and exceptional energy density, with a calorific value of approximately 120–142 MJ/kg. Notably, 1 kg of H_2 releases 4.1 times more energy than 1 kg of coal and 2.8 times more than 1 kg of gasoline. Moreover, its production is carbon-neutral, generating no CO_2 emissions. This gas can be sourced from abundant H_2O and readily converted into other forms of energy, making it an excellent choice for heat and power generation. (Clarizia et al., 2023; Dincer & Acar, 2015). The table 1 summarizes the energy contents among several fuels.

Fuel	**Fuel Energy Content (MJ Kg^{-1})**
Hydrogen	120-142
Natural gas	54.4
Gasoline	46.4
Diesel	45.6
Ethanol	29.6
Methanol	19.7

Table 1. Comparison of energy contents of various fuels.

Source: Adapted from (Ni et al., 2006).

Due to the environmentally friendly aspects and promising energy source, the hydrogen presents central hole to several industrial applications, such as ammonia production, oil refining, aircraft applications, in H_2 powered vehicles (Chisalita et al., 2020; Qazi, 2022). According to Hydrogen Council (2020), the use of hydrogen energy has been growing and could represent 8% of global energy demand (GED) with a production cost of \$2.50 USD per kilogram (*COUNCIL, Hydrogen. Path to Hydrogen Competitiveness: A Cost Perspective*, 2020). The expectations are that by 2030, the H_2 production cost will be lower i.e., 1.80 USD/kg, playing a vital role in several energy sectors. Fig. 1 illustrates how hydrogen is versatile, and as a result, has been receiving different application worldwide.

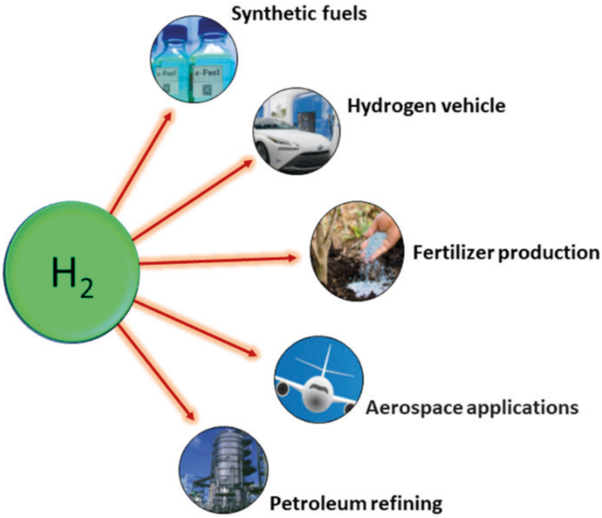

Fig. 1. Illustration of the common application of hydrogen gas.

Numerous studies explore sustainable methods for hydrogen production, highlighting its crucial role in fostering environmental sustainability. However, from an industrial perspective, the steam reforming of methane (SRM) is the most popular process. Currently, approximately 96% of hydrogen is derived from carbon-based sources such as natural gas, oil, and coal, while only 3.9% comes from water electrolysis, with the remaining 0.1% sourced from other methods (S. Li et al., 2020). Specifically, this endothermic (ΔH_{SR} = 206 kJ/mol) reaction takes place under high-temperature steam (700°C – 1,000°C) for the conversion of CH_4 into H_2 and CO (H. Zhang et al., 2021):

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \ \Delta H^0_{298} = +206 \text{ kJ/mol} \qquad (1)$$

This technology presents several challenges, including high temperatures, making it slow to start the process, catalyst deactivation and heavy greenhouse gas (GHG) emissions. Therefore, switching the hydrogen production to clean and environmentally benign methods could greatly reduce the CO_2 emissions and their adverse effect on global warming.

Considering that the sunlight reaching Earth's surface could supply approximately 10,000 times the global energy demand, developing systems that operate efficiently under solar irradiation is crucial for the practical production of "green" fuels. Research on solar water splitting using TiO_2 photoelectrodes has been actively pursued since the pioneering work of Fujishima and Honda (FUJISHIMA & HONDA, 1972). Since then, extensive efforts to promote water splitting to H_2 and O_2 became prominent in literature. The cost of H_2 produced by electrolysis is still significantly higher than that produced by fossil fuels. For large-scale deployment to be practical, the cost of solar hydrogen generation must be drastically reduced (Jia et al., 2016). To follow this motivation, this paper aims to compare the most relevant sunlight-driven technologies for renewable hydrogen production: Photovoltaic (PV) cells can convert photons into electricity, which can then be coupled with electrolyzers to convert electrical energy into carbon-free fuels (Clarizia et al., 2023) through a photoelectrochemical (PEC) process. The photoelectrochemical cells enable direct photo into-chemical energy conversion (Andrei et al., 2022), which allows H_2 and O_2 generation at distinct electrodes.

OVERVIEW OF WATER SPLITTING APPROACHES

This section compares two different sunlight-driven configurations for renewable hydrogen production: the photovoltaic (PV)-electrolysis system and the photoelectrochemical (PEC) approach.

Photovoltaic (PV)-electrolysis System

The use of photovoltaic energy for hydrogen production has garnered significant scientific interest. Essentially, photovoltaic (PV) cells convert photons into electricity, which can then be used to generate carbon-free fuel. Currently, over 90% of photovoltaic cells rely on conventional crystalline silicon technology. The efficiency of a PV cell is determined by the ratio of electrical power generated to the amount of sunlight incident on its surface (Hasan et al., 2022). Efficiency is the primary challenge in implementing PV systems, once the theoretical maximum efficiency is 29%, practical applications have achieved only up to 26% (Hasan et al., 2022; Jia et al., 2016). The efficiency of an individual solar cell is different when compared to the efficiency of solar panels as a whole system, which the solar panel efficiency is around 15-20%, while the solar cell efficiency reaches 42%.

Commercial photovoltaic panels consist of a series of PV cells encased in a protective glass front and a plastic backing. These cells are primarily made from semiconductor materials, with doped silicon variants being the most widely used due to their efficiency and suitability for energy conversion. A photovoltaic cell is composed of a p-n junction (adjacent layers of p-type and n-type semiconductor materials). As a p-n junction is illuminated, high-energy photons absorbed at the junction excite the electrons in the semiconducting material, generating the electrons transfer to higher energy states. These excited electrons will flow through the metallic contacts on the top surface of the photovoltaic cell (Roderick, 2021).

PV cells can be manufactured using various semiconductor materials, including silicon (Si), cadmium telluride (CdTe), copper indium gallium selenide (CIGS), perovskites, and certain organic compounds (OPV) (Bian et al., 2021; Jia et al., 2016). However, crystalline silicon remains the dominant choice, offering the best balance between performance and cost efficiency. The film's thickness is from few nanometers (nm) to tens of micrometres (μm), allowing thin, light and flexible PV modules. Significant research has been developed new PV cell materials technologies and also improving the performance, and decreasing the costs of existing technologies

Material composition	**Cell Commercial Efficiency**	**Cell Laboratory Efficieny**	**REF**
Monocrystaline Silicon (Si)	27.6 %	---	(*Photovoltaic Energy Factsheet*, n.d.)
GaInP/GaAs//Si	---	33%	(Cariou et al., 2018)
GaInAsP triple-junction	---	35.9 %	(Schygulla et al., 2022)
InGaP/GaAs/GaInNAsSb triple-junction	---	30 %	(Jia et al., 2016)
Perovskite	25.7 %	---	(*Photovoltaic Energy Factsheet*, n.d.)
CdTe	22.1 %	---	(*Photovoltaic Energy Factsheet*, n.d.)
GaAs	47.1 %	---	(*Photovoltaic Energy Factsheet*, n.d.)
$CuO/CdTe/CdS/TiO_2$	---	28.11 %	(Roy & Majumdar, 2022)
Copper indium gallium selenide solar **(**CIG**S)** cell	20 %	---	(Al-Ezzi & Ansari, 2022)

Table 2. Comparison of different commercial and laboratory PV cells efficiencies.

The PV cells have been also coupled with electrolyzers, which can convert electrical energy into “green” fuels (Fig. 2) (Vos, 1980). In these systems, several key steps occur to facilitate H_2 generation: (i) the semiconductor absorbs light, generating charge carriers; (ii) these charge carriers are separated and transported; and (iii) the charges are transferred to the electrolyte interface, where they drive light-induced reactions.

To enhance the overall efficiency of the PV-electrolysis system, research was conducted on each component, including the solar modules and the electrolysis compartment, focusing on electrodes and electrolytes (Gibson & Kelly, 2010). For example, the electricity generated from PV cells relies on the intensity of the sunlight, temperature and also in the performance of the cell, its cell type and size. Conversely, water splitting to produce H_2 and O_2 can be achieved through various electrolysis methods, including alkaline electrolysis, solid oxide electrolysis, anion exchange membrane (AEM) electrolysis, and proton exchange membrane (PEM) electrolysis (Calnan et al., 2022; Gibson & Kelly, 2010).

The main advantage of PEM electrolysis is the possibility to operate experiments at high current densities, generating hydrogen of high purity and pressure (Sánchez-Molina et al., 2021). The key components of a PEM electrolyzer include a proton exchange membrane, electrodes, gas diffusion layers, and bipolar plates. The electrodes, typically made of catalytic materials like platinum, facilitate the electrochemical reactions that generate H_2, while the bipolar plates serve as current collectors. A PEM electrolyzer operates based on electrolysis, where an electric current passes through the electrolyte to drive chemical reactions at the electrodes. Specifically, H^+ ions generated at the anode migrate through the proton exchange membrane. At the anode, water is oxidized, releasing O_2, while at the cathode, H^+ ions are reduced to form H_2 (*Proton Exchange Membrane (PEM) Electrolyzers for Green Hydrogen Production*, n.d.).

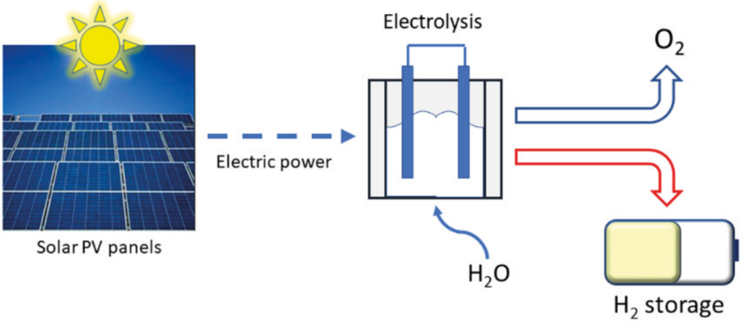

Fig. 2. PV-electrolysis power-source for hydrogen production.

In the case of PV-electrolysis systems and photoelectrochemical processes, the solar-to-hydrogen (STH) efficiency is an important parameter to determine the efficiency of hydrogen production through water splitting, and can be calculated by the following equation 2:

$$\text{STH (\%)}=\left[\frac{(\mathit{Standard\ Gibbs\ free\ energy\ of\ water{,}237\ kJmol}-1)\ x\ (\mathit{Rate\ of}\ \mathrm{H2}\ \mathit{evolved})}{(\mathit{Energy\ density\ of\ incident\ solar\ light})\ x\ (\mathit{Irradiated\ area})}\right]\text{ x 100 (2)}$$

According to the literature, an n/pn/p GaInP/GaAs junction configuration achieved a solar-to-hydrogen conversion efficiency of 16%. Meanwhile, when cost is a critical factor, a triple-junction a-Si cell demonstrated a solar-to-hydrogen conversion efficiency of 7.8% (Khaselev et al., 2001; Muhammad-Bashir et al., 2020). Additionally, a comparison between conventional silicon (Si) modules and experimental InGaP/GaAs/Ge PV-electrolysis systems revealed higher STH efficiencies of 18–21% for hydrogen production, whereas the Si module achieved approximately 9.4% (Muhammad-Bashir et al., 2020).

Other cost-effective catalysts, such as NiO, have been utilized in PV-electrolyzers (Bayrak Pehlivan et al., 2019), demonstrating that the combination of stable, low-cost thin-film PV materials and earth-abundant catalysts can achieve solar-to-hydrogen (STH) efficiencies exceeding 13%, even with moderately efficient PV modules. A second generation of the thermally-integrated device, using NiFe LDH nanomaterials combined with ACIGS modules, reached a solar-to-hydrogen (STH) module efficiency of 13.4% based on gas volume measurements. This system utilized a six-cell CIGS-electrolyzer module with an active area of 82.3 cm² (Bayrak Pehlivan et al., 2019).

PV-electrolyzer device designs play a critical role in the future deployment of solar water-splitting for sustainable green fuel production. Therefore, scaling up the entire system while maintaining high efficiency is essential for its practical implementation.

Photoelectrochemical (PEC) Application

The principle of the semiconductor in a photoelectrochemical (PEC) is similar to a PV cell. Specifically in PEC, the reaction occurs under light illumination when photons with energy greater than the semiconductor's band gap excite electrons, generating charge carriers through light absorption. The charge carriers move toward the interface between the semiconductor and electrolyte due to the electric field in the depletion layer. Once at the interface, they facilitate photoelectrochemical reactions at the semiconductor surface—oxidation occurring at the surface of an n-type semiconductor and reduction at the surface of a p-type semiconductor (see Fig. 3) (Ahmed & Dincer, 2019).

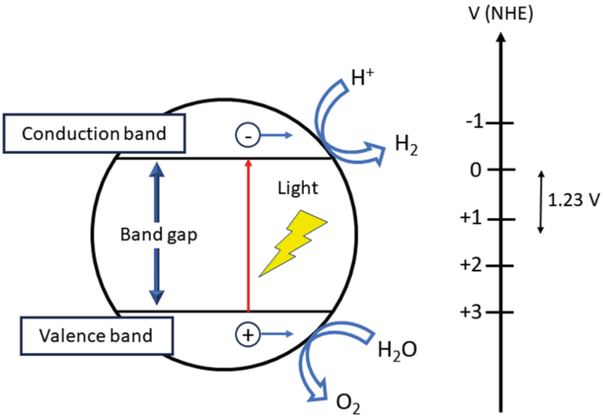

Fig. 3. Principle of water splitting photocatalysis on semiconductors.

The alignment of the band gap and the potentials of the conduction and valence bands is crucial. The band edge positions in semiconductors must be carefully considered for photoelectrocatalytic reactions, as they determine the most suitable semiconductor for a specific application. This approach has been successfully applied in various reactions, including CO_2 reduction, hydrogen production, ammonia generation, and glycerol reforming (Camargo et al., 2022; Romeiro et al., 2025; Prabhakar et al., 2025; Yu et al., 2022). The band gap must be ideally small, < 1.5 eV, to absorb enough visible light and, for water oxidation processes, the valence band potential of the materials must be more positive than the O_2/H_2O redox potential (1.23 V vs RHE at pH=0). Regarding the H_2 generation, the conduction-band (CB) of a semiconductor must be in a higher position than the reduction potential of H^+ to H_2, which is E_0=0.0 V vs NHE at pH=0 and -0.41 V vs NHE, at pH. The overall water splitting process into H_2 and O_2 is an uphill reaction and needs 1.23 V vs RHE at pH=0, as shown in eq 2. In this way, the band gap energy (Eg) of the semiconductor should be greater than 1.23 eV (400 nm).

$$H_2O \rightarrow \frac{1}{2} O_2 + H_2 \qquad (2)$$

In the literature, two primary configurations of PEC cells have been extensively studied: (i) hydrogen formation on the photocathode surface and (ii) hydrogen formation on the photoanode surface (see Fig. 4). The electrochemical process involves two half-reactions: water oxidation to O_2 at the photoanode surface and water reduction to H_2 at either the photocathode or the counter electrode (Clarizia et al., 2023). In the case of an n-type semiconductor, photoexcited electrons are transferred through an external circuit to the counter electrode (typically platinum) to facilitate the reduction of water to H_2. Meanwhile, the photo-generated holes migrate to the semiconductor surface, where they drive the oxidation of H_2O to O_2 (Romeiro et al., 2020). In contrast, for p-type semiconductor materials, the band bending at the semiconductor/electrolyte interface is downward. As a result, photoexcited electrons migrate to the semiconductor surface, where they reduce H_2O to H_2, while photoexcited holes are transferred to the counter electrode to drive the oxidation of H_2O to O_2 (Kalanur et al., 2018).

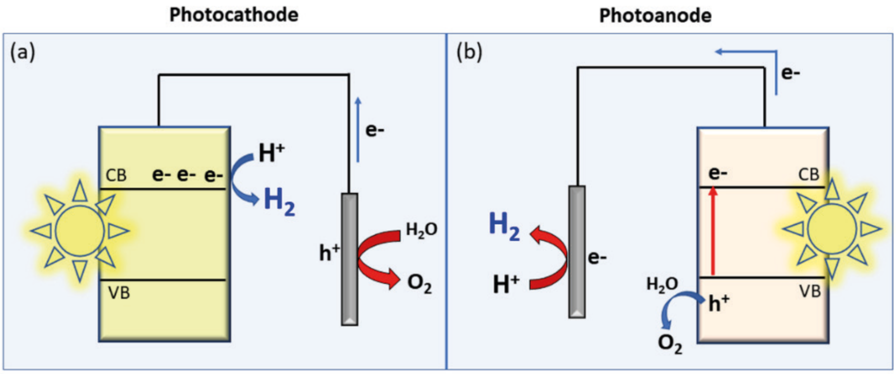

Fig. 4. Photoelectrochemical water splitting approaches using (a) p-type and (b) n-type semiconductors.

Some semiconductor materials lack the necessary properties, such as an optimal band gap, suitable band edge positions, and long-term stability, for efficient overall water splitting. Additionally, significant energy losses occur due to charge carrier recombination during the separation and transport of photoexcited electron-hole pairs in many PEC systems, leading to low energy conversion efficiency.

The selection of efficient semiconductor materials and optimized PEC cell configurations is crucial for maximizing performance. Key considerations include achieving high selectivity for H_2 generation and ensuring long-term stability during extended photoelectrocatalysis (Rumayor et al., 2023). The photoelectrocatalysts should effectively absorb sunlight and generate sufficient photovoltage to drive water-splitting reactions (Ahmed & Dincer, 2019). Band gaps between 1.23 eV and 3.0 eV are essential for effective adaptation to the terrestrial solar spectrum while providing sufficient energy to drive the 1.23 eV free energy requirement for water splitting (Teixeira et al., 2020). Therefore, efficient separation and high mobility of charge carriers, band gap, band edge positions in inorganic materials are highly desirable characteristics for efficient water splitting reaction (Cheng et al., 2022).

Incorporating impurity elements into semiconductor matrices through doping and synthesizing heterojunctions are effective strategies for band structure engineering, helping to suppress the recombination of photogenerated charge carriers and enhance overall performance (Lemos et al., 2017). Various semiconducting materials have been synthesized and utilized as photoelectrocatalysts for hydrogen evolution from water. The following section will highlight the most relevant material classes, including metal oxides (e.g., ZnO, TiO_2, SnO_2) and carbon-based materials (e.g., graphene, g-C_3N_4). Additionally, strategies for enhancing their performance, such as hybrid formation and heterojunction engineering, will be discussed, focusing on improving activity, selectivity, and stability for H_2 production.

NANOMATERIALS AND SEMICONDUCTORS FOR GREEN H_2 PRODUCTION

Photovoltaic (PV) Cells Composition

Photovoltaic (PV) cells are designed to generate electricity from sunlight. PV modules typically consist of a rectangular grid of 60 to 72 cells, connected through multiple parallel circuits and laminated between a transparent front surface and a structural back surface (*Photovoltaic Energy Factsheet*, n.d.). Most of the PV cells are constrcuted using a semiconductor material such as silicon (Si), having one side doped with pentavalent dopants forming n-type semicondutor, and another side doped with trivalent Chemical species forming a p-type semiconductor. The most usual material for commercial solar cell construction is Silicon (Si), but some can be built using Gallium Arsenide (GaAs) (Jia et al., 2016), Cadmium Telluride (CdTe) (Roy & Majumdar, 2022) and, Copper Indium Gallium Selenide (CIGS) (Bayrak Pehlivan et al., 2019).

Silicon (Si) solar cells are widely available in the market and are commonly used due to their competitive pricing and affordability. Silicon-based photovoltaic cells can be classified into three main types: monocrystalline silicon, polycrystalline silicon, and amorphous silicon. Monocrystalline silicon (Si) cells offer the highest efficiency, reaching approximately 27.6%, while polycrystalline silicon cells achieve around 23.3%. In contrast, amorphous silicon solar cells have a lower efficiency of about 10.0% (*Photovoltaic Energy Factsheet*, n.d.; Qarony et al., 2017). The optimal semiconductor band gap of the top cell required to reach a maximum conversion efficiency ranges around ~ 1.o to 1.8 eV.

Another emerging category of materials for photovoltaic cell production is perovskites (ABX_3). In these compounds, cesium serves as the A-cation, while lead or tin act as the B-cation, and chlorine, bromine, or iodine function as the X-anion. Perovskite materials exhibit excellent light absorption, high charge-carrier mobility, and long carrier lifetimes, leading to impressive energy conversion efficiencies. (Snaith, 2018). However, several challenges, including manufacturing costs, stability, and environmental compatibility, can limit the commercial viability of perovskite solar cells. Another promising technology is organic photovoltaic (OPV) cells, which offer unique advantages such as flexibility, transparency, and non-toxicity. Additionally, organic semiconductors present a cost-effective alternative to inorganic semiconductors for photovoltaic module production. However, like perovskites, OPV cells face long-term stability issues. Unlike conventional solar cells, OPVs are constructed using electron donor and acceptor materials instead of semiconductor p-n junctions. Currently, state-of-the-art OPV cells have achieved power conversion efficiencies exceeding 16% (Cui et al., 2020).

SEMICONDUCTORS IN PEC WATER SPLITTING

There is still a need for efficient photocatalysts that are able to (i) absorbing visible-light, (ii) generate charge carriers and avoid heat losses, and (iii) promoting the separation of photogenerated electrons and holes. Significant research efforts have been devoted to developing materials with improved photoelectrocatalytic activity.

Zinc oxide (ZnO)

Zinc oxide (ZnO) is an n-type semiconductor with a hexagonal wurtzite structure that presents intrinsic defects, such as zinc interstitial (Z_i) and oxygen vacancy (V_o) in its crystal structure and also a wide bandgap value of 3.37 eV (Gusmão et al., 2021). In addition, ZnO presents high exciton binding energy of ~ 60 meV (Gusmão et al., 2021; Rodrigues et al., 2023). These properties allow a variety of uses in electrochemical properties, solar cells, photocatalysts and photoelectrochemical applications (Guérin et al., 2012; Wolcott et al., 2009).

The ZnO presents properties such as, environmental friendliness, non-toxicity, abundance and efficiency for various photocatalytic reactions, and is considered a suitable photoanode for H_2 generation because of its appropriate band structure, photoactivity and high electron mobility (Ma et al., 2020). The practical applications of ZnO are usually limited by its high recombination rate of photogenerated electron–hole pairs, a challenge that can be addressed by optimizing its morphology, insertion of dopants and synthesis of heterostructures. Additionally, ZnO has a wide bandgap and an absorption edge at about 368 nm, limiting its utilization to ultraviolet light, which constitutes only 4% of the solar spectrum. The following section will address some of the published literature on the use of ZnO for photoelectrochemical cells (PECs). However, it is important to note that the protocols for assessing H_2 production can vary significantly, leading to different evaluations of PEC performance.

ZnO thin films with diferent loadings of Ag were synthesized, presenting hydrogen evolution rates of ~38 and ~24μmol/h under UV and visible light exposure respectively, which are almost five and tem fold higher than those of pristine ZnO (Trang et al., 2020). The outstanding performance was ascribed to the lower recombination rate of photogenerated charge carriers and (ii) the interaction between ZnO and Ag, facilitating the electron transfer from ZnO to Ag.

Considering heterostructures, an assembled nanoflower morphology of Bi_2S_3 decorated with ZnO nanoparticles, the L-Bi_2S_3/ZnO heterostructures produced 2791 mmol of H_2, a 2.74 fold enhancements compared to L- Bi_2S_3 (1020 mmol of H_2) under visible light (Bera et al., 2018).

$BiVO_4$/ZnO quantum dot (QD) heterostructures exhibited a remarkably reduced charge-transfer resistance across the interface between the $BiVO_4$ and ZnO particles when compared to the traditional $BiVO_4$/ZnO-S, the $BiVO_4$/ZnO QDs. The authors observed oxygen and hydrogen production rates of around 0.9 and 1.8 µmol/min for the quantum dot (QD) photoelectrodes and an average Faradaic efficiency of hydrogen and oxygen evolution was calculated to be over 90% (J. Li et al., 2021).

Titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) is considered a wide band gap semiconductor which has attracted interest due to its unique properties such as photoactivity, large surface area, non-toxicity and low cost (Romeiro et al., 2020). TiO_2 can be found in three crystalline polymorphs: Anatase, brookite and rutile. The rutile phase is the most stable at high temperatures, while the anatase and brookite phases are metastable and can be transformed into the rutile phase when heated to high temperatures (Kaplan et al., 2016). Due to the band gap values being around 3.2 eV for anatase, 3.0 eV for rutile TiO_2 and 3.3 for the brookite phase, TiO_2 material is photoactive in the ultraviolet region of the electromagnetic spectrum.

The structure of crystalline TiO_2 presents defects associated with non-stoichiometry between Ti and O atoms (1:2) when treated under high temperature conditions and vacuum or reduced in H_2 atmosphere. The most known defects are oxygen vacancies (V_O), Ti vacancies (V_{Ti}) or titanium interstitial (Ti_i). The presence of different defects can result in an improvement or worsening of the photocatalytic activity, depending on the type and location of yhe intrinsic defects.

TiO_2 in nanoscale have, generally, a higher photocatalytic activity due to the small diameter of the nanoparticles, in which the charge requires minimal effort to transfer to the surface. Additionally, with the decreasing of nanoparticles, the recombination of photoexcited electron hole pairs decreases once the electrons and holes can flow on the surface without recombine (Bakbolat et al., 2020).

The possibilities for technological applications of titanium dioxide are quite broad, specially involving the water splitting and therefore production of H_2. Fujishima and Honda (1972) first achieved UV-light assisted electrochemical water splitting using a TiO_2 photoanode in a PEC cell (FUJISHIMA & HONDA, 1972) and after their pioneering work, the interest in the field of photocatalysis for water splitting reached worldwide attention. For instance, Sun et al., 2011 have been obtained highly ordered TiO_2 nanotube arrays aiming the H_2 formation by electrochemical anodization of titanium sheets. In their work, the TiO_2 nanotubes photoanodes presented fast charge transfer, a maximum photoconversion efficiency of 4.13% and highest hydrogen production rate of 97 mmol h^{-1} cm^{-2} obtained from TiO_2 nanotubes anodized for 60 min (Sun et al., 2011).

Wang et al. (2011) employed an effective strategy to enhance the photoelectrochemical (PEC) performance of rutile TiO_2 nanowires by subjecting them to hydrogen treatment, thereby creating a high density of oxygen vacancies that act as electron donors. The authors hypothesized that annealing TiO_2 in a reducing gas atmosphere will substantially increase the density of oxygen vacancies and, therefore, enhance the electrical conductivity as well as the charge transportation of TiO_2. The optimized H:TiO_2 nanowire reached a photocurrent density of ~1.97 mA/cm^2 under simulated solar light and a solar-to-hydrogen (STH) efficiency of ~1.63% (Wang et al., 2011).

Brito, et al., (2018) developed CuO nanoparticles decorating TiO_2 nanotubes and observed an improvement in the photocurrent behavior and in H_2 generation through water splitting in a full PEC cell. The superior performance of CuO-TiO_2 can be attributed to the transient formation of a p–n junction, which enhances photocurrent density by facilitating efficient charge separation (de Brito et al., 2018).

Tin oxide (SnO_2 and Sn_3O_4)

Among the well-known semiconductor oxides, tin oxide has been extensively studied due to its wide range of potential applications, including in photoelectrochemical cells, sensors, and batteries. This material can exist in various forms, such as SnO, SnO_2, and Sn_3O_4, with the SnO_2 phase being the most thermodynamically stable. Both the monovalent SnO (p-type semiconductor, indirect band gap = 0.70 eV; direct band gap = 2.6 eV) and SnO_2 (n-type semiconductor, band gap = 3.6 eV) phases have attracted significant attention due to their distinct semiconductor properties (Romeiro et al., 2023). Recently, mixed valence tin oxide, Sn_3O_4 (Sn^{2+} and Sn^{4+}) was reported as the first non-stoichiometric tin oxide identified and its band structure has a band gap with energy in the visible light region (E_{gap} = 2.7 eV).

According to the potentials of the valence band (+1.81 V vs NHE) and the conduction band (-0.94 V vs NHE) of Sn_3O_4 (Pan & Yi, 2015), and its respective band gap value, this oxide shows great potential as a photocatalyst for energy conversion. Additionally, theoretical calculations have demonstrated that the valence and conduction band positions of SnO lie between the evolution potentials of hydrogen (H_2), with their exact placement depending on the number of layers of SnO (Zhou & Umezawa, 2015). Experimentally, Zhang, et al., 2018 observed that the band potentials valence and conduction values of SnO are +0.72 V and -1.89 V vs NHE respectively, presenting potential for the reduction of H^+ ions on its surface (R. Zhang et al., 2018). On the other hand, the SnO_2 conduction and valence bands are around +0.07 V and +3.67 V vs NHE (pH=7.0) respectively, and consequently oxidation reactions are susceptible on the fotoelectrocatalyst surface.

In the literature, Sn_3O_4 nanoflakes anchored on carbon fiber paper were synthesized using various concentrations of H_2O_2. The sample prepared with the highest H_2O_2 concentration achieved a H_2 production rate of 1.43 x 10^4 mmol h^{-1} g^{-1}. The authors found that H_2O_2 treatment played a critical role in shaping the morphology of Sn_3O_4, increasing both the diameter and thickness of the nanoflakes. As a result, the Sn_3O_4 treated with 1 mL of H_2O_2 exhibited a significantly larger active surface area compared to the untreated sample, leading to improved performance in hydrogen production (L. Li et al., 2022).

Romeiro, et al., (2022) investigated the performance of rGO-Sn_3O_4/SnO_2 heterostructure for H_2 generation under UV-vis irradiation and observed a higher H_2 generation (1.4 mmol L^{-1}) when using the nanocomposite as photocathode. However, a lower concentration of H_2 (0.4 mmol L^{-1}) was obtained under visible light irradiation for the nanocomposite, attributed to the presence of SnO_2 nanoparticles in the nanocomposite that absorbs light in the UV region. Therefore, using the open spectrum, the rGO-Sn_3O_4/SnO_2 heterostructure can reach the highest performance, indicating that H_2 production is dependent on the photo-absorption of the catalyst (Romeiro et al., 2022).

In the context of semiconductors, improving the efficiency, stability, and activity of photoelectrodes remains essential. This can be achieved by incorporating organic or non-metallic supports, as well as doping or functionalizing nanomaterials, to enhance hydrogen production from water splitting reactions. Research focused on material engineering is crucial for advancing photoelectrochemical technologies and enabling efficient H_2 generation in future applications.

A GENERAL ECONOMIC ANALYSIS OF H_2 PRODUCTION

Currently, 98% of hydrogen production relies on carbon-intensive energy sources, with steam methane reforming (76%) and coal gasification (22%) being the dominant methods. In contrast, only 2% of global hydrogen production comes from water electrolysis, the primary method for generating green hydrogen. The commercialization of green hydrogen faces significant challenges, including lower production efficiency compared to conventional methods and higher costs—reaching up to 15 euros per kilogram. This cost disparity is primarily due to the substantial investment required for electrolyzers, making green hydrogen less competitive with fossil fuel-based alternatives. Overcoming these barriers is crucial for the widespread adoption of sustainable hydrogen production (Terlouw et al., 2022).

The potential techno-economic advantages of photoelectrochemical (PEC) systems over photovoltaic (PV) electrolyzers for hydrogen production remain uncertain. According to a recent report, the levelized cost of hydrogen (LCOH) for PV electrolyzers was estimated at \$6.22 per kilogram of H_2, with a solar-to-hydrogen efficiency of 10.9%. In comparison, despite a similar efficiency of 10%, the LCOH for PEC systems was higher, at approximately \$8.43 per kilogram of H_2. These findings highlight the economic challenges associated with PEC technology and the need for further advancements to improve its competitiveness. (Grimm et al., 2020). Shaner et al. showed that the LCH using photovoltaic electrolysis (PV-E) and PEC water splitting are high \$12.1 and \$11.4 kg^{-1}, respectively, when compared to the price range of hydrogen obtained through steam methane reforming (SMR) ~\$1.4 kg^{-1} (Shaner et al., 2016). Therefore, hydrogen gas produced by electrolysis processes can still not economically compete with hydrogen produced by SMR.

Water electrolysis still faces technical challenges related to energy system integration and business operations, making large-scale deployment complex. Despite its global potential, hydrogen technology remains in its early stages of development. Although numerous studies highlight hydrogen's significant role in future energy systems, further advancements are needed to overcome existing barriers and accelerate its widespread adoption.

CONCLUSIONS

The synthesis of green hydrogen has obtained significant interest from researchers due to its economic potential and sustainability. To develop efficient systems for converting sunlight into valuable chemicals, a comprehensive understanding of chemical processes, transport phenomena, thermodynamics, electrochemistry, surface materials, and performance evaluation is essential. However, challenges remain in hydrogen storage, distribution, and transportation, which can hinder its widespread adoption as an energy source. Researchers worldwide are actively addressing these challenges, leading to continuous improvements. Significant progress has also been made to assist scientists in scaling up experimental lab-scale setups, contributing to the development of a cost-effective global hydrogen market.

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