Harnessing Solar Energy for Green Hydrogen Production in Algeria

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Abstract

The global energy sector remains the largest human-driven contributor to carbon dioxide emissions, making its transformation imperative in the fight against climate change. Transitioning to clean, renewable energy sources is not just an option—it is a necessity for a sustainable future. In this context, Algeria's exceptional solar potential presents a unique opportunity to maximize the efficiency of solar energy systems and accelerate the shift toward green solutions.

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Heterogeneous photocatalysis stands out as one of the most cost-effective methods for harnessing renewable energy and mitigating pollution. This study explores the potential of photocatalytic hydrogen (H_2) production—a game-changing clean energy solution that aligns with global decarbonization goals. Through light-driven water splitting, renewable hydrogen can be generated efficiently, offering a viable path to reducing greenhouse gas emissions. Despite extensive efforts in nanocomposite advancements, a major challenge persists: achieving high efficiency and selectivity in sunlight-driven catalytic hydrogen generation. Hydrogen, with its high energy density and zero-carbon footprint, represents a cornerstone for the clean energy transition. This study provides key insights for strategic investments in Algeria, identifying prime locations (with solar irradiance exceeding 100 mW cm^{-2}) for hydrogen production where solar energy can be harnessed at an unprecedented scale.

Keywords. Green hydrogen; Photocatalytic process; Solar energy; Renewable energy.

1. Introduction

Despite the dominance of traditional energy sources in the global energy market, there have been rapid advancements in both the quantitative and qualitative aspects of energy production and consumption [1]. This instability in energy markets is significantly impacted by numerous factors, such as the availability of reserves, energy prices, government regulations, and the actions of international energy organizations [2]. As a result, there is a noticeable global shift towards renewable energy, particularly solar power [3]. The most recent International Energy Outlook predicts a global increase in energy consumption within the industrial sector by 9% to 62%, while the transportation sector's energy consumption is anticipated to rise by 8% to 41% from 2022 to 2050 [4]. The control of fossil fuel usage is currently a significant challenge for governments, especially for countries like Algeria, where over 95% of the national income relies on hydrocarbon exports, making traditional energy sources crucial to its economy. In response, initiatives are underway to diminish the reliance of the electricity sector on fossil fuels and to diversify the economy in a sustainable manner [5].

Given that Algeria is not exempt from the challenges facing traditional energy sources; it has implemented strategies to harness its solar potential, advancing current and future projects to enhance both its utilization and export capabilities. Solar radiation, a plentiful supply of clean, renewable energy, is essential in tackling global energy and environmental issues [6]. Transforming solar energy into chemical energy is a highly efficient and economical method of harnessing solar power, offering a practical solution for energy storage and utilization. This process not only allows for the direct conversion of solar energy but also facilitates its transformation into fuels and chemicals, providing a sustainable pathway to meet global energy demands while reducing reliance and dependence on fossil fuels [7]. Hydrogen, often touted as a green fuel of the future, is not found in nature in significant quantities on Earth. However, it can be derived from renewable energy sources such as biomass [8], solar radiation [9], geothermal energy [10], and hydroelectric power [11]. In addition to these, hydrogen can also be recovered from other processes, making it a versatile and promising energy carrier [12].

Hydrogen is set to be a vital fuel and energy carrier of the future, with various applications across different sectors. Its combustion produces only water vapor, with no emission of greenhouse gases, positioning it as an eco-friendly alternative to conventional fuels. H_2 is used industrially for the production of methanol, hydrocracking in petroleum refineries, and synthesizing of ammonia and fertilizers [13]. Novel markets are developing for vehicles powered by hydrogen fuel cells [14], that produce electricity via an electrochemical reaction between hydrogen and oxygen from the air. Additionally, fuel cell systems for home heating are gaining a growing interest, further expanding the potential applications of hydrogen technology [15].

Photosynthesis has served as a fundamental process in nature for billions of years, supplying energy to the entire biosphere while regulating the levels of O_2 and CO_2 in the atmosphere. Similarly, photocatalytic water splitting represents a sustainable technology that produces green hydrogen, aligning with nature's approach to energy generation and environmental balance. Water splitting using solar radiation is one of the few promising carbon-free processes that can directly convert solar energy into chemical energy in the form of H_2. However, it is an endergonic reaction, characterized by a positive free energy change ($\Delta G°$) of +237 kJ mol^{-1} of H_2 produced under standard conditions (298 K, 1 atm) [16]. In this context, energy from sunlight is necessary to drive and catalyze the water splitting on low cost materials with small over-voltage [17, 18]. Solar hydrogen production can be classified into various ways based on the types of intermediate energy utilized. A solar hydrogen production plant will attain energy positivity only if the hydrogen-generating systems fulfill stringent efficiency and durability standards, ensuring that the energy input from sunlight is effectively converted and sustained over time.

Current research aims to enhance the performance, extending the lifetime and reducing the costs of H_2 production technologies, with the purpose of enabling large-scale implementation in the future. In this context, although various projects have been launched to invest in solar energy and explore export opportunities, Africa is still far from becoming a solar energy exporter.

Achieving this goal requires a strong and unwavering commitment to harnessing this clean, free, and renewable resource. This review explores the potential of green hydrogen production through solar photocatalytic processes, emphasizing Africa's immense solar energy advantage. With an abundance of sunlight, the continent has a unique opportunity to transform its solar exposure into a driving force for the clean energy transition. By conducting a comprehensive analysis of the technical and economic parameters of solar hydrogen production, this study highlights Africa's potential to emerge as a global leader in sustainable energy.

2. Hydrogen production pathways

As hydrogen production necessitates energy input, analogous to electricity generation, it is classified as a secondary energy carrier. The production of hydrogen invariably necessitates the utilization of primary energy sources. The primary energy sources that can be used for production of hydrogen include photoelectrochemical processes, electrochemical processes, biochemical processes, thermochemical processes or fuel processing processes [19-22].

Owing to the emerging demand of H_2 as a fuel, it is needed to increase its production. A broad spectrum of feedstocks, encompassing both fossil fuels and renewable resources, can be employed for hydrogen production. Hydrocarbon pyrolysis and hydrocarbon reforming are the main alternative methods available for hydrogen production compared to fossil fuels utilization. Biomass based process and water splitting are the techniques associated with renewable resources [23-25].

Water splitting is a two-step process, involving separate half-cell reactions: reduction of H^+ and H_2 (hydrogen evolution reaction (HER)) and the oxidation of the oxide ions to O_2 (oxygen evolution reaction (OER)), respectively, as given below for different pH conditions [26]:

$$2H^+(aq)+2e^- \rightarrow H_2 \ (E^0 = 0 \text{ V, pH } 0) \quad (1)$$

$$H_2O(l) \rightarrow \frac{1}{2}O_2(g)+2H^+(aq)+2e^-(E^0 = 1.23\text{V versus SHE, pH } 0) \quad (2)$$

$$2H_2O(l)+2e^- \rightarrow H_2(g)+2OH^-(aq)(E^0 = -0.83\text{V versus SHE, pH } 14) \quad (3)$$

$$2OH^-(aq) \rightarrow H_2O(g)+\frac{1}{2}O_2(g)+2e^- \ (E^0 = 0.40\text{V versus SHE, pH } 14) \quad (4)$$

The overall reaction is given by:

$$H_2O(l) \rightarrow H_2(g)+\frac{1}{2}O_2(g) \ (\Delta E = 1.23 \text{ V}) \quad (5)$$

The overall reaction of water splitting shows that external electricity input (equal to $\Delta G^0 = -$ n F $E^0 = 237$ kJ mol^{-1}) is required. Solar-powered water splitting is experiencing significant growth. Three primary solar-assisted methods are mainly used: photobiological, thermochemical, and photocatalytic [27-29]. The process carried by bacteria or algae under anaerobic conditions and light irradiation is referred to as photobiological water splitting method. However, it is not environmentally friendly due to the formation of carbon dioxide as a by-product. In thermochemical methods solar energy is captured using telecommunication devices. The captured solar energy is utilized for the temperature increase that facilitates the splitting of water. However, this method is not good because heat resistance devices are needed for practical applications. The photocatalytic splitting of water represents, instead, a hopeful approach for HER. Photocatalytic water splitting offers advantages over photobiological and thermochemical methods. The prominent ones include non-significant reactor systems, low-cost process and easy separation of H_2 and O_2.

3. Solar potential of Algeria

Solar energy provides a compelling alternative for electricity generation through photovoltaic technology. This transition not only lessens reliance on fossil fuels but also contributes to environmental preservation. Boasting the greatest solar potential in the Mediterranean region, estimated at 169,440 TWh annually, Algeria is ideally positioned for large-scale solar energy utilization [30]. The potential of Algeria's solar and wind resources has been subject to rigorous examination in the open literature. For example, Yaiche et al.[31] drawn a revised solar radiation maps for Algeria, identifying the province of Djanet as the area characterized by the highest levels of solar radiation. Kamel et al. [32] drawn up an updated map of solar irradiation in Algeria by leveraging data from the Modern-Era Retrospective Analysis for Research and Applications (MERRA-2) dataset. Belkhir et al. [33] introduced a novel methodology that integrates Geographical Information Systems (GIS) and the Analytical Hierarchy Process (AHP) to determine ideal locations for large-scale photovoltaic (PV) plants. Therefore, accurate solar irradiation data is the cornerstone of successful solar energy system design and management. Solar irradiation quantifies the amount of solar energy incident upon a unit area over a specified duration. The intensity of solar irradiation differs across regions and seasons and changes hourly due to the daily variations in the sun's elevation. The Solar-Med-Atlas, a freely accessible online database, was used to obtain Global Horizontal Irradiation (GHI) and Direct Normal Irradiation (DNI) data, which were validated against ground-based measurements across countries including Algeria. The database provides annual values, long-term monthly averages, and site-specific information to support the development of solar energy projects. As illustrated in **Fig. 1** [34], Algeria has a significant solar energy potential that varies considerably across different regions. The aggregate annual solar energy incident upon the earth at the sea level, also called the solar constant, is approximately 2 MWh/m² across most of Algeria's national territory. Additionally, the southern regions hold significant potential for harnessing solar resources for hydrogen production. Specifically, Tamanrasset and Illizi boast a high annual solar energy potential, with values of 2.4 MWh/m² and 2.2 MWh/m², respectively. The lowest annual solar energy availability is observed along the coastline and in certain northern regions, where it is approximately 1.6 MWh/m². This vast solar potential presents a strong case for utilizing solar energy in the hydrogen production, especially in regions with high solar irradiance. With such abundant solar resources, Algeria has the potential to assume a leadership role in green hydrogen production, thereby mitigating its dependence on fossil fuels and advancing global clean energy initiatives.

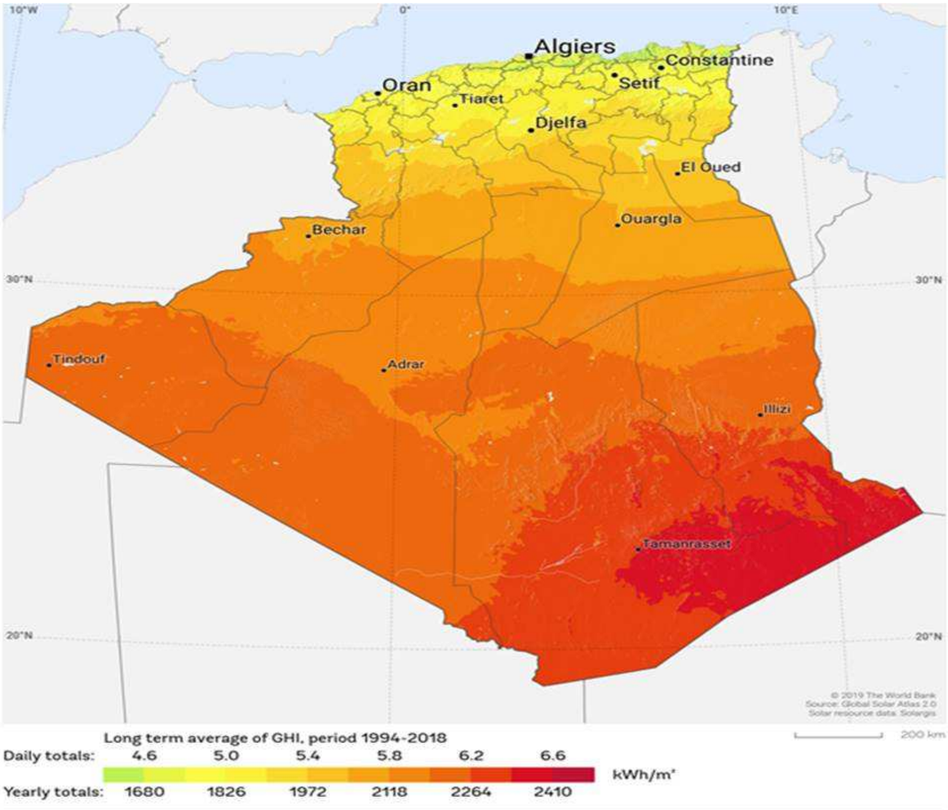

Fig.1. Global horizontal irradiation map (from Solar-Med-Atlas, a freely accessible online database).

4. Fundamental mechanism of photocatalysis in semiconductors

The photocatalytic process is initiated when a photocatalyst is exposed to light radiation of energy greater than its bandgap. When light is absorbed, electrons move from the valence band to the conduction band, creating electron-hole pairs and allowing charge separation [35, 36].

$$Semiconductor \xrightarrow{hv>Eg} e_{CB}^{-} + h_{CB}^{+} \qquad (10)$$

The photo-generated electron-hole (e^-/h^+) pairs subsequently move in different directions towards the surface of the photocatalyst giving rise to oxidation and reduction reactions (**Fig. 2**). Namely, in the presence of H_2O and O_2 hydroxyl radicals (•OH) are primarily produced by holes in the photocatalyst's valence band, whilst electrons in the conduction band reduce O_2 molecules to form superoxide radicals ($^{\bullet}O_2^-$). These reactive species then directly oxidize contaminant molecules in the solution. **Figure 2** illustrates the key processes involved in photocatalysis, highlighting the essential steps such as photon absorption, charge separation, and the generation of reactive species that drive oxidation and reduction reactions.

However, when e^-/h^+ recombination occurs the quantum yield decreases, reducing the overall photocatalytic efficiency.

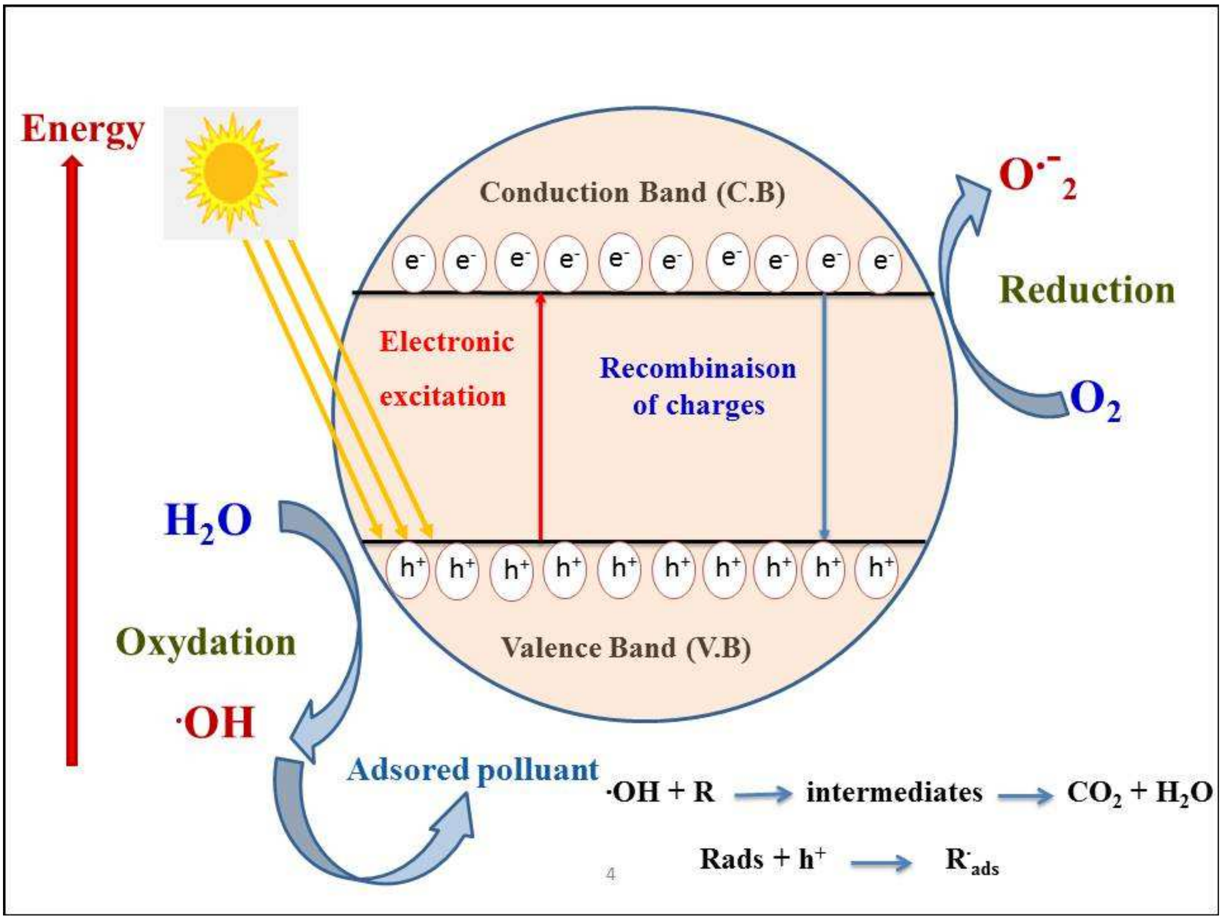

Fig. 2. Simplified mechanism of photocatalytic process.

5. Mechanistic Insights into Photocatalytic Water Splitting

When light hits the photocatalyst, it triggers a reaction that splits water to produce hydrogen [37]. The overall photocatalytic water-splitting process involves three key steps: (i) Absorption of photons with energy exceeding the bandgap of the semiconductor generates electron–hole pairs in the conduction band (CB) and valence band (VB), respectively. (ii) The photogenerated holes (h^+) participate in the oxidation of water, resulting in the release of protons (H^+) and molecular oxygen (O_2). (iii) The photogenerated electrons (e^-) migrate to the conduction band (CB), where they reduce protons (H^+) to produce hydrogen gas (H_2). A comprehensive understanding of heterogeneous photocatalytic water splitting necessitates insight into both the role of the photocatalyst and the function of sacrificial electron donors [38].

The "band gap" refers to the energy difference between the upper edge of the valence band (VB) and the lower edge of the conduction band (CB) in a semiconductor [39]. When a photocatalyst absorbs a photon with energy equal to or greater than its bandgap, it can initiate water splitting. However, the overall efficiency of this process is often limited due to low hydrogen yield, which is typically attributed to insufficient light absorption, rapid electron–hole recombination at the catalyst surface and semiconductors' suitable band edge energy.

To enhance the process efficiency, different strategies can be pursuit:

- The introduction of sacrificial electron donor agents capturing holes, thus facilitating a more efficient separation and utilization of charge carriers [40].
- the integration of co-catalysts as electrons sinker.The most effective species are generally noble metals such as Pt, Au, Ag.

Key factors influencing the bandgap potential—which is critical for efficient water splitting—include surface oxidation, available surface area, and ion adsorption. The overall mechanism of photocatalytic water splitting is illustrated in Figure 2. Thermodynamically, water splitting is an endothermic reaction that requires an energy input corresponding to a standard Gibbs free energy change ($\Delta G°$) of 237 $kJ \cdot mol^{-1}$. This translates to a minimum thermodynamic potential of 1.23 eV needed to drive the overall photochemical water splitting process [41]. Therefore, it is essential to employ an appropriate photocatalyst capable of generating electron–hole (e^-/h^+) pairs through the absorption of photons with sufficient energy. These charge carriers subsequently drive the redox reactions involved in the splitting of H_2O molecules.

The photocatalytic overall water splitting process faces several key challenges: (i) Many photocatalysts exhibit unfavorable band alignment, rendering them ineffective for complete water splitting. (ii) The oxygen evolution half-reaction is widely considered the rate-limiting step, primarily due to its complex mechanism involving a four-electron transfer and the removal of two protons to form an O–O bond, often leading to stoichiometric imbalances [42]. (iii) The recombination of photogenerated H_2 and O_2 on the catalyst surface—particularly on non-noble metals—further reduces efficiency, as the gases tend to react to reform water. At present, CdS-based photocatalysts achieve a maximum solar-to-hydrogen (STH) conversion efficiency of only 1.63%, which remains insufficient for practical applications [43].

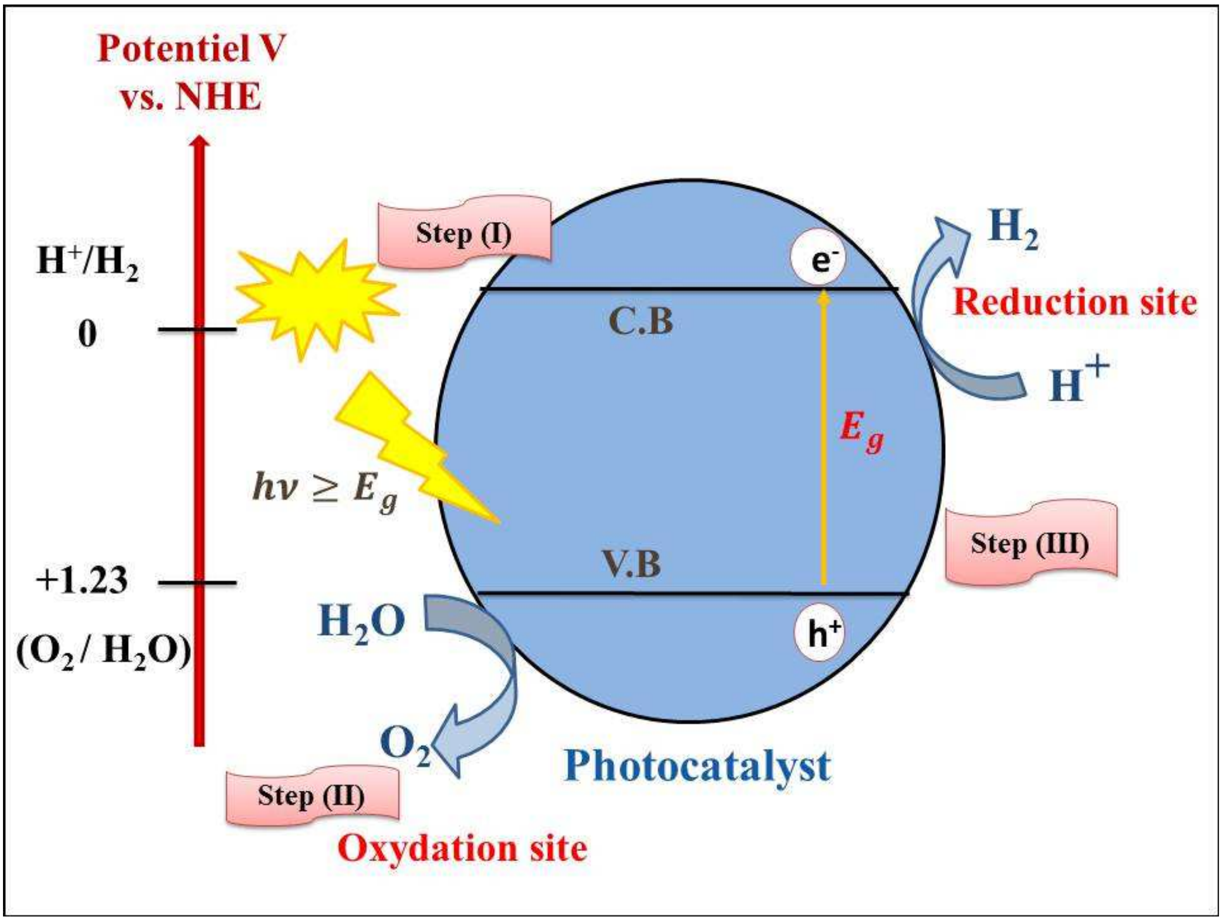

Fig. 3: Photocatalytic water splitting.

To achieve photocatalytic water splitting using solar energy, semiconductors like TiO_2 [44], $ZnCo_2O_4/ZnO$ [45], $SrTiO_3$ [46], $SrTiO_{3-\delta}$ [47], Mo_2C [48], $CuFeO_2$ [49], MoS_2/Ni_3S_2 [50], Pt/CuO [51], CuO [51] CuO/Activated carbon [52], CdS [53, 54], WO_3 [55], $CuIn_3Se_5/WO_3$ [56] etc. have obtained much attention.

Several modification approaches, including doping [35, 57], sensitization [58, 59], supported materials [60, 61] and the creation of hybrid composites, have been explored to enhance the performance of semiconductors in terms of both productivity and exploitation of sunlight. To date, in excess of 130 materials and their derivatives have been synthesized for the photocatalytic generation of H_2 and O_2, often employing external redox agents [62]. A combinatorial approach has been developed and demonstrated to be an effective approach for the expeditious selection of photocatalyst materials [63-65].

A semiconductor irradiated with a light flux Φ of energetic photons (E_g > hν) generates a photocurrent given by:

$$J_{ph} = e\,\Phi \left\{ \frac{1 - e^{\left[(E - E_{fb})^{1/2}\right]}}{1 + \alpha\, L_d} \right\} \quad (6)$$

where $\boldsymbol{e}$ is the electron charge, α the absorption coefficient of the semiconductor and δ the width of the space charge region and $\boldsymbol{L_d}$ the diffusion length; the width δ is given by:

$$\delta = \left(2\,\varepsilon\,\varepsilon_0\,\Delta U / e\, N_{A/D}\right)^{0.5} \quad (7)$$

ΔU is the optimal band bending, $N_{A/D}$ is the carrier density, ε the permittivity of the semiconductor, ε_o the permittivity of vacuum. Expression (7) is simplified for $\alpha L_d << 1$, and the photocurrent (J_{ph}) is given by:

$$J_{ph} = \int_0^{\infty} e\,\Phi \left\{1 - e^{-\alpha\delta (E - E_{fb})^{1/2}}\right\} \quad (8)$$

and the conversion yield is expressed by: η = 1.23 J_{ph}. The decomposition voltage of H_2O (1.23 V) comes from the free enthalpy ΔG° (= 2FΔE) of H_2O formation (= +237.19 kJ mol^{-1}), $\boldsymbol{F}$ is the universal constant (= 96485 C mol^{-1}).

If the potential is progressively varied, the photocurrent starts to flow for E_{on}> E_{fb} (resp. <E_{fb}) for ***n***-type (resp. ***p***-type). Here, E_{on} refers to the onset potential—the minimum external bias at which a measurable photocurrent is observed, indicating the activation of charge carrier separation and transport under illumination.

In the absence of sub-band states within the gap region, E_{on} can be assimilated to the flat band potential and this technique can be used to estimate the band bending at the solid/liquid interface. Another main issue to consider is the dissolution potential (E_d), i.e. the potential at which the semiconductor begins to degrade due to oxidation by its own photogenerated holes. Potential-driven dissolution and photo-corrosion are critical concerns for photocatalysts, as they can lead to catalyst deactivation over time. Several studies have attributed the decline in photocatalytic activity to self-oxidation processes, often linked to the chemical or photo-induced dissolution of the semiconductor material [66, 67]. Ensuring the stability of photocatalysts is essential, especially when they are used in corrosive environments. For example, Rao et al. [68] observed a gradual decrease in hydrogen production in a UV-irradiated ZnO/water suspension, which was attributed to the photocorrosion of ZnO.

If the standard potential for the anodic dissolution of the semiconductor, E_d is more negative than E_{VB}, h^+ can also cause oxidation of the crystal. The primary oxidation product, then, will depend on the relative rate of the two competing h^+ reactions. In other words, If E_d is more cathodic than the O_2/H_2O couple level, the material can undergo photo-corrosion, and this is true for small band gap binary semiconductors (M_xO_y):

$$M_xO_y + H_2O \rightarrow M^{x+}_{aq} + y/2\ O_2 + x\ e^- \qquad (9)$$

The photocatalyst's structure and surface modifications are crucial factors that affect the recombination of e^-/h^+ pairs, directly influencing the overall efficiency. The separation of charge carriers is improved by the interfacial electric field, with a band bending of approximately 0.5 V being optimal for the complete separation of the photogenerated charges. In photocatalytic systems devoid of external circuits, electric fields can be generated either through the inherent anisotropy of the photocatalyst's crystal structure or via the formation of semiconductor-semiconductor junctions (***p-p, n-n or p-n***) [69]. The advantageous effects of junctions have been shown to occur both between semiconductors of disparate chemical compositions and between various crystallographic phases of the same chemical composition. These junctions improve charge separation and enhance photocatalytic performance [70].

In photochemical water splitting, the hole-driven oxidation reaction constitutes the rate-determining step, thereby significantly impeding the overall efficiency of the water-splitting process. The low solar-to-hydrogen efficiency is frequently ascribed to a difference between the internal quantum efficiency of photon-excited hole generation and the apparent quantum yield for hydrogen production. The loss of photo-generated holes is undesirable but inevitable. Despite significant advancements, we are still far from mastering the challenges associated with these wasted holes and their chemical consequences, which remain one of the major bottlenecks in achieving high solar-to-hydrogen efficiency.

The low efficiency of hydrogen production in semiconductors with an otherwise suitable band gap is thought to result from several factors: 1) Rapid electron-hole recombination phenomena can occur both within the bulk of semiconductor particles and on their surfaces, diminishing the overall efficiency of the process, this recombination of electron-hole pairs results in a diminished quantum efficiency during the photocatalytic process [71]. 2) Fast oxygen-hydrogen back reaction on the catalyst surface, leading to the reformation of water and reducing hydrogen yield [72], and 3) The significant limitation of inefficient visible light utilization, as photo-generated electrons tend to quickly recombine with holes within the semiconductor, reducing overall photocatalytic efficiency [73].

Loading noble metals onto the semiconductor can help suppress charge recombination to some extent by forming a Schottky barrier, which facilitates charge separation and improves photocatalytic efficiency [74, 75]. More frequently, a diverse range of sacrificial agents, including inorganic salts and organic compounds, are introduced into the reaction medium to efficiently prevent charge recombination and enhance quantum efficiency [76]. The separation of hydrogen gas from oxygen is imperative, as both gases are generated concurrently during the photocatalytic process. If not properly managed, this can result in safety issues and a reduced hydrogen yield. The separation of H_2 and O_2 can be accomplished through a photoelectrochemical system, in which hydrogen and oxygen are produced at separate electrodes.

6. Hydrogen as a Sustainable Energy Source and Its Existing Production Methods

Hydrogen is undoubtedly the fuel of the future and, as mentioned earlier, is currently produced using several methods, including reforming of methanol [77] and methane [78], partial oxidation [79], plasma cracking [80], auto-thermal reforming [81] are not only expensive but also lead to the emission of greenhouse gases. Approximately 95% of hydrogen is produced globally through steam reforming [82, 83]. The production of hydrogen from fossil fuels contributes to a rise in greenhouse gas emissions [84, 85]. On the other hand, non-reforming processes like gasification [86], biological [87], dark fermentation [88] can only give a low production and therefore not well-suited. As a result, due to the numerous disadvantages associated with these hydrogen production methods (**Table 1**), they are not financially feasible for large-scale applications. Renewable H_2 production is a promising approach that integrates renewable energy sources. These methods not only help in generating hydrogen but also support sustainability by reducing reliance on fossil fuels and minimizing environmental impact [89]. Therefore, it is crucial to identify a hydrogen production process that is both cost-effective and environmentally friendly, ensuring long-term sustainability and reduced environmental impact.

7. Need for solar renewable energy in Algeria

In Algeria, hydrocarbons play a pivotal role in the nation's economic development. Algeria ranks as Africa's leading producer of natural gas, the continent's third-largest oil producer, and the second-largest supplier of natural gas to Europe. However, the production of crude natural gas and crude oil has steadily declined in recent years (Fig. 4), primarily due to repeated delays in new production projects and infrastructure development. In response to the declining fossil fuel output and the need to diversify the energy mix, Algeria launched the National Program for the Development of Renewable Energy 2011–2030 as a strategic shift toward sustainable energy solutions. The National Program for the Development of Renewable Energy 2011–2030, adopted by the Algerian government in February 2011, initially focused on implementing pilot and test projects across various available technologies. Insights gained during this phase, particularly regarding technological advancements in the energy sector, prompted a revision of the program.
Many technologies of renewable energy exist, including solar [90], biomass [91], wind [92], waste to energy [93] and co-generation bagasse [94] and hydrogen can be generated from renewable energy sources through various pathways and techniques [95]. Therefore, numerous research has been carried out on hydrogen production using solar energy. Boudries [96] assessed the H_2-production at various sites in Algeria using an electrolyzer integrated with a concentrating photovoltaic system.

Currently, solar energy is utilized in many ways, e.g. heating [97], cooking [98], electricity generation [99, 100], desalination [101], drying [102] …etc. Among these applications, electricity generation stands out as a significant and primary sector. Solar cells are primarily utilized for generating solar electricity [103, 104]. However, photochemical production requires several sequences with a low yield of the order of 1% [105] while the thermochemical decomposition of water into hydrogen and oxygen requires high temperatures (2200 K) with a high recombination rate of these two gases [106].

Given that Algeria receives abundant sunlight nearly year-round [31, 107], it is crucial to maximize the utilization of this solar energy for hydrogen production via the photocatalytic process. This renewable method provides an excellent approach for producing hydrogen through the photocatalytic process. Hydrogen recovery through renewable solar photocatalytic technology offers a more advantageous alternative to the Claus process. As a tropical country rich in solar energy resources, Algeria should focus on utilizing this renewable energy source for hydrogen production through the photocatalytic process in a cost-effective manner.

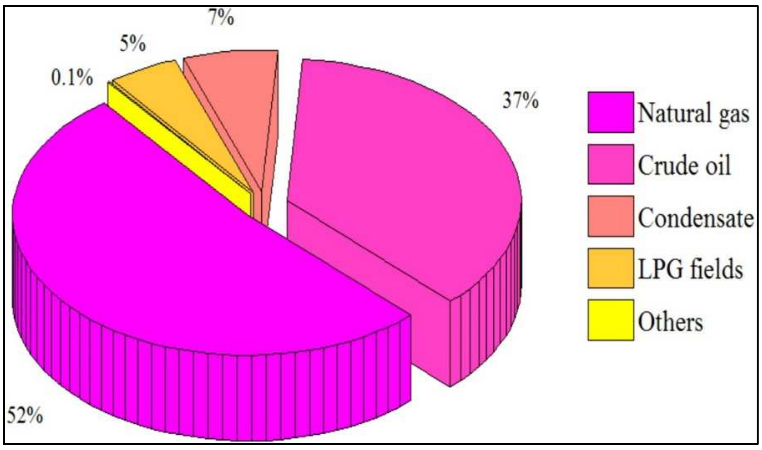

Fig. 4. The production of primary energy in Algeria [108]

8. Solar photocatalytic H_2 production

The band gap is a key characteristic of nano-photocatalytic materials, as it dictates the amount of solar energy that can be absorbed and converted for photovoltaic [109] or storable form namely hydrogen [110]. Wide band gap semiconductor oxides are attractive for photocatalytic hydrogen H_2-production because of the high stability and a conduction band (CB) enough cathodic to reduce water. However, the quantum efficiency is low unless other strategies are used. Semiconductors with wider band gap demonstrate greater stability compared to those with smaller gap, but tend to have low hydrogen production efficiency under solar light due to their limited ability to absorb visible light [111] and small carrier mobility [112]. Thus, combining semiconductors with different band gaps is an effective strategy for developing photocatalysts that offer both high activity and good stability, optimizing solar energy absorption and improving H_2 production [113]. In coupled semiconductors, excited electrons are transferred from the more negative CB of one semiconductor to the less negative CB of the other semiconductor, resulting in more efficient separation of photogenerated electron–hole (e^-/h^+) pairs, which enhances photocatalytic performance. Improved solar photocatalytic H_2 production using coupled semiconductors encompasses a broad spectrum of oxides, sulfides and phosphates: CdS/TiO_2 [111], WO_3/ SiC–TiO_2 [114], Pt/TiO_2/activated carbon [115], Ta_2O_5/TiO_2 [116], and $CuO/Al_2O_3/TiO_2$ [117], TiO_2/g-C_3N_4 [118], $Bi_2MoO_6/Mn_{0.2}Cd_{0.8}S$ [119], Pt–g-C_3N_4–(Au/TiO_2) [120], Zn-doped $CuInS_2$ [121] which have been investigated for the unbiased water splitting.

9. Photoreactor used for solar photocatalytic H_2 production

Photoactivity depends on the geometry of the photoreactor and its engineering. Numerous investigations into photocatalytic water splitting assess the performance of photocatalysts in magnetically agitated tank reactors. In these reactors, a catalyst suspension is irradiated through a quartz or glass window, and the gaseous byproducts are gathered using a manifold connected to the reactor. Typically, the slurry volume is under 1 L, with less than 1 g of photocatalyst producing only a few millimoles of hydrogen per hour. The rate of hydrogen evolution in a photocatalytic process is contingent upon not only the activity of the photocatalyst but also the design of the photoreactor [122]. Ideally, a photo-reactor should efficiently absorb incident light to facilitate photo-reactions while minimizing photonic losses. The design of large-scale photoreactors for hydrogen generation is fraught with numerous technical challenges and cost considerations. A key challenge is the development of efficient photocatalysts that operate under visible light, which accounts for ~ 45% and which has seen significant progress in recent years [35, 123-125]. Another critical issue pertains to the effective use of solar light, which is closely tied to the design of the photocatalytic reactor.

Researchers have investigated two primary types of photoreactors at the laboratory scale: slurry photoreactors and immobilized photoreactors. The landmark paper by Doede and Walker (1955) [126] marked a pivotal moment in the evolution of photoreactor analysis and design, setting the stage for future advancements. **Table 4** presents a list of various photocatalytic reactors utilized for hydrogen recovery from water. A well-designed solar photocatalytic reactor is essential to efficiently convert incident solar light photons into chemical energy. Despite the extensive published research on photocatalysis, much of it focuses on the exploration of photocatalysts and the analysis of their kinetics [127]. However, limited information is available on the configuration, design, and scalability of photoreactors.

To address the scalability challenges associated with photocatalytic hydrogen production, a pilot-scale photoreactor was employed to evaluate the solar-driven reforming of biomass-derived compounds using Cu_2O–TiO_2 (P25) photocatalysts synthesized via a facile ball milling method [41]. Unlike typical laboratory-scale setups, this system featured a 10 L stainless-steel storage tank coupled with a 14.25 L Compound Parabolic Collector (CPC) inclined at 37°, offering a total sun-exposed surface area of 2.10 m². Operated at the Plataforma Solar de Almería (latitude: 37.0909° N, longitude: 2.357° W), the photoreactor enabled testing under real. TiO_2 based composites with varying Cu_2O content were synthesized by adjusting milling speed and duration. The optimal sample—3% Cu_2O–P25 milled at 150 rpm for 2 hours—demonstrated the highest photocatalytic performance, yielding approximately 94 mmol of hydrogen, which is six times greater than that produced by pure P25. This sample also achieved a solar-to-hydrogen (STH) conversion efficiency of 1.71% using glycerol as a sacrificial agent. Glycerol outperformed glucose and ethanol due to its lower redox potential, simpler structure, and higher number of hydroxyl groups, which facilitated faster oxidation and more efficient electron transfer. However, increasing the Cu_2O loading beyond 3% was found to hinder light absorption by blocking the TiO_2 surface, thereby reducing photocatalytic efficiency. These findings underscore the significance of optimizing both photocatalyst composition and reactor design to enable efficient green hydrogen production from biomass derivatives at pilot scale.

For semi-pilot applications requiring large-scale production (in cubic meters per hour), a scale-up of at least 1,000 times is necessary. While the low activity of photocatalysts has typically been seen as the primary barrier to the practical implementation of this technology, the engineering aspects of the problem have received insufficient attention. In our opinion, these engineering challenges are equally important and complex large-scale operations necessitate the evacuation and recharging of reactors, resulting in extended periods of downtime and significant variations between batches due to the highly non-linear nature of heat and mass transport, particularly in wet chemical processes. Consequently, continuous processes are favored for industrial production. During laboratory evaluations of photocatalysts, an even slurry distribution is achieved through vigorous magnetic stirring, enhancing light absorption and mass transfer for the H_2-production. However, mechanical stirring is impractical for large-scale operations due to high energy costs. Continuous flow reactors, especially tubular reactors with solar concentrators, have been successful and larger-scale applications, leveraging experience from solar thermal engineering. Recent studies have shown an improvement in apparent quantum efficiency (AQE) using fluidized bed reactors, although they require larger photocatalyst beads.

Sub-atmospheric operation and sacrificial reagents are common to avoid reverse reactions, but can incur energy penalties. Therefore, photoreactor designs must maximize solar exposure, which leads to increased capital costs and material challenges, especially for UV transparency. To concentrate sunlight, various reflector geometries are used, which allow for smaller reactor sizes but potentially decrease quantum efficiency due to increased recombination of (e^-/h^+) pairs.

Conclusions

This review highlights the immense potential of hydrogen production via solar water splitting as a cost-effective and environmentally sustainable pathway for green energy generation. While various hydrogen production methods exist, most are energy-intensive and generate toxic by-products. In contrast, solar photocatalysis presents a clean and efficient alternative, leveraging abundant sunlight to drive hydrogen recovery from water without harmful emissions. Algeria's vast solar resources make this approach particularly promising, offering a sustainable and economically viable solution for large-scale hydrogen production. The dual benefits of solar heterogeneous photocatalysis—zero waste generation and minimal external energy input—position it as a key player in the global transition to clean energy. With ongoing advancements in photocatalytic reactor design, the field has made remarkable progress. Beyond laboratory-scale studies, research efforts are expanding toward large-scale implementation, bringing solar hydrogen production closer to economic feasibility. However, critical challenges remain. Maximizing solar-to-hydrogen conversion efficiency, ensuring the long-term stability of materials, and achieving consistent large-scale performance are the key hurdles to overcome. Addressing these limitations will be essential to unlocking the full potential of solar-driven hydrogen production and positioning it as a cornerstone of the global clean energy landscape.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used Open AI / chatGPT in order to improve language and readability. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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Table. 1. Methods for hydrogen generation

N°	Methods	Process	Disadvantage	Ref.
1	Steam reforming	It is utilized in industrial processes to extract hydrogen by separating it from carbon within methane molecules.	Result in greenhouse gas emission	Tong et al.[128], HARYANTO et al. [82]
2	Methanol Reforming	Methanol can also be reformed to produce hydrogen in a process similar to ammonia reforming but at lower temperatures	Results inCO_2 emissions, dependency on fossil-derived methanol, and catalyst degradation, which increase costs and limit sustainability	Mei Deqing et al. [129]
3	Partial oxidation	Converts methane and limited oxygen into syngas, producing hydrogen.	production of toxic carbon monoxide, the requirement for high temperatures, and the potential formation of by-products like CO_2 and soot	Osman et al. [130], Kumar et al. [131]

4	Ammonia reforming	$2NH_3 \rightarrow N_2 + 3H_2$ $(500\ °C\ and\ 250\ atm)$	high temperatures, catalyst deactivation, nitrogen by-products, and ammonia's toxicity	Kim et al. [132], Yousefi et al. [133],
5	Pyrolysis	The hydrocarbons are broken down into hydrogen and carbon without the involvement of water or air.	Buildup of carbon fouling	Vuppaladadiyam et al. [134], Alvarez et al. [135], Brandon José Leal Pérez et al. [136]
6	Gasification	The process of gasifying biomass at a temperature of 1400 °C involves heating organic materials in an oxygen-limited environment to produce valuable gases such as hydrogen, carbon monoxide, and methane.	High costs, feedstock variability, complex cleanup, lower efficiency, and CO_2 emissions.	Chang et al. [86], Asadullah et al. [137]
7	Dark fermentation	Anaerobic bacteria use biomass waste to produce hydrogen.	Hydrogen pressure increases, H_2 production decreases	Łukajtis et al. [138], Guo et al. [88]
8	Coal cracking	Coal gasification produces hydrogen by breaking down coal into syngas, but it generates significant CO_2 emissions,	Carbon-intensive process, releasing significant greenhouse gases and relying on	Boruah et al. [139]

		making it less environmentally friendly compared to renewable hydrogen production methods.	finite fossil fuel resources, which limits its environmental sustainability.	
9	Biological	Certain algae and bacteria produce hydrogen.	Large-scale production has not yet been demonstrated.	Das et al. [27], Gavala et al. [140]
10	Photobiological	Microbes harness solar energy to facilitate the reaction of water with iodine and sulfur dioxide, yielding hydrogen iodide and sulfuric acid, which are subsequently thermally decomposed to generate hydrogen and oxygen.	Large-scale production has not been established.	Poudyal et al. [141], Ghirardi et al. [142], Dasgupta et al. [143]
11	Photochemical	Utilize solar thermal energy to drive a cycle that converts water into hydrogen.	High cost	Reverberi et al. [144], Lei et al. [145]
12	Biophotolysis	Biological systems, such as microbes and bacteria, are utilized to produce H_2.	low efficiency, slow production rates, environmental sensitivity, complexity in	Javed, Muhammad Asad, et al. [146]

			cultivation, contamination risks, limited substrate range, by-product formation, and scalability challenges.	
13	Photofermentation	Fermentation process triggered by light exposure.	Low hydrogen yield, reliance on specific microorganisms, sensitivity to light conditions, complexity in maintaining optimal growth conditions, risk of contamination, potential by-product formation, and challenges in economic viability.	Adessi et al.[147]
14	Microwave-assisted methane pyrolysis	This method uses microwaves to heat methane in a reactor, resulting in the separation of hydrogen and solid carbon.	requires further development to reach commercial viability and improve efficiency	Deng, Wenyi, et al. [148]

15	Electrolysis	Electrolysis, to facilitate the electrolysis of water into hydrogen and oxygen using electricity, is most efficient when paired with renewable energy sources.	Electrolysis faces challenges due to high costs, energy demands, and reliance on stable renewable power, hindering large-scale, cost-effective green hydrogen production.	Zeng, Kai, and Dongke Zhang [149]
16	Solar-to-Fuels or Artificial Photosynthesis	This process imitates natural photosynthesis by using solar energy to break down water molecules and produce hydrogen.	Low efficiency, high production costs, scalability issues, and dependence on sunlight availability	HL. Tuller [150]

Table 2. Hydrogen production through photocatalysis using different catalysts.

N°	Catalyst	Sacrificial agent	H_2 produced	Ref.
1	$ZnFe_2O_4/SrTiO_3$	$Na_2S_2O_3$	9.2 $cm^3\ h^{-1}$	Boumaza et al. [151]
2	$FeGaO_3$	H_2S	2945 µmol/h	Subramanian Esakkiappan et al. [152]
3	AMn_2O_4 (A=Cu and Zn)	Na_2S	0.089286 µmol/h	Bessekhouad and Trari [153]
4	CdS/ZnS/n-Si	Na_2S / Na_2SO_3	1584.821 µmol/h	Atif and Musa [154]
5	CuM_2O_4 (M=Al, Cr, Mn, Fe and Co)	Na_2SO_3	3.6 ml $h^{-1}\ g^{-1}$	Saadi et al. [155]
6	CuO/ZnO	Na_2SO_3	340 µmol $h^{-1}\ g^{-1}$	Haddad Meriem et al. [156]
7	Mg doped MnO_2	Na_2SO_3	506.67 µmol $h^{-1}\ g^{-1}$	Laksaci et al. [35]
8	La_2NiO_4/SnO_2	Na_2SO_3	15.1 µmol $g^{-1}min^{-1}$.	Laouici et al. [157]
9	3% CuO/TiO_2	Glycerol	0.17 mmol $h^{-1}\ g^{-1}$	Pecoraro, Claudio M. et al. [158]
10	CNT/Cerium doped TiO_2	sulphide wastewater	14,500 µmol/h	Raja, M. Anthony, and V. Preethi [159]
11	Cu_2MoS_4	Na_2S / Na_2SO_3	4.25 µmol	Liang Huirong and Liejin Guo [160]

12	MoS_2 peroviskite based composit	HI / H_3PO_2	13.6 mmol g^{-1} h^{-1}	Zhao, Xiaole, et al. [161]
13	N-doped $ZnIn_2S_4$	Na_2SO_4	1575.71 µmol·g^{-1}	Chong, Wei-Kean, et al. [162]
14	$CuFe_2O_4$/g-C_3N_4	Na_2S / Na_2SO_3 / TEOA	700 µmol/h	Mehtab Amir et al. [163]
15	$CuLaO_{2.62}$	Na_2SO_3	0.465 mL/h per mg	Koriche N., A. Bouguelia and M. Trari. [164]
16	Pt/$SrTiO_3$/TiO_2	Oxalic acid	5.1 mmol g cat^{-1} h^{-1}	Yan Jian-Hui et al. [165]
17	SnO_2/TiO_2	Methanol	Up to 1000 µmol in 12 h	Sasikala R. et al. [166]
18	TiO_2/CuO	Methanol	8.24 $mmolh^{-1}g^{-1}$	Jong Min Kum et al. [167]
19	Pt/TiO_2	Glucose	1700 µmol in 7 h	Marianna Bellardita et al. [168]
20	SiO_2/TiO_2/g-C_3N_4	Not mentioned	686.83 $\mu molh^{-1}g^{-1}$	Sijia Sun et al. [169]

Table 3. Phtocatalytic reactor types

N°	Types of reactor	Sacrificial agent	Experimental conditions	Important findings	Ref.
1	200 mL Pyrex cell	Na_2S	Xenon lamp 500 W. Photocatalyst used : 0.1 g $Cd_{0.44}Zn_{0.56}S$. Aqueous solution (0.35 M Na_2SO_3 and 0.25 M Na_2S)	Highest H_2 recovery rate 2640 µmol/h/g was achieved without any co-catalysts.	Wang et al. [170]
2	Cylindrical reactor	Na_2S	Mercury lamp 400 W. Photocatalyst used : CuO/CdS. 500 mL in 0.175 mol Na_2S and 0.125 mol Na_2SO_3	238 µmol/h of hydrogen production was achieved	Cheng et al. [171]

3	4L Trapezoidal reactor	H_2S	Direct solar light and LED lamp 7W. Photocatalyst used : 0.2 g/L CNT doped $dZnS - Fe_2O_3$	Direct solar irradiation results in a maximum hydrogen production of 450 mL, corresponding to a quantum yield of 100%. Artificial light gives 60 mL at quantum yield of 23.5 %.	Anthony and Preethi [172]
4	50 mL photocatalytic reactor	H_2S	300 W Xe lamp with a cut-of flter (k>420 nm). 50 mL Na_2S (0.1 mol/L) and Na_2SO_3 (0.6 mol/L) solution as well as 2.5 mg MnS/In_2S_3	The introduction of PdS into the MnS/In2S3 composite significantly enhances the hydrogen production rate of the system, reaching 22.7 $mmol.g^{-1}\ h^{-1}$ with a maximum apparent quantum efficiency of 34% at approximately 395 nm.	Li et al. [173]
5	100 mL Batch reactor	Na_2S	tungsten flament lamp 300 W Photocatalyst used : 0.03 g PbS–MCM-41 and 30 ml of an aqueous solution (0.02 M of Na_2S)	The hydrogen evolution rate was significantly enhanced to 30 mmol/(gh) with the incorporation of PbS, representing a 15-fold increase compared to bulk PbS (2 $mmol.g^{-1}\ h^{-1}$).	Pourahmad [174]
6	600 mL a double-jacketed Pyrex reactor	Na_2SO_3	3 tungsten lamps, each of 200 W	3.6 ml $h^{-1}\ g^{-1}$	Saadi et al. [155]

			Photocatalyst used : CuM_2O_4 (M = Al, Cr, Mn, Fe and Co)		
7	40-mL doublewalled Pyrex reactor	$Na_2S_2O_3$	300-W halogen lamp 50 mg of photocatalyst at pH 13.6 in 40 mL of 0.1 M $Na_2S_2O_3$ Photocatalyst used : $CuGaO_2$	Maximum H_2 production 4300 µmol/h	Gurunathan, K., et al. [175]
8	19-mL Pyrex vial	Na_2S	450-W Xe lamp Photocatalyst used : ZnS/SiO_2 and CdS/SiO_2	The silica-supported catalyst exhibited significantly greater activity than both ZnS/SiO_2 and CdS/SiO_2 in an aqueous solution of 0.1 M Na_2S	Ueno A. et al. [176]
9	14.25 L parabolic Collector	Biomass : glycerol and ethanol	Solar light Photocatalysts used : Cu_2O/P25 prepared by ball milling at 150 rpm (2h)	The 3%Cu_2O-P25 sowed the maximum production rate with 94 mmol of H_2	Umair et al. [41]