Review

Synthesis and Performance of Photocatalysts for Photocatalytic Hydrogen Production: Future Perspectives

Salvador Escobedo and Hugo de Lasa *

Chemical Reactor Engineering Centre (CREC), Faculty of Engineering, Western University, 1151 Richmond Street, London, ON N6A 5B9, Canada; sescobe@uwo.ca
* Correspondence: hdelasa@uwo.ca; Tel.: +1-519-661-2144; Fax: +1-519-850-2931

Abstract: Photocatalysis for “green” hydrogen production is a technology of increasing importance that has been studied using both TiO$_2$–based and heterojunction composite-based semiconductors. Different irradiation sources and reactor units can be considered for the enhancement of photocatalysis. Current approaches also consider the use of electron/hole scavengers, organic species, such as ethanol, that are “available” in agricultural waste, in communities around the world. Alternatively, organic pollutants present in wastewaters can be used as organic scavengers, reducing health and environmental concerns for plants, animals, and humans. Thus, photocatalysis may help reduce the carbon footprint of energy production by generating H$_2$, a friendly energy carrier, and by minimizing water contamination. This review discusses the most up-to-date and important information on photocatalysis for hydrogen production, providing a critical evaluation of: (1) The synthesis and characterization of semiconductor materials; (2) The design of photocatalytic reactors; (3) The reaction engineering of photocatalysis; (4) Photocatalysis energy efficiencies; and (5) The future opportunities for photocatalysis using artificial intelligence. Overall, this review describes the state-of-the-art of TiO$_2$–based and heterojunction composite-based semiconductors that produce H$_2$ from aqueous systems, demonstrating the viability of photocatalysis for “green” hydrogen production.

Keywords: green hydrogen; photocatalysts synthesis; electron/hole scavengers; energy efficiencies; artificial intelligence

1. Introduction

Today, the increased energy demands of a growing world population, as well as the need to drastically reduce the environmental impact of energy production, represent a major technical challenge [1,2]. These higher energy demands lead to the overexploitation of nonrenewable resources, such as oil and natural gas, and to a steady increase in greenhouse gas emissions, which may result in both health problems [3] and climate change [4,5].

Recent studies recommend the use of hydrogen as a “green energy fuel”. Hydrogen is the simplest and most abundant element in the universe, and yet it is not easily available on the planet. Hydrogen does not occur alone naturally, and can always be found combined with other elements, such as water and organic compounds [6,7]. Furthermore, hydrogen is high in energy density (120–143 MJ/kg), with this being approximately three times greater than in fossil fuels [8–10].

Hydrogen is a very important chemical for numerous chemical industries. It is believed that hydrogen could provide a future source of energy for the residential, transportation, and industrial sectors [11,12]. Unfortunately, approximately 95% of the hydrogen generated today requires the use of fossil fuels, such as methane, for its production [13,14]. Thus, the development of clean renewable technologies for hydrogen production is needed to provide the clean energy that is so urgently needed.

In recent years, photocatalytic hydrogen production has attracted the attention of the scientific community because it is a new sustainable technology that can generate...
green hydrogen from near-UV and visible light (i.e., solar energy) [15–18]. Furthermore, hydrogen can be produced by using photocatalysis, which removes a wide range of organic pollutants from water, such as phenols, ketones, alcohols, alkenes, carboxylic acids, and others compounds [19]. However, to be a viable source of energy, and for its successful implementation, green hydrogen production from photocatalysis needs to overcome important technical barriers [11,14]: (a) It must be economically competitive and scalable, as compared to other available technologies that generate hydrogen from nonrenewable sources; and (b) It must produce hydrogen with high photon conversion efficiency [20].

Fujishima and Honda [21] were the pioneers of photocatalytic water splitting. These researchers discovered that TiO$_2$ and Pt behave as the anode and cathode in a photoelectrochemical cell, respectively, splitting water into hydrogen and oxygen, under UV irradiation. This concept has been broadly applied to the development of TiO$_2$-based semiconductors that are used to produce hydrogen from water, under both near-UV and visible light [22]. One should note that TiO$_2$-based semiconductors are environmentally friendly, reliable, corrosion-free, photostable, and inexpensive materials [23–26]. Photocatalysis for hydrogen production is also a process that is simple to engineer and that operates at near to atmospheric pressure and temperature. On this basis, it is believed that photocatalysis for hydrogen production, using TiO$_2$-based semiconductors, could provide, in the short term, a valuable alternative energy source for isolated communities around the world.

However, hydrogen production rates using TiO$_2$ are still low and the photon efficiencies must be enhanced. In this respect, photocatalytic efficiencies can be improved by: (a) Increasing the semiconductor specific surface area [27,28]; (b) Depositing or doping metals (Pt, Pd, Au, Rh, Ag, Ni, Cu, Co) [29–39] or nonmetals (N or S) [40,41] on the TiO$_2$ photocatalyst; (c) Coupling TiO$_2$ with other semiconductors [42–44]; (d) Dye-sensitizing TiO$_2$ [45–48]; and (e) Adding chemical additives or sacrificial agents (i.e., electron/hole scavengers) to the aqueous photocatalytic suspension [49–53]. These anticipated changes to photocatalysts for hydrogen production are of great importance to radically increase the “green” hydrogen availability.

Sacrificial agents (SAs) can transform the thermodynamically inhibited water splitting reaction ($\Delta G^0 = 237$ KJ mol$^{-1}$) into a feasible reaction for hydrogen production [58]. As a result, the addition of e$^-$/h$^+$ scavengers allows the hydrogen production to proceed, with an increase in the photon utilization efficiency. There are two types of e$^-$/h$^+$ SAs: (a) Organic chemical species (hydrocarbons, alcohols, and organic acids); and (b) Inorganic chemical species (sulfides, sulfites, iodates, iodides). These e$^-$/h$^+$ SAs have the following functions: (1) They capture photogenerated holes (h$^+$), which minimizes the probability of e$^-$/h$^+$ recombination; (2) They suppress the formation of water (back reaction), avoiding water splitting with O$_2$ production; and (3) They act as additional sources of protons [59,60]. Organic sacrificial agents are likely the ones with better chances of being adopted, given their permittivity and oxidation potential [60]. Furthermore, the use of SAs for hydrogen production must also be evaluated vis-à-vis of their availability and cost. For instance, organic chemicals from biomass waste, or, alternatively, ethanol obtained from the fer-
mentation of agricultural residues, may offer good and inexpensive options as sacrificial agents [41,61–64].

Hydrogen production via photocatalysis must be evaluated on the basis of photon utilization using quantum yields (QYs). QYs represent the ratio of the moles of hydrogen radicals (H\(^{\bullet}\)) produced, over the moles of photons absorbed [27,65,66]. With regard to the moles of photons absorbed, they can be calculated using macroscopic irradiation energy balances (MIEB) [67–69]. Furthermore, the hydrogen production efficiencies can be gauged using the photocatalytic thermodynamic efficiency factors (PTEFs), which determine the photon energy utilization efficiency [39,70]. In this respect, both QYs and PTEFs have become the standard key parameters for the evaluation of photocatalytic reactors for hydrogen production. These parameters provide a comprehensive basis from which to establish the optimal design and operation of scaled-up photocatalytic reactors units [28,71–74].

Photocatalysis for hydrogen production, as well as for other applications, has been impacted by artificial intelligence (AI). This new cognitive system is usually demonstrated with two subsets: machine learning (ML), or artificial neural networks (ANNs) [75]. ML or ANN models can be evaluated by considering the photocatalytic process inputs and the desired outputs, leading to more informed and accurate decisions. Furthermore, these methods can consider unstructured experimental data, which allows for accurate predictions for complex and large-scale chemical processes [76]. In photocatalysis for hydrogen production, these techniques can lead to identifying the optimal operational parameters required to obtain the maximum hydrogen generation [77]. This is critical for the future scaling up of “green hydrogen” technologies.

This review reports and compares the most up-to-date research and background information on photocatalysis for hydrogen production. Special emphasis is given to new approaches in photocatalysis accounting for sacrificial agents, reaction networks, kinetic models with included adsorption phenomena, energy efficiency, and possible AI applications. Our objective is to provide a comprehensive guide, as a reference for future research, in the field of photocatalytic hydrogen production.

2. Synthesis and Characterization of Heterojunction Composite Photocatalysts for Hydrogen Production

This section reviews the most widely studied photocatalysts and designed heterojunction semiconductors, including those that are based on TiO\(_2\), sulfides (CdS, CuInS\(_2\)), graphite carbon nitride (g-C\(_3\)N\(_4\)), and perovskite (La\(_2\)Ti\(_2\)O\(_7\)). Our objective is to identify the semiconductors that are more responsive to visible light, and the ones that are most effective for photocatalytic hydrogen generation. Appendix A Table A1 and Appendix B Table A2 report the morphologies, the optical properties, the H\(_2\) reaction rates, and the energy efficiencies of different photocatalysts.

2.1. TiO\(_2\)-Based Photocatalysts

TiO\(_2\) is one of the most commonly studied materials in photocatalysis. This oxide semiconductor material is not consumed during the photoinduced reaction and assists in accelerating chemical reactions by absorbing photons on its surface. Then main features that influence the activity of a photocatalyst are set during the synthesis of the semiconductor. These include: (1) Wavelength activation; (2) Resistance to mechanical stress and photocorrosion; (3) Crystallinity; and (4) Surface properties [71,78,79].

TiO\(_2\) naturally exists in three different microcrystal structures, including rutile, anatase, and brookite [80–82]. Table 1 reports: (a) The band gap energy (E\(_{BG}\)), the difference between the valence band (VB) and the conduction band (CB); and b) The wavelength activation required to excite TiO\(_2\), in its various polymorphic phases. E\(_{BG}\) can be estimated with Equation (1). Thus, the E\(_{BG}\) determines the photon energy required to activate a photocatalyst, promoting excited electrons (e\(^{-}\)) to move from the VB to the CB. Furthermore, the result-
ing \((e^-/h^+\) pairs migrate to the surface of the semiconductor and initiate photocatalytic reduction/oxidation reactions with adsorbed organic species (refer to Figure 1) [6,71].

\[ E_{BG}(eV) = \frac{1240}{\lambda(nm)} \] (1)

Table 1. \(\text{TiO}_2\) polymorphic phases as described via physical and optical properties [6,82].

| Semiconductor Phase | Crystalline Form | Density (g cm\(^{-3}\)) | Wavelength (nm) | Band Gap Energy (eV) |
|---------------------|-----------------|-------------------------|----------------|---------------------|
| Rutile              | Tetragonal      | 4.27                    | 413            | 3.0                 |
| Anatase             | Tetragonal      | 3.90                    | 388            | 3.2                 |
| Brookite            | Orthogonal      | 4.13                    | 365            | 3.4                 |

Figure 1. Schematic diagram of the \(\text{TiO}_2\) particle activation with photons and through the photocatalytic oxidation (O)/reduction (R) process.

\(\text{TiO}_2\), however, presents two main drawbacks: (1) The photoactivation is limited, given that it can only use 4 to 5% of the sunlight spectrum; and (2) The recombination rate of \((e^-/h^+)\) pairs is relatively quick, even though the light absorption time (ca. \(10^{-15}\) s) occurs faster than the recombination time (ca. \(10^{-10}\) s) [81]. To address these issues, the \(\text{TiO}_2\) has been modified by combining different methods and preparation steps, such as the impregnation/doping with metals [65,83,84] and nonmetals [85], the preparation of composite materials containing \(\text{TiO}_2\) heterojunctions [86], the control of the polymorphic phases [87], and porosity (micro or meso) [27,66,88,89].

Escobedo et al. [65] loaded platinum (Pt) particles onto \(\text{TiO}_2\) Evonik Degussa-P25 (DP25), designated as Pt/DP25, using the incipient wetness impregnation method to improve both the semiconductor optical properties and the agglomerate particle size distribution. First, DP25 was dried at 140 °C for 6 h, to desorb the water and other gas species. Following this, hexachloroplatinic acid hydrate (\(\text{H}_2\text{PtCl}_6 \times H_2\text{O}\)) was dissolved in 4 mL of distilled water. Next, a first 2 mL of Pt solution volume was added dropwise on 5 g DP25. The resulting slurry was dried at 140 °C for 2 h, and fine ground. Then, the remaining 2 mL of promotor solution was further impregnated on the \(\text{H}_2\text{PtCl}_6/\text{DP}25\) precursor. The resulting powder was dried at 160 °C for 3 h, and then calcined at 450 °C for 3 h to ensure chlorine removal. Finally, the samples were reduced using an \(\text{Ar}/\text{H}_2\) (90/10% Praxair composition) gas blend at 1 cm\(^3\) s\(^{-1}\), in a flow reactor unit, and heated at 400 °C for 3 h. This method allowed for the obtainment of well-dispersed metallic Pt\(^0\) particles, formed on the \(\text{TiO}_2\) outer surface. A similar wetness impregnation method was employed by Bahruiji et al. [90]. These authors loaded different Pd amounts on DP25 by dissolving \(\text{PdCl}_2\) in 1.5 mL of deionised water. This was acidified at a pH of 1, using a HCl solution. Then, the precursor solution was added dropwise onto 2 g of DP25 powder. The samples were dried at 120 °C for 2 h, followed by 3 h of calcination at 500 °C [91]. Montoya et al. also used a DP25 surface-modified semiconductor. These authors loaded DP25 with copper...
(Cu) and nickel (Ni), at different metal loadings, by using a UV photodeposition method, in a methanol solution. The prepared solution was degassed with Ar. This was performed to favor the reduction conditions of the DP25 photocatalysts loaded with Cu and Ni.

Guayaquil-Sosa et al. [27] proposed a sol-gel method to synthesize a new mesoporous TiO2 (mpTiO2) semiconductor and obtained an improved photocatalyst surface area and pore size. These authors employed pluronic F-127 as a structure-directing template, as well as titanium (IV) isopropoxide, ethanol, citric acid, hydrochloric acid, and a hexachloroplatinic acid hydrate dopant as reagents for the solution. The doped sol-gel phase was loaded with different Pt amounts and agitated for 24 h. Then, it was calcined gradually at 550 °C for 6 h. The resulting doped mesoporous powder was designated as x wt.% Pt/mpTiO2-550 °C, where x was the loaded amount of metallic Pt. A similar sol-gel method was employed by Rusinque et al. [88]. However, in this case, a palladium (II) chloride (H2(CdS:ZnS:DP25). This resulted in a designated photocatalyst which was synthesized by template synthesis, in a blend of titanium butoxide (Ti(OBu)4), ethylene glycol, acetone, distillate water, and acetic acid. This was stirred at 35 °C for 3 h, resulting in a precipitate of titanium glycolate. Then, the resulting slurry was filtered, washed, and dried overnight at 110 °C. The mixture was purged with N2 for 15 min to remove dissolved or adsorbed oxygen. Next, the sample was stirred at 500 rpm, and irradiated for 3 h with a 20 W Black-Ray mercury lamp to achieve Pt photodeposition. Finally, the Pt/DP25 photocatalyst was filtered, washed, and dried overnight at 110 °C.

Rayees Ahmad et al. [92] prepared a mesoporous Cu-TiO2 (mpCu-TiO2) photocatalyst for H2 production that was shown to be active under direct solar irradiation. This photocatalyst was first synthesized by template synthesis, in a blend of titanium butoxide (Ti(OBu)4), ethylene glycol, acetone, distillate water, and acetic acid. This was stirred at 35 °C for 3 h, resulting in a precipitate of titanium glycolate. Then, the resulting slurry was stirred at 80–100°C for 8 h, and washed with H2O and ethanol. Following this, it was dried at 100 °C, and finally calcined at 250 °C for 5 h to produce mesoporous TiO2 (mpTiO2). The deposition of copper nanoparticles (Cu NPs) was achieved by wet impregnation. A total of 100 mg of mpTiO2 was suspended in 10 mL of water and sonicated for 10 min. The 3 wt.% Cu NP loadings were added to the suspension and stirred for 24 h. Finally, the mpCu-TiO2 photocatalyst was separated by centrifugation and dried at room temperature.

Similarly, Choi and Kang [93] synthesized a TiO2 photocatalyst with an anatase structure using a sol-gel method, and added Cu particles while utilizing the impregnation method. Ruban and Sellappa [94] also synthesized core-shell nanoparticles (NPs) by using a Cds-ZnS/DP25 photocatalyst. This photocatalyst was developed in two steps: (1) Through the hydrothermal synthesis of TiO2; and (2) By the coprecipitation of Cds-ZnS NPs on TiO2. First, 500 mL of 0.1M of cadmium acetate and zinc acetate were mixed and stirred. Next, 3.5 g of DP25, 7.6 g of thiourea, and 0.2 M of Na2S were added to it. The formed crystals were separated by ultracentrifugation, washed thoroughly (deionized water and isopropanol), and dried at 110 °C. The final weight ratio of this new photocatalyst was 1:1:1 (Cds:ZnS:DP25).

Rivero et al. [95] prepared a Pt/graphene-TiO2-based photocatalyst in order to improve the photocatalytic properties of simple TiO2-based materials for H2 production. First, the polyol method was employed for the synthesis of Pt/DP25. Then, the Pt precursor (H,6PtCl6,6H2O) and DP25 were slurred in ethylene glycol. The resulting suspension was mixed, stirred, and heated at 140 °C for 2 h. The residual solids were washed, recovered by centrifugation, and dried overnight at 50 °C. Then, the synthesis of 5 wt.% of rGO/DP25
was developed using a hydrothermal method. In this case, DP25 was added to a reduced graphene oxide (rGO) solution, stirred for 2 h, and then maintained at 120 °C for 3 h (in a Teflon-lined stainless-steel autoclave). The remaining particulate material was recovered by centrifugation, rinsed, washed with ultrapure water, and dried overnight at 50 °C. The solid powder was designated as a Pt/rGO/DP25 photocatalyst. Other photocatalysts have also been studied for the preparation of junction materials, such as NiO (p-type)/TiO₂ (n-type) for photocatalytic hydrogen production.

Ruixia Lui et al. [96] and Fujita et al. [97] loaded NiOₓ on TiO₂. To accomplish this, TiO₂ powder (Catalyst So. of Japan) was doped using an impregnation method: 1 g of TiO₂ was dispersed in a 10-mL Ni(NO₃)₂ solution at 0.15 M. The formed slurry was continuously stirred during an overnight period to ensure adequate impregnation. Then, it was dried at 80 °C for 12 h and ground. Finally, the resulting powder was calcined at 450 °C for 3 h, under a flow of air of 50 cm³, to obtain the NiOₓ/TiO₂ photocatalyst.

Sadanandam et al. [98] prepared a cobalt (Co)-doped DP25 photocatalyst for H₂ production under solar light irradiation. These authors synthesized the photocatalyst by using the impregnation method. DP25 was added to a 1 wt.% cobalt (Co(CH₃COO)₂·4H₂O) solution in distilled water. The solution was constantly stirred under slow heating to evaporate excess water till dryness was obtained. Then, the dry powder was calcined at 400 °C in 5 h. Finally, the photocatalyst was reduced using a 30% H₂/N₂ gas blend at 450 °C for 5 h. These procedures allowed the Co (II) formation on the DP25 surfaces.

Another subject of critical importance for H₂ production is the particle concentration of various TiO₂-based photocatalysts. The following, Figure 2, reports the importance of the photocatalyst particle concentration, used to produce H₂ at different experimental conditions, as previously explained in this section.

**Figure 2.** H₂ Production with various photocatalyst particle concentrations using different TiO₂-based photocatalysts. Notes: (1) bars report hydrogen production; (2) red crosses show photocatalyst concentration (g/mL); and (3) various photocatalysts are referred to with numbers, as reported in Appendix A Table A1.

### 2.2. Assorted Frames (No TiO₂)-Based Photocatalysts

Recent studies report the development of graphitic carbon nitride (g-C₃N₄) [55–57,99–101] and sulfide-based (CdS, CuInS₂) [40,102–104] photocatalysts. Although metal sulfides usually present photocorrosion issues, their strong visible light absorption, narrow band gaps, and excellent electronic charge transfer have attracted significant researcher attention [58]. Wang et al. [60] studied Zn₀.₅Cd₀.₅S and g-C₃N₄. These materials were prepared in several steps. First, a solution of diethylthiocarbamate trihydrate (DDTC) was prepared to form Cd(DDTC)₂ and Zn(DDTC)₂. These two chemicals were equimolarly mixed in 100 mL of oleylamine (80–90%). The resulting slurry was stirred, heated at 240 °C (at 5 °C/min), and
kept for 1h under a N\textsubscript{2} atmosphere. The resulting blend was later separated by centrifugation, and the formed precipitate was washed with ethanol. The products were collected and stored using cyclohexane. Following this, 35 mL of acetic acid was added to form Zn\textsubscript{0.5}Cd\textsubscript{0.5}S. The formed slurry was stirred for 10 h, in a heating bath at 70 °C, with the photocatalyst precursor, which was initially hydrophobic but became hydrophilic. In the case of the formed g-C\textsubscript{3}N\textsubscript{4} powder, fine melamine powder was added. The resulting solid blend was heated up to 550 °C (at 2.5 °C/min) and kept for 4h under a N\textsubscript{2} atmosphere.

Katsumata et al. \cite{105} synthesized a WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} photocatalyst by a simple calcination method for hydrogen generation (refer to Figure 3). A commercial Aldrich reagent of tungsten trioxide (WO\textsubscript{3}) nanoparticles was used. The formation of g-C\textsubscript{3}N\textsubscript{4} powders was obtained by heating urea at 500 °C for 2 h, in a covered alumina crucible, at a heating rate of 20 °C/min. Further heating treatment was performed at 520 °C for 2 h. The acquired product was cooled down to room temperature, fine ground, and collected. The WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} photocatalyst was prepared by blending and grinding WO\textsubscript{3}, with g-C\textsubscript{3}N\textsubscript{4}, in an agate mortar for 30 min. The resulting powder mixture was calcined at 450 °C for 4 h, with a temperature ramp of 20 °C/min and was then fine ground again. Jiang et al. \cite{106} also prepared a g-C\textsubscript{3}N\textsubscript{4}-based photocatalyst, but loaded it with silver sulfide (Ag\textsubscript{2}S) by employing the precipitation method. The g-C\textsubscript{3}N\textsubscript{4} was synthesized by thermal treatment. A total of 10 g of urea was dried at 80 °C for 24 h. Then, the precursor was calcined at 550 °C for 4 h, at a heating rate of 2.3 °C/min. The resultant yellowish powder was washed twice with nitric acid [0.1M], and three times with deionized water and absolute ethanol. The final product was dried at 60 °C for 12 h. The Ag\textsubscript{2}S/g-C\textsubscript{3}N\textsubscript{4} photocatalyst was prepared in situ, at room temperature. With this end, 0.092 g of g-C\textsubscript{3}N\textsubscript{4} powder and Ag\textsubscript{2}S were dispersed (depending on the x wt.% desired) in 50 mL of absolute ethanol, and were ultrasonicated for 20 min. Next, thioacetamide (TAA) was incorporated into the mixture, and was stirred for 4 h. The final product was collected by centrifugation, washed with distilled water and absolute ethanol, and dried at 60 °C, for 12 h, to obtain the Ag\textsubscript{2}S/g-C\textsubscript{3}N\textsubscript{4} photocatalyst.

Z. Shen et al. \cite{107} successfully prepared cadmium sulfide (CdS) nanocrystals, embedded in molybdenum trioxide (MoO\textsubscript{3}) core-shell nanospheres, for both H\textsubscript{2} production and photodegradation under visible light irradiation. These authors used a sonochemistry method at room temperature and normal pressure, with no templates or surfactants required. The synthesis of MoO\textsubscript{3}/CdS was carried out at different molar ratios. A mixture of Cd(AC)\textsubscript{2} 2H\textsubscript{2}O [3 mmol], (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24} 4H\textsubscript{2}O [0.0143 mmol], and thioacetamide [6.2 mmol] was dissolved in 8 mL of acetone. The mixed solution was immersed in the reaction solution and sonicated at room temperature for 1 h. During the selected reaction
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with titanium disulfide (TiS$_2$) and tantalum (IV) sulfide (TaS$_2$). The TiS$_2$ was prepared with a blend of Ti metal and sulfur powder. The blend was then heated at 800 °C for 72 h. In the case of the TaS$_2$, a commercial powder was used (Alfa Aesar, 99.8% metal basis). The few-layers of TaS$_2$ and TiS$_2$ were formed by soaking 1 g of metal disulfides in 3.5 mL of n-butyl lithium [1.6 M] in a 12-mL hexane solution. The solution was heated at 27 °C for 72 h. Next, the samples were exfoliated by ultrasonication in distilled water, in a closed vial, for 4 h. The suspension was centrifuged, and the resulting solid product was collected. The resulting product was washed and centrifuged with ethanol three times, and dried in air.

Other authors, such as Gupta et al. [108], developed two CdS-based photocatalysts with titanium disulfide (TiS$_2$) and tantalum (IV) sulfide (TaS$_2$). The TiS$_2$ was prepared with a blend of Ti metal and sulfur powder. The blend was then heated at 800 °C for 72 h. In the case of the TaS$_2$, a commercial powder was used (Alfa Aesar, 99.8% metal basis). The few-layers of TaS$_2$ and TiS$_2$ were formed by soaking 1 g of metal disulfides in 3.5 mL of n-butyl lithium [1.6 M] in a 12-mL hexane solution. The solution was heated at 27 °C for 72 h. Next, the samples were exfoliated by ultrasonication in distilled water, in a closed vial, for 4 h. The suspension was centrifuged, and the resulting solid product was collected. The few-layer TaS$_2$ and TiS$_2$ nanocomposites, together with the CdS nanoparticles, were prepared by adding 10 mL of sodium sulfide (Na$_2$S) [0.1 mM] to 10 mL of cadmium acetate (Cd(CH$_3$COO)$_2$) [0.1 mM], and stirring this mixture steadily until it resulted in a precipitate material. The formed precipitate was centrifuged and dried at 60 °C. To prepare the nanocomposite photocatalyst of Ti(Ta)S$_2$/CdS, with a mass ratio of 1:1.4, 10 mg of TaS$_2$ or TiS$_2$ was dispersed in 10 mL of water by sonication for 1 h. Then, [0.1 mM] of Cd(CH$_3$COO)$_2$ was added to it, and the mixture was mixed for 8 h, followed by the addition of [0.1 mM] Na$_2$S in 10 mL of water. The final product, which consisted of yellow CdS particles, was centrifuged and dried in air at 60 °C for 12 h.

S. Chen et al. [109] synthesized a CuNi@C=O/g-C$_3$N$_4$ photocatalyst for hydrogen production, which was found to be active under visible light. The preparation for this photocatalyst started with the development of CuNi@C=O nanoparticles. In order to obtain these, a blend of 0.755 g of copper (II) nitrate (Cu(NO$_3$)$_2$ 3H$_2$O), 1.210 g of nickel (II) nitrate (Ni(NO$_3$)$_2$ 6H$_2$O), and 1.876 g of tartaric acid (C$_4$H$_6$O$_6$) was stirred in 20 mL of deionized water to form solution A. Next, 5 g of polyethylene glycol was dissolved in a mixture of 48 mL glycerol, and 12 mL of water to produce solution B. The two solutions (A and B) were mixed and sonicated for 1 h, until a uniform blend was reached. Then, this new solution was transferred into a hydrothermal reactor, and kept at 150 °C for 2 h. The resulting product was washed and centrifuged with ethanol three times, and dried at 100 °C. Finally, the dried sample was calcined at 800 °C for 2 h, under an inert Ar atmosphere, in order to obtain black CuNi@C=O (CN) nanoparticles. The CN samples with different concentrations of Cu and Ni were achieved by adding two different mole ratios of Cu(NO$_3$)$_2$ 3H$_2$O and Ni(NO$_3$)$_2$ 6H$_2$O. The g-C$_3$N$_4$ material was prepared by a calcination method, with 20 g of urea being placed in a crucible and calcined in air, at 600 °C for 2 h, resulting in a pale-yellow powder. Then, the CuNi@C=O/g-C$_3$N$_4$ photocatalyst was developed using a grinding-calcination-grinding method. Typically, to obtain this material, CuNi@C=O and g-C$_3$N$_4$ were ground in an agate mortar for 1 h, and then calcined under a N$_2$ flow at 150 °C for 2 h, and finally ground again.

Other types of photocatalysts, such as Fe/Al$_2$O$_3$-MCM-41 and In$_2$O$_3$/Ta$_2$O$_5$, were also studied and developed as efficient materials for hydrogen production, under visible light. Pradhan et al. [110] synthesized the mesoporous (mp) Fe/Al$_2$O$_3$-MCM-41 photocatalyst by sol-gel, followed by the application of an incipient wetness impregnation method. The mp-Al$_2$O$_3$ was prepared by using sucrose as a template. In order to obtain the mp-Al$_2$O$_3$-MCM-41, mp-Al$_2$O$_3$ was incorporated into the MCM-41. A surfactant consisting of cetyltrimethylammonium bromide (CTAB, C$_{15}$H$_{31}$NBr), and a source of silica consisting of tetraethyl orthosilicate (TEOS, C$_4$H$_{10}$O$_4$) were used. The Si/Al ratio in the mp-Al$_2$O$_3$-MCM-41 material was maintained at 10. The preparation of MCM-41 was adopted from Trens et al. [111]. The loads of x wt.% iron (Fe) were introduced onto the mp-Al$_2$O$_3$-MCM-41 by using an incipient wetness impregnation method, using a ferrous sulphate (FeSO$_4$) solution. Finally, the Fe/Al$_2$O$_3$-MCM-41 photocatalyst was calcined at 600 °C for 6 h.

Leilei et al. [112] formulated the indium (III) oxide/tantalum (V) (In$_2$O$_3$/Ta$_2$O$_5$) photocatalyst for hydrogen production. The tantalum pentoxide (Ta$_2$O$_5$) microphases were prepared by adding 0.4 g of Ta$_2$(OC$_2$H$_5$)$_6$ to 10 mL of ethylene glycol in a N$_2$ chamber,
while stirring for 8 h at room temperature, until the formation of a transparent solution was obtained. Then, the solution was poured into a bath of 100 mL of acetone, containing 0.5 vol.% of water, and was stirred for 10 min. After aging for 30 min, the obtained white precipitate was removed by centrifugation. It was then washed with ethanol and deionized water (threefold). Finally, the resulting clean material was dried in a vacuum oven at 60 °C for 24 h to obtain well-dispersed Ta$_2$O$_5$ microspheres. To acquire the resulting photocatalyst of In$_2$O$_3$/Ta$_2$O$_5$, an amount of 0.22 g of Ta$_2$O$_5$ microspheres was ultrasonically dispersed in 50 mL of water for 10 min. Next, an $x$ amount of indium nitrate (In(NO$_3$)$_3$ $n$H$_2$O) was added to this, while stirring at ambient temperature. To obtain a precipitate, a solution of ammonia was added with constant stirring until the pH > 9. Subsequently, the obtained precipitate was separated by centrifugation, and washed with ethanol and deionized water. Then, the resulting solids were dried at 60 °C for 24 h and annealed at 800 °C for 2 h to obtain a white powder of In$_2$O$_3$/Ta$_2$O$_5$ photocatalyst.

Figure 4 reports the hydrogen evolution and the photocatalyst particle concentrations for different heterojunction composite photocatalysts. For codes for different photocatalysts, refer to Appendix B Table A2.

![Figure 4](image_url)

**Figure 4.** H$_2$ Production and photocatalyst concentrations employed by different heterojunction composites. Notes: (1) bars represent hydrogen production; (2) cross-marks describe photocatalyst concentration (g/L); (3) for codes for various photocatalysts, refer to Appendix B Table A2.

In summary, this section reports the great diversity in the currently employed methods used to synthesize new TiO$_2$-based and heterojunction composite photocatalysts for hydrogen formation, at near ambient temperature and pressure. These photocatalysts have the important property of being active under both near-UV and visible light irradiation. It is our view that TiO$_2$-based photocatalysts are significantly more effective than heterojunction-based composites. In principle, the preparation methods for the TiO$_2$-based photocatalysts are simpler, and the photochemical reaction for H$_2$ production uses both small concentrations of photocatalyst loadings and less costly scavenger reagents (e.g., organic pollutants or ethanol at low concentrations). These features, we believe, make TiO$_2$-based photocatalysts preferable for the development of new semiconductor materials and for reaction processes for the photocatalytic production of hydrogen.

### 3. Photocatalytic Reactors for Hydrogen Production

A central issue in the development of new technologies for hydrogen production is the availability of suitable kinetics. The rate equations that are involved in such kinetic modeling should allow one to evaluate the energy efficiencies and the photocatalytic reactor scale-up. In addition, and for a successful reactor scale-up, the following is recommended: (a) Homogeneous and uniform reactor light irradiation distribution; (b) A significant
number of absorbed photons promoting $e^−/h^+$ formation; and (c) Adequate mixing flow conditions for the slurry.

Given the above, photocatalytic reactors can be classified using the following criteria: (1) The type of irradiation used; (2) The position of the light sources; and (3) The photocatalyst deposition method [71]. Thus, and to address this matter, several photocatalytic reactor configurations and light sources are described in this literature review. These descriptions are accompanied by a comparison of their various photoreactor performances, as relevant for the degradation of different organic compounds with hydrogen production.

3.1. Type of Light Source

Photocatalytic hydrogen production relies heavily on the light source used. Most of the experimental data reported in this review were produced using different types of synthetic light sources, such as near-UV lamps and visible light lamps, which provide a limited fraction of the sun spectrum. Photocatalytic reactors using sunlight are, in principle, the best ones, given that the sun is a renewable source of photon energy (refer to Figure 5).

![Figure 5. Solar energy spectrum distribution. This figure is reproduced with the permission of Catalysts, an MDPI research journal [113].](image)

Table 2 summarizes the wavelength and power of an assortment of different types of commercial lamps, which are regularly employed for photocatalytic processes, including hydrogen generation, air purification, and water/wastewater pollution oxidation, and are reported in the technical literature.

3.2. Location of Light Source

Photoreactor design and performance are influenced by the position and the location of incident light sources. Figure 6a–d report the photon flux irradiation patterns when using different types of light irradiation distributions. In photoreactors, the effect of radiation in Pyrex transmission walls is a minor one (less than 10% for near-UV), as documented in [27,39,71].

Figure 6a,b describe two possible tubular reactor configurations: (a) a single-lamp annular unit; and (b) a multilamp annular unit. These units show an enhanced photon absorption, with transmitted photons being transported through inner or outer lamp sources [115]. Furthermore, one can also see that the symmetrical light irradiation distributions facilitate the evaluation of the photons absorbed via the calculation of the macroscopy irradiation energy balances [39,65,66,116,117].

On the other hand, Figure 6c,d show asymmetric light irradiation distributions. These light irradiation distributions are typical of photoreactor units using sun irradiation, with
asymmetrical light irradiation making the evaluation of the absorbed light irradiation much more complex [118–121].

Table 2. Wavelengths and powers of different types of commercial light sources used in photocatalytic reactors for water and air treatment, as well as for hydrogen generation processes.

| Reference | Lamp Type                        | \(\lambda\) = Wavelength (nm) | Nominal Output Power (W) |
|-----------|----------------------------------|--------------------------------|--------------------------|
| [60]      | Xe lamp                          | \(\lambda \leq 420 \) or \(\lambda \geq 420\) | 300                      |
| [114]     | Xe arc lamp                      | Simulated solar light          | 300                      |
| [103]     | High-pressure Hg lamp            | -                              | 400                      |
| [27,65,66]| USHIO polychromatic blacklight blue (BLB) | 340 to 410                   | 15                       |
| [88]      | Hg Philips visible light lamp     | 300 to 700                     | 15                       |
| [90]      | Hg lamp Ace-Hanovia              | -                              | 450                      |
| [93]      | Shinan UV-lamp                   | 365                            | 180                      |
| [75]      | Black-Ray mercury lamp           | 340 to 410                     | 20                       |
| [94]      | Philips Sun-lamp                 | 400 to 700                     | 100                      |
| [95]      | Philips PL-S                     | 315 to 400                     | 9                        |

Figure 6. Light sources in photocatalytic reactors can be placed as follows: (a) internal-annular radial irradiation (top view); (b) external-annular radial irradiation (top view); (c) external-side radial irradiation (top view); and (d) top axial irradiation (side view). Cylindrical geometries are not exclusive, and rectangular geometries can also be applied [122–125].
Furthermore, it is important to mention that the photocatalytic reactor efficiency depends on the irradiation distribution on the photocatalyst surface. This irradiated photocatalyst surface can be available in a photoreactor as: (1) A film or; (2) Suspended particles in a slurry [113].

### 3.3. Experimental Photocatalytic Reactors for the Photocatalytic Production of Hydrogen

Escobedo et al. [65] employed a Photo-CREC Water-II (PCW-II) reactor to photodegrade organic pollutants and to produce hydrogen. This reactor includes an inner Pyrex glass tube with a black light blue lamp of 15 W, with an emission range of 340–410 nm placed inside the inner tube. This photoreactor configuration produces a radial and axial symmetric radiation field. The PCW-II unit operates at standard room conditions (pressure and temperature), with a slurry solution being recirculated with a centrifugal pump in an annular space between the inner lamp in the Pyrex tube and an outer opaque polyethylene tube, resulting in fluid dynamic conditions without mass transfer processes limiting the overall photoconversion rate [71]. It also involves a sealed mixed hydrogen storage tank. The main reactor components and accessories are described in Figure 7. This system also facilitates the spectroradiometer measurements to obtain the macroscopic irradiation energy balances. Prior to the experiments, 0.9 g of a slurried photocatalyst was sonicated. This was performed to ensure good particle distribution, before the slurry was poured into a 6-L solution in the hydrogen storage tank. The 6-L solution was prepared with 2 vol.% ethanol (electron/hole scavenger) in water, and tested at different pH concentrations: 4, 7, and 10. The pH solution was adjusted to the level of 4, with 1-mL aliquots of H₂SO₄ [2M]. This acidic process in the 2 vol.% ethanol solution with DP25 (TiO₂) or 1 wt.% of Pt/TiO₂ (DP25) photocatalysts, resulted in the best hydrogen-producing conditions, yielding up to 202 µmol and 1536 µmol of hydrogen, respectively, during 6 h of irradiation time. The pH of 4 in the aqueous solution appears to promote a high concentration of H⁺ ions, favoring water dissociation and the formation of hydronium ions. Furthermore, the excess of protons absorbed on the photocatalyst can interact more easily with the produced and stored electrons, boosting H• radicals formation and, consequently, hydrogen production [65,126].

Figure 7. Schematic representation of the PCW-II reactor: (i) annular internal reactor view with lamp and photocatalyst slurry suspension; (ii) external tubular reactor view; and (iii) hydrogen storage tank view. Figure is reproduced with permission of the I&EC Research journal [39].

Enhanced results were observed by Guayaquil-Sosa et al. [27] with a mesoporous TiO₂ photocatalyst. When loaded with 2.5 wt.% Pt/mpTiO₂-550 °C, this yielded up to 1372 µmol of H₂. Furthermore, hydrogen production was 2.7 times higher for a photoconversion process of 6 h. Rusinque et al. [66] also improved these findings by loading palladium (Pd) as a noble metal in mesoporous TiO₂. These authors observed a large H₂ evolution of
1617 µmol and 5660 µmol, for mesoporous TiO$_2$ and for 1 wt.% Pd/mpTiO$_2$-500 °C, respectively [66]. Furthermore, Rusinque et al. [88] tested the Pd/mpTiO$_2$-500 °C under visible irradiation, and found that the 0.25 wt.% Pd/mpTiO$_2$-500 °C photocatalyst displayed the best performance under visible light irradiation, producing 323 µmol of H$_2$.

Rayees Ahmad et al. [92] developed a reactor that was comprised of a simple Pyrex tube of a 20-cm$^3$ volume, which was horizontally placed under direct sunlight. This reactor contained 6 g/L of 3 wt.% Cu on TiO$_2$ in a mixture of water/methanol (4:1). The reactor was purged with Ar and irradiated with direct sunlight during the months of May and August 2016, with an average solar energy flux of ~637 W/m$^2$ and a temperature of ~35 °C. These conditions generated, respectively, 400 µmol of H$_2$, or up to 1000 µmol of H$_2$ by using 3 wt.% of Cu on TiO$_2$ (DP25), or, alternatively, by employing 3 wt.% of Cu on mpTiO$_2$ during 6 h of irradiation.

Wang et al. [60] used a gas-closed system with a top-window Pyrex cell under visible light ($\lambda > 420$ nm). These authors added 0.02 g of photocatalyst powder (Zn$_{0.5}$Cd$_{0.5}$S or g-C$_3$N$_4$) to 100 mL of a liquid containing a mixture of sacrificial agents. The Na$_2$S/Na$_2$SO$_3$ photocatalyst mixed with Na$_2$S/Na$_2$SO$_3$ (1.4 M ratio), at a pH~13, resulted in ~235 µmol of H$_2$ produced. The second g-C$_3$N$_4$ photocatalyst was added to a solution of triethanolamine (20 vol.%) at a pH~11, which generated ~28 µmol of H$_2$.

Kumaravel et al. [114] utilized g-C$_3$N$_4$ and CdS photocatalysts to evaluate H$_2$ production in a tightly closed immersion-type reactor of 1000 mL total volume (refer to Figure 8a). The experiments were carried out in 500 mL of double distilled water, mixed with a concentration of either a 10 vol.% of any alcohol (methanol, ethanol, etc.), or 0.1 M of glucose, Na$_2$S, Na$_2$SO$_3$, or a sulfide/sulfite mixture with 0.25 g of several photocatalysts. The highest H$_2$ yields were reported when a triethanolamine (TEAO) solution was mixed with g-C$_3$N$_4$ or CdS photocatalysts, showing 247 µmol and 283 µmol of H$_2$ produced, respectively, at a pH of 12. These results suggest the absence of surface hydrophilicity and the poor binding affinity with alcohols on the surface of g-C$_3$N$_4$ and CdS.

Ruban and Sellappa [94] designed a 5-L bench-scale plexiglass tubular reactor (refer to Figure 8b). The geometry of the system was selected to optimize the photocatalyst exposure to light, with three Philips lamps surrounding the reactor. These lamps consisted of two visible light lamps of 100 W (400–700 nm), and one near-UV lamp of 8 W (365 nm). The reactor consisted of two inlets (for N$_2$ purging and for solution feeding) and two outlets (for H$_2$ and for residual solution collection). These authors slurried the CdS-ZnS/DP25 photocatalyst in a solution of sodium sulfide (Na$_2$S) and sodium sulfite (Na$_2$SO$_3$). The photocatalyst-water suspension was degassed with N$_2$ for O$_2$ removal. Then, 1 L of the suspension was recycled by a peristaltic pump and was maintained at 25 °C. These
experiments studied the influence of different operating variables, obtaining an optimum H₂ yield of 384 mL during 90 min of irradiation. The optimal conditions for the operation of this reactor were determined to be as follows: (a) Concentration of sulfide ion = 0.05 M; (b) Concentration of sulfite ion = 0.2 M; (c) pH = 11; (d) Catalyst concentration = 0.5 g/L; (f) Volume of wastewater = 250 mL; and (g) Recycle flow rate = 18 L/h.

A different approach was adopted by Akihiko Kudo [103], where tantalate photocatalysts were synthesized by solid-state reactions or, alternatively, by using a flux method. This author found that a 0.2 wt.% NiO on NaTaO₃: La (1.5 mol%) yielded a highly active photocatalyst, producing up to 882 mmol of H₂. This amount of H₂ was obtained, after 400 h, using a quartz cell, irradiated with a 400-W high-pressure lamp, with 1 g of suspended photocatalyst in 390 mL of water, and with 1 mM of added NaOH. The 4.1-eV-wide band gap and the O₂ generation did not significantly hinder the high H₂ production without sacrificial reagents.

In summary, the photocatalytic reactors reported in this review strongly suggest that the photocatalytic hydrogen yield is influenced by e⁻/h⁺ scavengers, the pH, the irradiation source, the photocatalyst type, and the reactor configuration. These parameters, however, should be examined further, in our view, in order to improve the photocatalytic reactions and the reactor performance for hydrogen production.

4. Reaction Engineering of Photocatalytic Hydrogen Production

The quantification of the liquid- and gas-phase intermediates and their evaluation are critical to the development of adequate kinetic models for photocatalytic hydrogen production. There are three important kinetic parameters required to assess photocatalytic performance: (i) The photoreaction rates; (ii) The adsorption constants; and (iii) The intrinsic kinetic constants. These parameters can be influenced by: (a) humidity, (b) temperature, (c) wavelength, (d) radiation intensity, (e) gas velocity, (f) residence time, (g) photocatalyst loading, (h) oxygen, and (i) the organic pollutant concentration. The improvement of these parameters can help us to advance the scale-up of photocatalytic processes [127].

4.1. “Series-Parallel” Reaction Networks

Photocatalytic reactions for hydrogen production can be described by using the formation of various by-products as a basis. Formed by-products are the result of photoinduced reduction and oxidation reactions. Furthermore, differences of kinetics are closely dependent on the photocatalyst type, and the electron/hole scavenger. Escobedo et al. [65] described a “series-parallel model”, as reported in Figure 9. These authors modeled the photoconversion of ethanol (electron/hole scavenger) in water, with suspended Pt/DP25 photocatalyst particles, in the PCW-II reactor. The quantified by-products were acetaldehyde (C₂H₄O), acetic acid (CH₃COOH), methane (CH₄), ethane (C₂H₆), and carbon dioxide (CO₂). In this case, by identifying several key formed chemical species, the reaction mechanism was adequately formulated. This was given the expected chemical changes occurring when the ethanol was consumed and the hydrogen was formed, under variable photon density, in the PCW-II reactor. In agreement with this, Dey and Pushpa [128] also found CH₄- and CO₂-formed products using a suspension of TiO₂ in alcohol solutions.

Later, Escobedo et al. [129] proposed a few modifications to the original “series-parallel” model by including hydrogen peroxide (H₂O₂) to the formed by-products. Figure 10 describes the observable chemical species and the proposed reaction network during the photocatalytic generation of hydrogen.

Other interesting reaction networks of a similar nature were proposed by Guayaquil-Sosa et al. [130]. These authors also describe hydrogen formation with ethanol as a scavenger, while using a Pt/mpTiO₂-550 °C photocatalyst. The “series-parallel” model was also considered, as described in Figure 11. This process included the generation of H₂O₂ and the details of the oxidation/reduction network on the mpTiO₂ and Pt sites, respectively.
**Figure 9.** “Series-parallel” reaction network for photocatalytic H₂ production when ethanol is the organic source pollutant (electron/hole scavenger), and when a Pt/DP25 photocatalyst is used. Note: the stoichiometric coefficients are designated as $\gamma_i$ and $\tau_i$. Figure is reproduced with the permission of the APCATB: Environmental research journal [65].

**Figure 10.** New proposed “series-parallel” reaction network for the photoconversion of ethanol during hydrogen generation using a Pt/DP25 photocatalyst. Note: $\gamma_1$ being $\gamma_1 = 2$ for path 1, and $\gamma_3 = 0$ for path 2 are the stoichiometric coefficients for steps 1 and 3, respectively. Figure is reproduced with the permission of the Fuel research journal [129].

**Figure 11.** Alternative “series-parallel” reaction network for the photoconversion of ethanol during hydrogen formation using a Pt/mpTiO₂-550°C photocatalyst: (a) oxidation on the mpTiO₂ site, and (b) reduction on the Pt site. Figure is replicated with permission of the MDPI Catalysts research journal [130].

As shown in Figure 12a, Rusinque et al. [126] further considered a similar “series-parallel” reaction network. These authors propose a reaction mechanism with suspended Pd/mpTiO₂ photocatalyst particles reacting with a solution of 2 vol.% ethanol. This mechanism involved a number of formed by-products, such as methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄), acetaldehyde (C₂H₅O), carbon monoxide (CO), and carbon dioxide (CO₂).
In agreement with this, Bahruji et al. [91] report that the decomposition of the several alcohols on well-defined and pure Pd surfaces plays an important role in modified TiO$_2$ activity. The findings obtained by Bahruji et al. were not limited to alcohols, but also pertain to a variety of oxygenates [91]. In this way, these authors emphasize the role of Pd particles deposited on DP25 during irradiation, preventing CO poisoning on the photocatalytic surface, while allowing alcohol adsorption and reforming at ambient conditions. The decomposition scheme of CH$_3$OH suggested by Bahruji et al. is shown in Figure 12b.

![Figure 12. Conceptual diagrams of two different reaction schemes for the decomposition of alcohols: (a) “in-series-parallel” hydrogen reaction network for the photoconversion of ethanol using a Pd/mp-TiO$_2$-500 °C photocatalyst, and (b) photocatalytic cycle of CH$_3$OH, using a of 5 wt.% Pd/DP25. Photocatalyst figures are replicated with the permission of the MDPI Catalysts research journal [126] and the APCATB: Environmental research journal [91]. Note for (a): the OH$^\bullet$ and H$^\bullet$ radical species refer to the OH$^\bullet$ and H$^\bullet$ adsorbed species on the photocatalyst surface.](image1)

To address the role of the scavenger, other authors have studied the influence of the incorporation of metal oxides to the mp-TiO$_2$, as well as the use of different electron/hole scavengers, such as methanol (CH$_3$OH), in the hydrogen formation reaction network. On this basis, Rayees et al. [92] propose a mechanism, as shown in Figure 13a, for a Cu/mp-TiO$_2$ photocatalyst. A similar pathway for a reaction network was proposed by Montoya and Gillan [90] using a Cu or a Ni/DP25 (TiO$_2$) photocatalyst, as described in Figure 13b.

![Figure 13. Hydrogen formation reaction network consisting of the photoconversion of CH$_3$OH by two photocatalysts: (a) a Cu/mp-TiO$_2$ [92], and (b) a M/DP25 (TiO$_2$) [90]. Note that the metal promotor, designated with “M”, represents either Cu or Ni.](image2)

Furthermore, other important photocatalytic routes for hydrogen production involved other scavengers, such as glycerol (C$_3$H$_8$O$_3$). Fujita et al. [97] propose an overall stoichiometry using NiO$_x$/TiO$_2$ photocatalysts, as shown in Figure 14a. This reaction was also described at the more basic mechanistic level by Panagiotopoilou et al. [131], as shown in Figure 14b. The proposed mechanism displays the different possible reactions that might occur while using a Pt/TiO$_2$ photocatalyst.
4.2. Adsorption Models

4.2.1. Langmuir Isotherm

It is essential that the adsorption constants of all the chemical species involved in photocatalytic hydrogen production processes be assessed. Adsorption models, including Langmuir isotherms, are recommended to accomplish this. Thus, the Langmuir adsorption isotherm can also be considered a suitable expression to determine the adsorbed species on the TiO\textsubscript{2}, at equilibrium [71,129,132,133]. This equation is represented as follows:

\[
\theta_A = \frac{Q_{eq,ads}}{Q_{eq,max}} = \frac{K^A_{eq,i}C_{eq,i}}{1 + K^A_{eq,i}C_{eq,i}} \tag{2}
\]

where \(\theta_A\) stands for the dimensionless surface species concentration; \(Q_{eq,ads}\) and \(Q_{eq,max}\) represent the existing and maximum equilibrium adsorption surface concentrations (mol/g\textsubscript{cat}), respectively; \(C_{eq,i}\) denotes “\(i\)”, which is the species equilibrium concentration in the gas/liquid phase (mol/L); and \(K^A_{eq,i}\) is the adsorption equilibrium constant (L/mol). In this respect, only a few studies estimate the adsorption constants using independent equilibrium experiments. Adsorption parameters can be assessed using “dark” conditions (without irradiation). This precondition allows for independently calculated adsorption parameters, minimizing the cross-correlation of the intrinsic kinetic parameters. Therefore, it is acceptable to independently calculate the Langmuir adsorption parameters in order to minimize both the cross-correlation and the uncertainty of the parameter calculations [134–136]. Bahruji et al. [91] confirmed that the adsorption of alcohols (methanol, ethanol, n-propanol, i-propanol) is, indeed, carried out at ambient conditions, on Pd/TiO\textsubscript{2} photocatalysts.

Interesting studies have been developed to understand the photocatalytic performance of alcohols (electron/hole scavengers). This has led to extensive surface studies, with different photocatalyst materials. Escobedo et al. [6,129] present an adsorption study using 2 vol.% ethanol on Pt/DP25, at a pH of 4. The authors recirculated the photocatalyst slurry in the PCW-II reactor, under “dark conditions” (no irradiation provided), to measure the equilibrium adsorption of ethanol (C\textsubscript{2}H\textsubscript{5}OH), with a regression coefficient (R\textsuperscript{2}) of 0.998. Rusinque et al. [126] also determined the adsorption isotherm parameter of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) in the liquid phase, using a Pd/mpTiO\textsubscript{2} in the PCW-II reactor, with an R\textsuperscript{2} of 0.995. Rivero et al. [95] calculated the adsorption parameter of CH\textsubscript{3}OH for a Pt/rGO/DP25 photocatalyst, with an R\textsuperscript{2} of 0.993. Table 3 presents the Langmuir parameters assessed in the different studies.
Table 3. Langmuir adsorption parameters obtained when using different sacrificial agents and photocatalysts for H₂ generation.

| Ref.   | Photocatalyst  | Adsorbate | Adsorption Constants | R²  |
|--------|----------------|-----------|----------------------|-----|
| [6,129]| 1 wt.% Pt/DP25| C₂H₅OH    | 1.427                | 0.998|
| [126]  | 0.25 wt.% Pd/mpTiO₂ | H₂O₂  | 31.633 × 10³        | 0.995|
| [95]   | 0.5 wt.% Pt/(5 wt.%) rGO/DP25 | CH₃OH | 1.138                | 0.993|
| [52,95]| Pt/TiO₂        | C₂H₅OH   | 1.521                | 0.990|
| [97]   | 2 wt.% NiO/TiO₂ | C₃H₈O₃   | 3.000                | 0.930|

4.2.2. Langmuir–Hinshelwood Kinetic Model

It is important to establish kinetic models for photocatalytic hydrogen production. These studies help us to design, develop, and scale-up high-efficiency photoreactors. It is proposed that, for this type of model development, the rate equations should include the organic pollutant (e.g., CH₃OH, C₂H₆OH, etc.) adsorption and conversion, as well as the formation of H₂ and other by-products [129]. In general, it is also valid to use the empirical rates of the chemical species during the oxidation/reduction process, without considering the detailed reaction networks or mechanistic steps [137].

In most studies, the photocatalytic hydrogen production is a heterogeneous process. These processes take advantage of organic chemical pollutants (or electron/hole scavengers). The photocatalytic activities of these systems can also be easily and commonly described with the Langmuir–Hinshelwood (L-H) model, which is represented with the following equation:

$$ r_i = \frac{LVRPA f[H^+]}{1 + \sum_{j=1}^{n} K_{A,j} C_j} = \frac{K_{A,i} k^* C_i}{1 + \sum_{j=1}^{n} K_{A,j} C_j} $$

(3)

The parameters involved are: (a) The LVRPA, which denotes the local volumetric rate of photon absorption; (b) $f[H^+]$, which represents the variability of the pH on the photocatalytic reaction; (c) $K_{A,i}$, which is the adsorption constant (L/mol); (d) $k^*$, which denotes the apparent reaction kinetic constant (mol/g₉cat h); and (e) $C_i$, which stands for the concentration of chemical species (mol/L).

Escobedo et al. [129] studied a PCW-II photoreactor, operated in the batch mode. This unit allows one to account for the chemical species balances for each observable individual chemical species, “$i$”, which can be represented with the following photoreaction rate equation:

$$ r_i = \frac{1}{W_{irr,cat}} \frac{dN_i}{dt} = \frac{V}{W_{irr,cat}} \frac{dC_i}{dt} $$

(4)

with $W_{irr,cat}$ being the irradiated photocatalyst mass (g₉cat); V being the total reactor volume (L); $N_i$ being the moles of the “$i$” chemical species; and $t$ being the irradiation time (min).

By combining Equations (3) and (4), as well as by incorporating an apparent constant photoreaction rate, $k^{app}_i$, for the “$i$” chemical species, one can obtain Equation (5):

$$ r_i = \frac{dC_i}{dt} = \frac{k^{app}_i C_i}{1 + \sum_{j=1}^{n} K_{A,j} C_j} $$

(5)

Equation (5) is useful for describing the chemical changes of species, “$i$”, in the PCW-II reactor, including the organic pollutants and intermediate species [71]. Escobedo et al. [129] modeled the various reaction steps of the photocatalytic hydrogen production, from a solution of ethanol and a Pt/DP25 photocatalyst, using the L-H equation. These authors considered some specific assumptions: (a) The organic pollutant and by-products can be adsorbed on the surface of the photocatalyst; (b) The adsorption is considered to be in
dynamic equilibrium; and (c) No chemical species are affected by the photolysis process. The kinetic model for this photocatalytic system was described with a set of ordinary differential equations (ODEs). These equations were established based on the “series-parallel” reaction network presented in Figure 9, assuming that the ethanol batch mode photoreactor was the dominant adsorbed species, such as \[ \sum_{j=1}^{n} K_j^A C_j \approx K^A_{\text{EtOH}} C_{\text{EtOH}} \]

(1) Ethanol (EtOH)

\[ r_{\text{EtOH}} = \frac{dN_{\text{EtOH}}}{dt} = -V C_{\text{EtOH}} (k_1 + k_2 + k_4 + k_5) \]

(6)

(2) Acetic Acid (AA)

\[ \frac{dN_{\text{AA}}}{dt} = \frac{V C_{\text{EtOH}} (k_2 C_{\text{EtOH}} - k_3 C_{\text{AA}})}{1 + K^A_{\text{EtOH}} C_{\text{EtOH}}} \]

(7)

(3) Carbon Dioxide (CD)

\[ \frac{dN_{\text{CD}}}{dt} = \frac{V [C_{\text{EtOH}} (k_1 + k_4) + k_3 C_{\text{AA}}]}{1 + K^A_{\text{EtOH}} C_{\text{EtOH}}} \]

(8)

(4) Ethane (E)

\[ \frac{dN_{\text{E}}}{dt} = \frac{V C_{\text{EtOH}} \left( \frac{1}{2} k_4 + k_5 \right)}{1 + K^A_{\text{EtOH}} C_{\text{EtOH}}} \]

(9)

(5) Methane (M)

\[ \frac{dN_{\text{M}}}{dt} = \frac{V (k_1 C_{\text{EtOH}} + k_3 C_{\text{AA}})}{1 + K^A_{\text{EtOH}} C_{\text{EtOH}}} \]

(10)

(6) Hydrogen (H)

\[ \frac{dN_{\text{H}}}{dt} = \frac{V C_{\text{EtOH}} (2k_1 + 2k_2 + 2.5k_4)}{1 + K^A_{\text{EtOH}} C_{\text{EtOH}}} \]

(11)

The results obtained for the five kinetic constants, after solving the set of ODEs, are reported in Table 4. These are optimized values that are reported with their 95% confidence intervals (CI) and standard deviations (±SD). These results confirm the adequacy of the model approach for obtaining reliable kinetic parameters.

Table 4. Optimized kinetic parameters calculated with a set of ODEs, using the L-H Equation to obtain the “series-parallel” reaction network of Figure 9, for the photoconversion of ethanol during H$_2$ generation [129].

| Parameter | Value (h$^{-1}$) | 95% CI (%) | ±SD (%) |
|-----------|-----------------|-------------|---------|
| $k_1$     | $2.01 \times 10^{-6}$ | 21.6        | 11.5    |
| $k_2$     | $2.23 \times 10^{-6}$ | 23.5        | 10.4    |
| $k_3$     | $1.63 \times 10^{-2}$ | 4.6         | 83.0    |
| $k_4$     | $5.18 \times 10^{-6}$ | 3.9         | 2.3     |
| $k_5$     | $6.63 \times 10^{-6}$ | 4.4         | 2.2     |

In this respect, Rivero et al. [95] described a similar simplification of the L-H kinetic model with methanol scavenger, used to obtain the maximum generated rate of hydrogen as follows:

\[ \frac{dN_H}{dt} = \frac{k_H K^A_{\text{MeOH}} C_{\text{MeOH}}}{1 + K^A_{\text{MeOH}} C_{\text{MeOH}}} \]
The experimental data was fitted with the initial methanol (MeOH) concentrations, ranging from 1.23 to 27.27 mol/L (5–70 vol.%), and with a photocatalyst of Pt/rGO/DP25. The value of $k_{H_2}$ was $1.37 \times 10^{-4}$ mol/h, and that of $K_{MeOH}^A$ was 1.1138 L/mol [95].

5. Energy Efficiency Studies in Photoreactors for Hydrogen Production

In this review, we summarize some of the efficiency parameters in photocatalytic processes. These parameters are the quantum yields (QYs or $\phi$), and photocatalytic thermodynamic efficiency factors (PTEFs), which are the key energy efficiency performance estimators in photocatalysis. Furthermore, these parameters help us to evaluate the photoreactor’s efficiency during the hydrogen formation. Appendices A and B Table A2 report a comparison of the QYs and the PTEFs, using different doped and nondoped TiO$_2$-based photocatalysts, as well as heterojunction photocatalysts, for photocatalytic H$_2$ production.

While one can understand the relevance of energy efficiencies to establish the photocatalytic reactor design performance to produce hydrogen, their evaluation remains a challenge. This is due to the lack of information about the following key parameters: (1) The photocatalyst absorbed irradiation; (2) The reaction mechanism (or networks); (3) The adsorption constant ($K_{eq,i}$); and (4) The intrinsic kinetic constants ($k_i$).

5.1. Quantum Yields (QYs or $\phi$)

The quantum yield (QY or $\phi$) is known as an important energy-efficiency estimator used to determine the efficiency of photocatalytic photoconversion processes. This parameter can be defined as the photoreaction rate (photoconverted molecules per unit time) divided by the photon absorption rate (number of photons entering the reactor) [71]. The quantum yield designation, which has been used by several authors, can be classified into several subcategories: (a) The primary quantum yield; (b) The overall quantum yield; (c) the apparent or global quantum yield; and (d) The quantum yield.

In this respect, Cassano et al. [138] consider a primary quantum yield always smaller than 1, as follows:

$$ \text{Primary QY} = \frac{\text{moles of pollutant degraded from a primary process/s}}{\text{moles of photons absorbed/s}} \quad (13) $$

Cassano et al. [138], and Davydov et al. [139] proposed and implemented an overall quantum yield, with interesting prospects for photocatalytic processes, which, in principle, could be greater than 1:

$$ \text{QY} \text{Overall} = \frac{\text{moles of pollutant degraded via primary and a secondary process/s}}{\text{moles of photons absorbed/s}} \quad (14) $$

Furthermore, and in cases where the moles of the absorbed photons were not available, an apparent quantum yield ($QY_{app}$) was considered as an alternative by using the photons irradiated into a reactor unit. While this approach is one frequently considered in the literature because of its relatively easy application, it is not very accurate [90,92,137,140–142]. The apparent QY$_{app}$ can be defined as follows:

$$ QY_{app} = \frac{\text{moles of pollutant degraded via a primary process/s}}{\text{moles of incident photons entering the photoreactor/s}} \quad (15) $$

Finally, a valuable variation of the quantum yield definition was proposed by Salaices et al. [67] as the ratio of the OH* radical consumption rate over the absorbed photons rate ($P_a$). The $P_a$ was primarily measured in photocatalytic reactors to determine the organic pollutant conversion in water, by developing MIEBs (macroscopic irradiation energy balances), and by accounting for the back and forward photon-scattering, using spectrophotodiometers and collimators [67,143]. Later, these measurements were adapted in the
Photo-CREC-Air Reactor (PCAR) by Garcia et al., using the ratio of the rate of \( \cdot \) OH radicals consumed over the rate of photons absorbed by TiO\(_2\) (\( \lambda \leq 388 \) nm) [73,144].

Furthermore, this QY definition was modified by Escobedo et al. [65] to account for photocatalytic hydrogen production in the Photo-CREC Water-II reactor. Thus, the QY definition becomes the rate of \( H^* \) molecules produced over the number of photons absorbed by the photocatalysts [27,64–66,88].

\[
QY = \frac{\text{rate of } H^* \text{ produced}}{\text{rates of photons absorbed}} = \frac{\left( \frac{dN_{H^*}}{dt} \right)}{P_a} = \frac{2 \left( \frac{dN_{H}}{dt} \right)}{P_a} \tag{16}
\]

Alternatively, one can define the "Theoretical QY" on the basis of the photon stoichiometric requirements for the formation of a \( H^* \) radical, as follows [65]:

\[
QY_{\text{theor}} = \frac{\text{moles of } H^*}{\text{moles of photons}} \tag{17}
\]

The \( QY_{\text{theor}} \) can be used to determine the complete mineralization of the organic pollutants (electron/hole scavengers) in water. This parameter can be used as a reference only and represents the maximum QY that the photocatalytic process can yield. Escobedo et al. [65] calculated the "Theoretical QY" for the "series-parallel" model, postulated in Figure 6 of Section 4.2. These authors report these \( QY_{\text{theor}} \) in Table 5. These values assume that ethanol was fully mineralized with an 80% efficiency.

| Reaction Path | Reactant | Product | # Photons | \( H_2 \) Generated | \( QY_{\text{theor}} \) |
|--------------|----------|---------|-----------|---------------------|----------------|
| 1            | \( C_2H_5OH \) | \( CH_4, CO_2 \) | 5         | 2                   | 0.80           |
| 2            | \( C_2H_5OH \) | \( C_2H_4O \) | 2         | 1                   | 1.00           |
| 3            | \( C_2H_2O \) | \( C_2H_3OOH \) | 4         | 2                   | 1.00           |
| 4            | \( C_2H_2O \) | \( C_2H_3OOH \) | 2         | 1                   | 1.00           |
| 5            | \( C_2H_2O \) | \( CH_4, CO_2 \) | 1         | 0                   | 0.00           |
| 6            | \( 2C_2H_3OOH \) | \( C_2H_5, CO_2 \) | 3         | 1                   | 0.66           |
| 7            | \( 2C_2H_3OOH \) | \( C_2H_5, CO_2 \) | 2         | 2                   | 1.00           |

While the assessment of the \( QY_{\text{theor}} \) on the basis of stoichiometric considerations, as reported in Table 5, is valuable, more recent results from Escobedo et al. [39], which are based on thermodynamic considerations (refer to Section 5.2), show that the \( QY_{\text{max}} \) is limited to 0.5 for both near-UV and visible light irradiation.

Effect of Platinum Loading and pH on the Quantum Yields for \( H_2 \) Production

QYs can be studied under different pHs and Pt loading conditions. This research is very important given that it allows one to determine the optimum Pt loadings and pH parameters, at ambient pressure and temperature. Escobedo et al. [65] found that the 1 wt.\% Pt/DP25, using ethanol as an electron/hole scavenger and an acidic pH, are the most favorable conditions for hydrogen production. This leads to a progressive and steady \( H_2 \) formation, reaching maximum values after 30 min of 8% QYs. These experimentally observed QYs are lower than the maximum “Theoretical QY”. These results can be justified given that the photocatalytic conversion of \( H^* \) radicals using organic scavengers requires a two-photon one-photocatalyst site quasi simultaneous interaction [6].

Figure 15a reports the variations of the QYs at different pHs (acidic, alkaline, and neutral) and Pt loadings. Figure 15b reports the QYs for various photocatalysts at an optimal pH of 4, as well as for two sources of irradiation: (i) near-UV, and (ii) visible light.
Recent research by our team also determined the QYs for the optimum pH of 4, under near-UV light. Guayaquil-Sosa et al. [27] calculated QYs of 9.3% and 22.6% for a mpTiO$_2$-550 °C and a 2.5 wt.% Pt/mpTiO$_2$-550 °C, respectively. Similarly, Rusinque et al. [66,88] determined QYs of 5% and 10.9% for a mpTiO$_2$-500 °C and for a 1 wt.% Pd/mpTiO$_2$-550 °C, respectively. Furthermore, a 1.13% QY for 0.25 wt.% Pd/mpTiO$_2$-500 °C, under visible light, was obtained.

Other authors, such as Montoya et al. [90], observed apparent QY$_{app}$s of 7% and 2.8% for TiO$_2$ loaded with 1 wt.% Cu and 1 wt.% Ni, respectively, under near-UV light conditions. Similarly, Rayees Ahmad et al. [92] calculated a 4.1% QY$_{app}$ and an 11.4% QY$_{app}$ for DP25 and -mpTiO$_2$ photocatalysts, respectively, containing 3 wt.% Cu, under sunlight irradiation. One should mention that the QY$_{app}$s calculated by these authors, while important, provide solely an approximate efficiency value, given that they are based on incident photons, instead of on the absorbed photons, as required by the QYs presented in Equation (16).

5.2. Photochemical Thermodynamic Efficiency Factors (PTEFs)

The PTEF was first defined for water decontamination by Serrano and de Lasa [145]. Then, it was adapted for air purification by Garcia-Hernandez et al. [73] as the product of the experimental quantum yield (QY$_{Exp}$) and the fraction of the photon energy utilized ($n_{\left[H^\bullet+OH^\bullet\right]}$) to form OH$^\bullet$ radicals. The maximum value of $n_{\left[H^\bullet+OH^\bullet\right]}$, assigned to the organic pollutant conversion in photocatalytic processes, was 1.33.

The following expressions represent the PTEFs for hydrogen production in photocatalytic reactors. They include both generated radicals, H$^\bullet$ and OH$^\bullet$, resulting in the fraction of photon energy ($n_{\left[H^\bullet+OH^\bullet\right]}$), as follows [39]:

$$ PTEF = QY_{Exp} \times n_{\left[H^\bullet+OH^\bullet\right]} $$

$$ n_{\left[H^\bullet+OH^\bullet\right]} = \frac{\Delta H_{\left[H^\bullet+OH^\bullet\right]}}{(E_{av})} $$

where $\Delta H_{\left[H^\bullet+OH^\bullet\right]}$ is the enthalpy of the formation of the H$^\bullet$ and OH$^\bullet$ radicals (kJ/mol), and $E_{av}$ stands for the average emitted photon energy.

Calculations of PTEFs for hydrogen production were first established by Escobedo et al. [39], with the thermodynamic consideration that, for the photocatalytic reaction to take place, it should involve a QY smaller than a QY$_{max}$ of 0.5, given that two absorbed photons are required for the simultaneous formation of one H$^\bullet$ radical and one OH$^\bullet$ radical.
Figure 15 reports the maximum experimental PTEFs for different optimum photocatalysts, under near-UV and visible light irradiation. It was determined that the PTEF for bare TiO$_2$ under near-UV light, was near to seven times larger for the mpTiO$_2$-550 °C than for the DP25. This suggests that a larger photocatalyst specific surface area favors the better utilization of the formed e$^-$/h$^+$ pairs under a higher concentration of adsorbed OH$^-$ and H$^+$ species. The PTEF also increased significantly, with the presence of dispersed Pt or Pd crystallites, in the structures of the DP25 and the mpTiO$_2$ photocatalysts (see Figure 16). Similar activity was observed for visible light. Therefore, by increasing the surface area of the photocatalyst, and by adding dispersed transition metals (Pt or Pd) to TiO$_2$, an enhancement of the photocatalytic production of hydrogen was obtained.

![Figure 16. Experimental maximum PTEFs for photocatalytic hydrogen production under two types of energy irradiation: (1) near-UV, and (2) visible light. Note: PTEFs were calculated as per Equation (19).](image)

6. Future Opportunities for the Photocatalytic Conversion of Hydrogen

**Artificial Intelligence in Photocatalysis**

The establishment of the optimized operating parameters is of importance for chemical processes, such as the photocatalytic production of hydrogen and its scale up. It is expected, in this respect, that artificial intelligence (AI) will help considerably to optimize the operating conditions, increasing the photon conversion efficiency in solar-light-irradiated photoreactors [146–149].

Estahbanati et al. [75] used artificial neural network (ANN) models to predict the photocatalytic hydrogen production from glycerol, using Pt/DP25. To evaluate the performance of the ANN, the coefficient of determination ($R^2$), the adjusted coefficient of determination ($R^2_{adj}$), the root mean squared error (RMS), the mean absolute error (MAE), and the absolute average deviation (AAD) were determined using the following equations:

$$R^2 = 1 - \sum_{i=1}^{n} \left( \frac{(x_{i,cal} - x_{i,exp})^2}{(x_{ave,exp} - x_{i,exp})^2} \right)$$  \hspace{1cm} (20)

$$R^2_{adj} = 1 - \left[ (1 - R^2) \frac{n - 1}{n - K - 1} \right]$$  \hspace{1cm} (21)

$$RMS = \sqrt{\frac{\sum_{i=1}^{n} (x_{i,cal} - x_{i,exp})^2}{n}}$$  \hspace{1cm} (22)

$$MAE = \frac{\sum_{i=1}^{n} |x_{i,cal} - x_{i,exp}|}{n}$$  \hspace{1cm} (23)
AAD = \frac{\sum_{i=1}^{n} \left( \frac{|x_{i,\text{cal}} - x_{i,\text{exp}}|}{x_{i,\text{cal}}} \right)}{n} \times 100 \quad (24)

where \( n \) is the number of data points; \( K \) represents the number of input variables; and \( x_{i,\text{cal}} \), \( x_{i,\text{exp}} \), and \( x_{\text{ave},\text{exp}} \) are the predictive response, the experimental, and the arithmetic mean of all the experimental data, respectively. These equations could help to reveal the most influential parameters during the photoconversion of \( \text{H}_2 \).

Estahbanati et al. [75] investigated the individual and interactive operating parameter effects in the photocatalytic process by taking the following into account: (1) The glycerol concentration; (2) The photocatalyst loading; (3) \( \text{Pt} \) %; and (4) The pH. A generic algorithm (GA) was developed, together with an ANN model, for process optimization. This study found that the overall optimum parameters of the system were 50 vol.% glycerol, 3.9 g/L photocatalyst, 3.1 wt.% Pt, and a pH of 4.5. Figure 17a shows the experimental data obtained for the cumulative hydrogen produced during 4 h, while operating at the identified optimum conditions. Furthermore, these results demonstrate that \( \text{H}_2 \) increases quasi-linearly during the experiments. Figure 17b reports the relative importance of the various operating parameters to produce hydrogen, on a percentual basis.

![Figure 17](image_url)

**Figure 17.** (a) Hydrogen formation rate after 4 h of photoconversion, with the reactor operating at optimum experimental conditions, and (b) optimal operating parameters determined with the generic algorithm. Duplicated with the permission of the APCATB: Environmental research journal [75].

Ren et al. [77] developed a “memetic” algorithm integrating the advantages of a “whale” optimization method and those of a simulated “annealing” random algorithm. This was performed to find a high-quality model solution. The authors also employed a “Sobol” variance-based method to find the most influential input parameters and to quantify how these factors affect the maximum generation of \( \text{H}_2 \). In this regard, these authors found that the most important parameters were: (a) The photocatalyst volume fraction, (b) The inlet velocity of the photocatalyst suspension; and (c) The diameter of the photocatalytic particles (see Figure 18a–c).

Masood et al. [146] present a “holistic” approach for machine learning (ML) in order to research a new solar-photocatalytic-driven process for hydrogen production (see Figure 19). These authors established that one can consider an empirical data domain, with numerous experiments being required, to validate the existing model assumptions. Given this, the authors advised the following: (a) Training of the ML models by integrating theoretical and empirical knowledge; (b) Incorporating the established knowledge in the ML space; and (c) Employing a current material database to constrain the ML predictions. It is envisioned that this combination of ML and empirical knowledge may pave the way towards the development of robust data collection and the selection of the best photocatalyst reactors.
Alyaa K. Mageed [150] also modeled the production of hydrogen using various ML techniques, including an ANN, a support vector machine (SVM), a nonlinear regression model (NLM), and a response surface model (RSM). This author considered the input effects of parameters, such as the irradiation time, the CuO content, the photocatalyst dosage, and the electron/hole scavenger (C$_2$H$_5$OH) concentration, in the proposed modeling process. On this basis, Alyaa K. Mageed [150] observed that the ANNs have a superior ability to predict H$_2$ production, compared to SVMs, NLMs, and RSMs, as indicated by the higher R value of 0.998 obtained. These types of results demonstrate the importance of ML applications to predict and optimize models for complex photochemical processes, which would otherwise be expensive and time-consuming.

As reported throughout this technical review, the scarcity of consistent research data in heterogeneous photocatalysis, with a proper definition of QYs, is still a major issue for the scaling up of hydrogen production. This review also introduces future perspectives and the importance of applying and adapting AI in future research. These computational advancements, supplemented with accurate data, may assist in accelerating the discovery of new solar photocatalyst processes. These hybrid techniques could promote new technologies to improve photocatalytic hydrogen production, and future opportunities that might help to speed up industrial applications.
7. Conclusions

This review reports a detailed description of the preparation of several TiO$_2$-based and heterojunction composite photocatalysts with assorted frames. It is observed that sol-gel, and other methods, have been commonly employed for the synthesis of TiO$_2$-based and complex composite photocatalysts, with the sol-gel method being the most viable method for the scaling-up of photocatalyst applications. Furthermore, impregnation, doping, and precipitation have been frequent metal and nonmetal precursor deposition methods used to enhance the physicochemical properties of photocatalysts to produce “green” hydrogen. This review also reports a classification of the different lamp types, on the basis of the wavelength spectrum and the nominal output power. On this basis, the criteria for photoreactor design are discussed by helping to identify the most suitable and efficient light-source positions for new photoreactor units. Moreover, the illustration and description of the different configurations of the current lab- and bench- scale photoreactors, their operation, and their experimental procedures are provided. Kinetic models for “green” H$_2$ production are also assessed by analyzing and evaluating the observed reaction rates on the basis of: (a) the reaction mechanisms, (b) the adsorption constants, and (c) the intrinsic rate constants. Furthermore, the photon utilization efficiencies, such as the QYs and the PTEFs of photoreactors for photocatalytic H$_2$ production, are taken into account. This review is completed with a discussion of new modeling tools, such as AI and ML, and the future opportunities of these approaches to improve and optimize photocatalytic scaled-up processes for “green” hydrogen production.

8. Directions for Future Works on “Green” H$_2$ Production

While the implementation of photocatalytic H$_2$ production will certainly benefit from low costs and stable photocatalysts, better reaction engineering will strongly contribute to the successful process scale up. Thus, future reaction engineering research for H$_2$ production should consider reliable and consistent measurements of both the photon transmission and the photon absorption fluxes. This will allow the photon utilization ranking of different photoreactor designs, taking as a reference meaningful efficiency parameters, such as the QY. In addition, validated and scalable kinetic models, such as the ones reviewed in this article, will also help in the ranking of photoreactors, using as the basis the organic scavenger conversion and the hydrogen formation. These findings will similarly facilitate the engineering of large-scale units and their operation, while taking advantage of AI and ML methods.

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Nomenclature

| Symbol | Description                     |
|--------|---------------------------------|
| A      | Uniformly irradiated mesh area holding an optimum loading of TiO$_2$ (m$^2$) |
| Ag     | Silver                          |
| Ar     | Argon                           |
| Au     | Gold                            |
| c      | Speed of light ($3 \times 10^8$ m/s) |
| C      | Carbon                          |
CH₄ Methane
CH₃COOH Acetic Acid
CO Carbon Monoxide
CO₂ Carbon Dioxide
C₂H₄ Ethylene
C₂H₃O CO₂ Carbon Dioxide
C₂H₆ Ethane
C₃H₈O₃ Glycerol
Cu Copper
Co Cobalt
Cₐ Acetone concentration (kg/m³)
Cᵢ Concentration of chemical species, “i”, in the liquid phase (mol/L)
Dₚ-BJH Pore diameter (nm)
e⁻ Electron
Eₐv Average photon energy (kJ/mol photon).
E₉BG Energy band gap (eV)
eV Electron volts
f [H⁺] Influence of pH
h Planck’s constant (6.63 × 10⁻³⁴ J/s))
h⁺ Hole
H⁺ Hydrogen ions
H• Hydrogen radicals
H₂ Hydrogen in gas phase
HCl Hydrochloric Acid
H₂O Water
kᵢ Apparent reaction kinetic constant of species, “i” (mol/g_cat h)
kᵢ¹ Overall apparent reaction kinetic constant
Kᵢ Adsorption equilibrium constant (L/mol)
L Liters
n[OH•+H⁺] Fraction of photon energy
Na₂S Sodium sulfide
Na₂SO₃ Sodium sulfite
Ni Nickel
Ni(NO₃)₂ Nickel Nitrate (II)
OH• Hydroxyl radicals
Pₑ Rate of absorbed photons (mol of photons/s).
Pᵢ Incident radiation
Pᵣ Reflected radiation
Pᵣ Transmitted radiation
Pd Palladium
Pt Platinum
q(θ,λ) Radiation measured (W/cm² nm)
Qₑq,ads Existing equilibrium adsorption surface concentration (mol/g_cat)
Qₑq, max Maximum equilibrium adsorption surface concentration (mol/g_cat)
Qₑq, max-1 Langmuir maximum equilibrium adsorption surface concentrations (mol/g_cat)
Qₑq, max-2 Freundlich maximum equilibrium adsorption surface concentrations (mol/g_cat)
R⁺ Reduced
S_BET Surface Area (m²/g)
t Time (s, min, or h)
Ti Titanium
TiCl₄ Titanium tetrachloride
TiO₂ Titanium dioxide
V Total volume of the PCW-II reactors (L)
Vₚ-BJH Pore volume (cm³/g)
w t.% Weight percent (%)
Acronyms

A  Anatase
AAD  Absolute Average Deviation
AI  Artificial Intelligence
ANN  Artificial Neural Network
BET  Brunauer–Emmett–Teller
BJH  Barrett–Joyner–Halenda
BTX  Benzene–Toluene–Xylene
CB  Conduction Band
CFD  Computational Fluid Dynamics
CREC  Chemical Reactor Engineer Centre
CVD  Chemical Vapor Deposition
DDTC  Diethyldithiocarbamate Trihydrate
DB  Debye–Scherrer
DP25  Degussa P25 (Commercial TiO$_2$)
EtOH  Ethanol
GA  Generic Algorithms
GO  Graphene Oxide
LED  Light-Emitting Diode
L-H  Langmuir–Hinshelwood
LVRPA  Local Volumetric Rate of Photon Absorption
MeOH  Methanol
MAE  Mean Absolute Error
MIEB  Macroscopic Irradiation Energy Balances
mp  Mesoporous
NLM  Nonlinear Regression Model
PAHs  Polycyclic Aromatic Hydrocarbons
PCW-II  Photo-CREC Water-II Reactor
PTEFs  Photocatalytic Thermodynamic Efficiency Factors
QYs  Quantum Yields
QY$_{app}$  Apparent Quantum Yield
QY$_{overall}$  Overall Quantum Yield
QY$_{theor}$  Theoretical QYs
R  Rutile
R$_2$  Coefficient of determination
R$_2^{adj}$  Adjusted coefficient of determination
RMS  Root Mean Squared Error
RSM  Response Surface Model
RVE  Representative Volume Element
SVM  Support Vector Machine
TEAO  Triethanolamine
UV  Ultraviolet
VB  Valence Band

Symbols

$\theta$  Angular position (°)
$\theta_A$  Dimensionless surface species concentration
$r_i$  Rate of photoconversion of the model pollutant “$i$” (mol/t g$_{cat}$)
$\Delta H_{OH^{\bullet}}$  Enthalpy invested in the formation of the OH$^{\bullet}$ radicals (J/mol)
$\lambda$  Radiation wavelength (nm)
$\rho$  Fluid density (kg/m$^3$)
$v$  Stoichiometric coefficient
$r$  Radial position (cm)
$n_{OH^{\bullet}}$  Fraction of photon energy used to form OH$^{\bullet}$ radicals

Appendix A

This Appendix shows a list of different TiO$_2$-based photocatalyst for H$_2$ production and their most relevant features.
Table A1. Characterization of different TiO₂-based photocatalysts, and evaluation of hydrogen production using these photocatalysts, as reported in recent research literature.

| No. | Ref. Year | Photocatalyst | Dopant (wt.%) | Load (g L⁻¹) | Crystalline Phase (%) | Sₐ₅₅₀ (m²/g) | Eᵦₕ (eV) | e⁻/h⁺ Scavenger | pH | Source of Light | λ (nm) | H₂ Production (μmol h⁻¹) | QYS% | PTEFs% |
|-----|-----------|---------------|---------------|-------------|----------------------|--------------|----------|----------------|----|----------------|--------|----------------------|------|--------|
| 1   | [39,65] 2013 | TiO₂ (DP25)   | -             | -           | A: R                  | 87: 13       | 54       | 3.20           | 2.73| Near UV        | 340–410 | 34                  | 0.7  | 0.57   |
| 2   | [114] 2019  | Pt/TiO₂ (DP25)| 1             | -           | A: R                  | 80: 20       | 45       | 3.1            | -   | Visible        | 300–700 | 54                  | 1.13 | 1.04   |
| 3   | [27] 2017   | mp/TiO₂-550°C | -             | 0.15        | A: R                  | 100          | 168      | 3.10           | 2.34| Sunlight       | 400–500 | 167                 | 11.4  | -      |
| 4   | [108] 2014  | Cu/TiO₂ (DP25)| Ni/TiO₂ (DP25)| 1           | A: R                  | 80: 20       | 45       | 3.1            | -   | Visible        | 400–500 | 167                 | 11.4  | -      |
| 5   | [39,66] 2019 | Pt/mp/TiO₂    | -             | -           | A: R                  | 100          | 123      | 2.55           | 2.34| Visible        | 300–700 | 269                 | 5     | 3.85   |
| 6   | [39,88] 2020 | Cu/mp/TiO₂    | -             | -           | A: R                  | 100          | 123      | 2.55           | 2.34| Visible        | 300–700 | 269                 | 5     | 3.85   |

Note: Acronyms are also provided in the “Nomenclature” section. S₂₅₅₀ = Brunauer–Emmett–Teller surface area; Eᵦₕ = energy band gap; A = anatase; R = rutile; B = brookite; λ = wavelength; α = QYS_app.

Appendix B

This Appendix shows a list of different non TiO₂-based photocatalyst for H₂ production and their most relevant features.

Table A2. Characterization of different assorted frame-based photocatalysts and evaluation of hydrogen production obtained using these photocatalysts, as reported in recent research literature.

| No. | Ref. Year | Photocatalyst | Dopant (wt.%) | Load (g L⁻¹) | Crystalline Phase (%) | Sₐ₅₅₀ (m²/g) | Eᵦₕ (eV) | e⁻/h⁺ Scavenger | pH | Source of Light | λ (nm) | H₂ Production (μmol h⁻¹) | QYS% | PTEFs% |
|-----|-----------|---------------|---------------|-------------|----------------------|--------------|----------|----------------|----|----------------|--------|----------------------|------|--------|
| 17  | [60] 2017  | ZnO/CDs-5S    | -             | 0.2         | A: R                  | 70: 30       | 55       | 2.88           | 13 | Near UV        | 420 ≤ λ < 420 | 47                  | -    | -      |
| 18  | [114] 2019 | CdS           | g-C₃N₄        | -           | A: R                  | 75: 25       | 48       | CH₃OH          | -  | Near UV        | 315–400 | 505                 | 1.57 | -      |
| 19  | [114] 2019 | CdS           | g-C₃N₄        | -           | A: R                  | 70: 30       | 54       | 2.4            | -   | Near UV        | 340–460 | 2054                | -    | -      |
| 20  | [105] 2014 | WO₃/g-C₃N₄  | 10            | 1           | A: R                  | 80: 20       | 50       | 2.9            | -   | Visible        | 300–700 | 1102                | -    | -      |
| 21  | [106] 2014 | Ag₂S/g-C₃N₄| 5             | 0.625       | A: R                  | 13: 02       | 2.58     | CH₃OH          | -   | Visible        | 420 ≤ λ < 420 | 47                  | -    | -      |
| 22  | [106] 2014 | Ag₂S/g-C₃N₄| 5             | 0.625       | A: R                  | 13: 02       | 2.58     | CH₃OH          | -   | Visible        | 420 ≤ λ < 420 | 47                  | -    | -      |
| 23  | [106] 2014 | NiO/NiTa₂O₃,l| -             | 0.2         | A: R                  | 75: 25       | 48       | CH₃OH          | -   | Near UV        | 315–400 | 505                 | 1.57 | -      |
| 24  | [106] 2014 | NiO/NiTa₂O₃,l| -             | 0.2         | A: R                  | 75: 25       | 48       | CH₃OH          | -   | Near UV        | 315–400 | 505                 | 1.57 | -      |
| 25  | [107] 2012 | MoO₃/Cds     | -             | 9           | A: R                  | 80: 20       | 42       | 2.9            | -   | Visible        | 300–700 | 1102                | -    | -      |
| 26  | [108] 2014 | TiO₂/CdS     | Ta₂O₅/CdS     | 42          | 0.05                | 20.8         | 42.2     | CH₃OH          | -   | Visible        | 300–700 | 420                 | 47.2  | 21.5   |
| 27  | [109] 2021 | CuSnO₂/CdS   | g-C₃N₄        | 8           | A: R                  | 80: 20       | 50       | TEAO           | -   | Visible        | 340–780 | 47.2                 | 21.5  | 10.22  |
| 28  | [110] 2014 | Fe/Al₂O₃-MCM-41| 5            | 2           | 834                   | 1.9          | CH₃OH    | -              | -   | Visible        | 300–700 | 146                 | 6.1   | -      |
| 29  | [112] 2014 | IrO₂/Ta₂O₅  | 5             | 1.5         | A: R                  | 780          | -        | Xe Lamp        | >420| Visible        | 300–700 | 146                 | 6.1   | -      |

Note: Acronyms are also provided in the “Nomenclature” section. S₂₅₅₀ = Brunauer–Emmett–Teller surface area; Eᵦₕ = energy band gap; A = anatase; R = rutile; B = brookite; λ = wavelength; α = QYS_app.
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