

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

Salvador Escobedo 厄 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



Citation: Escobedo, S.; de Lasa, H. Synthesis and Performance of Photocatalysts for Photocatalytic Hydrogen Production: Future Perspectives. *Catalysts* **2021**, *11*, 1505. https://doi.org/10.3390/ catal11121505

Academic Editor: Vasile I. Parvulescu

Received: 9 November 2021 Accepted: 4 December 2021 Published: 10 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).



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 TiO₂ 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 TiO₂ photocatalyst; (c) Coupling TiO₂ with other semiconductors [42–44]; (d) Dye-sensitizing TiO₂ [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.

The activity of TiO₂-based semiconductors depends on their surface properties, as well as on other added components (transition or noble metals). Thus, new approaches are required to achieve: (1) Reduced electron/hole (e^-/h^+) recombination; (2) Diminished energy band gap (E_{bg}); and (3) Increased specific surface area for both enhanced organic pollutants adsorption, and the effective absorption of photon energy. These desirable changes on TiO₂-based semiconductors are expected to diminish both the manufacturing and the operational costs of new technologies to produce photocatalytic hydrogen. In addition, other TiO₂-based semiconductors, including heterojunction photocatalysts consisting of graphitic carbon nitride (g-C₃N₄), sulfur-contained species (CdS, CuInS₂), and other materials, can also be valuable to achieve these goals. These new types of semiconductors can lead to enhanced charge separation and to the increase in the photogenerated pair charge duration under visible light [54–57].

Sacrificial agents (SAs) can transform the thermodynamically inhibited water splitting reaction ($\Delta G^0 = 237 \text{ KJ mol}^{-1}$) 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 O₂ 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•) 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, CuInS₂), graphite carbon nitride (g-C₃N₄), and perovskite (La₂Ti₂O₇). 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 H₂ reaction rates, and the energy efficiencies of different photocatalysts.

2.1. TiO₂-Based Photocatalysts

TiO₂ 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].

TiO₂ 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 TiO₂, 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].

$$E_{BG}(\text{eV}) = \frac{1240}{\lambda(\text{nm})} \tag{1}$$

Table 1. TiO₂ 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 TiO₂ particle activation with photons and through the photocatalytic oxidation (O)/reduction (R) process.

TiO₂, 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 TiO₂ 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 TiO₂ 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 TiO₂ 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 ($H_2PtCl_6 \times H_2O$) 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 $H_2PtCl_6/DP25$ 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 Ar/H_2 (90/10%) Praxair composition) gas blend at 1 cm 3 s $^{-1}$, in a flow reactor unit, and heated at 400 $^\circ$ C for 3 h. This method allowed for the obtainment of well-dispersed metallic Pt⁰ particles, formed on the TiO₂ outer surface. A similar wetness impregnation method was employed by Bahruji et al. [90]. These authors loaded different Pd amounts on DP25 by dissolving PdCl₂ 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 Rusingue et al. [88]. However, in this case, a palladium (II) chloride (PdCl₂) dopant was incorporated instead. The calcination step took place under an air atmosphere at 500 °C for 6 h. Furthermore, and considering that Pd oxidizes during the calcination step, the resulting semiconductor powder had to be reduced. The reduction was controlled in two consecutive steps: (1) The Pd species reduction took place in a flow reactor unit, under a 1 cm³/s of Ar/H₂ (90/10% Praxair composition) gas blend, at 500 °C for 3 h; and (2) Following this, further photoreduction of the photocatalyst took place in the PCW-II reactor by exposing the photocatalyst to near-UV light at room temperature for 1 h. This resulted in a designated x wt.% Pd/mpTiO₂-500 °C photocatalyst. A photodeposition method for Pt on DP25 was also considered by Establanati et al. [75]. These authors suspended 1 g of DP25 in 120 mL of a 10 vol.% ethyl alcohol solution. Then, the precursor material was sonicated for 30 min and a hexachloroplatinic acid solution was poured on it. The mixture was purged with N_2 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 (H₆PtCl₆ 6H₂O) and DP25 were slurried 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 NiO_x 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 NiO_x/TiO₂ photocatalyst.

Sadanandam et al. [98] prepared a cobalt (Co)-doped DP25 photocatalyst for H_2 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 H_2 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 H_2 at different experimental conditions, as previously explained in this section.



Figure 2. H_2 Production with various photocatalyst particle concentrations using different TiO₂based 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 $Zn_{0.5}Cd_{0.5}S$ and g-C₃N₄. These materials were prepared in several steps. First, a solution of diethyldithiocarbamate 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°/min), and

kept for 1h under a N₂ 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 $Zn_{0.5}Cd_{0.5}S$. 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-C₃N₄ 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 N₂ atmosphere.

Katsumata et al. [105] synthesized a $WO_3/g-C_3N_4$ photocatalyst by a simple calcination method for hydrogen generation (refer to Figure 3). A commercial Aldrich reagent of tungsten trioxide (WO₃) nanoparticles was used. The formation of $g-C_3N_4$ 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 $WO_3/g-C_3N_4$ photocatalyst was prepared by blending and grinding WO_3 , with g- C_3N_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. [106] also prepared a g- C_3N_4 -based photocatalyst, but loaded it with silver sulfide (Ag₂S) by employing the precipitation method. The g-C₃N₄ 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 Ag₂S/g-C₃N₄ photocatalyst was prepared in situ, at room temperature. With this end, 0.092 g of g-C₃N₄ powder and Ag₂S 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 $^{\circ}$ C, for 12 h, to obtain the Ag₂S/g-C₃N₄ photocatalyst.



Figure 3. Schematic diagram of the particle activation for heterojunction photocatalyst of $WO_3/g-C_3N_4$ during the production of hydrogen using a TEAO aqueous solution [105].

Z. Shen et al. [107] successfully prepared cadmium sulfide (CdS) nanocrystals, embedded in molybdenum trioxide (MoO₃) core-shell nanospheres, for both H₂ 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 MoO₃/CdS was carried out at different molar ratios. A mixture of Cd(Ac)₂ 2H₂O [3 mmol], (NH₄)₆Mo₇O₂₄ 4H₂O [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 time, the suspension temperature was maintained at lower than 50 °C. This time period helped to generate the precipitates of MoO_3/CdS photocatalyst that were collected by centrifugation, washed with ethanol, and air-dried for several hours.

Other authors, such as Gupta et al. [108], developed two CdS-based photocatalysts with titanium disulfide (TiS₂) and tantalum (IV) sulfide (TaS₂). The TiS₂ was prepared with a blend of Ti metal and sulfur powder. The blend was then heated at 800 $^\circ$ C for 72 h. In the case of the TaS₂, 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-butyllithium [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 (Na₂S) [0.1 mM] to 10 mL of cadmium acetate $(Cd(CH_3COO)_2)$ [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)S₂/CdS, with a mass ratio of 1:1.4, 10 mg of TaS₂ or TiS₂ was dispersed in 10 mL of water by sonication for 1 h. Then, [0.1 mM]of Cd(CH₃COO)₂ was added to it, and the mixture was mixed for 8 h, followed by the addition of [0.1mM] Na₂S in 10mL 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-C₃N₄ 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(NO₃)₂ 3H₂O), 1.210 g of nickel (II) nitrate (Ni(NO₃)₂ 6H₂O), and 1.876 g of tartaric acid ($C_4H_6O_6$) 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 3 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 $Cu(NO_3)_2$ 3H₂O and Ni(NO₃)₂ 6H₂O. The g-C₃N₄ 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_3N_4 photocatalyst was developed using a grinding-calcination-grinding method. Typically, to obtain this material, CuNi@C=O and g-C₃N₄ were ground in an agate mortar for 1 h, and then calcined under a N₂ flow at 150 °C for 2 h, and finally ground again.

Other types of photocatalysts, such as Fe/Al₂O₃-MCM-41 and In₂O₃/Ta₂O₅, were also studied and developed as efficient materials for hydrogen production, under visible light. Pradhan et al. [110] synthesized the mesoporous (mp) Fe/Al₂O₃-MCM-41 photocatalyst by sol-gel, followed by the application of an incipient wetness impregnation method. The mp-Al₂O₃ was prepared by using sucrose as a template. In order to obtain the mp-Al₂O₃-MCM-41, mp-Al₂O₃ was incorporated into the MCM-41. A surfactant consisting of cetyltrimethylammonium bromide (CTAB, C₁₉H₄₂NBr), and a source of silica consisting of tetraethyl orthosilicate (TEOS, C₈H₂₀O₄) were used. The Si/Al ratio in the mp-Al₂O₃-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-Al₂O₃-MCM-41 by using an incipient wetness impregnation method, using a ferrous sulphate (FeSO₄) solution. Finally, the Fe/Al₂O₃-MCM-41 photocatalyst was calcined at 600 °C for 6 h.

Leilei et al. [112] formulated the indium (III) oxide/tantalum (V) (In_2O_3/Ta_2O_5) photocatalyst for hydrogen production. The tantalum pentoxide (Ta_2O_5) microspheres were prepared by adding 0.4 g of $Ta_2(OC_2H_5)_5$ to 10 mL of ethylene glycol in a N₂ 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 Ta₂O₅ microspheres. To acquire the resulting photocatalyst of In₂O₃/Ta₂O₅, an amount of 0.22 g of Ta₂O₅ microspheres was ultrasonically dispersed in 50 mL of water for 10 min. Next, an *x* amount of indium nitrate (In(NO₃)₃ *n*H₂O) 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 In₂O₃/Ta₂O₅ 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. 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 TiO₂-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 TiO₂-based photocatalysts are significantly more effective than heterojunction-based composites. In principle, the preparation methods for the TiO₂-based photocatalysts are simpler, and the photochemical reaction for H₂ 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 TiO₂-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).





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	λ = 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 Photocatalytc 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 H_2SO_4 [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 TiO_2 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 TiO_2 . These authors observed a large H₂ evolution of

1617 µmol and 5660 µmol, for mesoporous TiO₂ and for 1 wt.% Pd/mpTiO₂-500 °C, respectively [66]. Furthermore, Rusinque et al. [88] tested the Pd/mpTiO₂-500 °C under visible irradiation, and found that the 0.25 wt.% Pd/mpTiO₂-500 °C photocatalyst displayed the best performance under visible light irradiation, producing 323 µmol of H₂.

Rayees Ahmad et al. [92] developed a reactor that was comprised of a simple Pyrex tube of a 20-cm³ volume, which was horizontally placed under direct sunlight. This reactor contained 6 g/L of 3 wt.% Cu on TiO₂ 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/m² and a temperature of ~35 °C. These conditions generated, respectively, 400 µmol of H₂, or up to 1000 µmol of H₂ by using 3 wt.% of Cu on TiO₂ (DP25), or, alternatively, by employing 3 wt.% of Cu on mpTiO₂ 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-C₃N₄) to 100 mL of a liquid containing a mixture of sacrificial agents. The Na₂S/Na₂SO₃ photocatalyst mixed with Na₂S/Na₂SO₃ (1.4 M ratio), at a pH~13, resulted in ~235 µmol of H₂ produced. The second g-C₃N₄ photocatalyst was added to a solution of triethanolamine (20 vol.%) at a pH~11, which generated ~28 µmol of H₂.

Kumaravel et al. [114] utilized $g-C_3N_4$ 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_2S , Na_2SO_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_3N_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_3N_4 and CdS.



Figure 8. Schematic representation of two types of batch photocatalytic reactors for H₂ production: (**a**) immersion unit, and (**b**) tubular unit. Figures are reproduced with permission of the MDPI journals, *Catalysts* [114] and *Energy* [94].

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 N₂ purging and for solution feeding) and two outlets (for H₂ and for residual solution collection). These authors slurried the CdS-ZnS/DP25 photocatalyst in a solution of sodium sulfide (Na₂S) and sodium sulfite (Na₂SO₃). The photocatalyst-water suspension was degassed with N₂ for O₂ 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 H_2 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(C_2H_4O), acetic acid (CH₃COOH), methane (CH₄), ethane (C_2H_6), 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 (H_2O_2) 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 H_2O_2 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 γ_i and τ_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: γ i being γ_1 = 2 for path 1, and γ_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 "seriesparallel" 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 (C₂H₄O), 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_3OH 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-seriesparallel" hydrogen reaction network for the photoconversion of ethanol using a Pd/mpTiO₂-500 °C photocatalyst, and (b) photocatalytic cycle of CH₃OH, 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[•] and H[•] radical species refer to the OH[•] and H[•] adsorbed species on the photocatalyst surface.

To address the role of the scavenger, other authors have studied the influence of the incorporation of metal oxides to the mpTiO₂, as well as the use of different electron/hole scavengers, such as methanol (CH₃OH), in the hydrogen formation reaction network. On this basis, Rayees et al. [92] propose a mechanism, as shown in Figure 13a, for a Cu/mpTiO₂ photocatalyst. A similar pathway for a reaction network was proposed by Montoya and Gillan [90] using a Cu or a Ni/DP25 (TiO₂) photocatalyst, as described in Figure 13b.

(a)	(b)
(i) $CH_3OH \xrightarrow{hv/photocatalyst} HCHO + H_2$ (ii) $HCHO + H_2O \xrightarrow{hv/photocatalyst} HCOOH + H_2$ (iii) $HCOOH \xrightarrow{hv/photocatalyst} CO_2 + H_2$	a) $TiO_2 + hv(> E_g) \rightarrow e^-(TiO_2CB) + h^+(TiO_2VB)$ b) $e^-(TiO_2CB) + Surface (M^+/_{M^{2+}}) \rightarrow \frac{TiO_2}{M_{(reduced)}}$ c) $2e^-(TiO_2CB) + \frac{TiO_2}{M_{(reduced)}} + 2H^+ \rightarrow H_2 + \frac{TiO_2}{M_{(reduced)}}$ d) $2h^+(TiO_2VB) + CH_3OH \rightarrow CH_2O + 2H^+$

Figure 13. Hydrogen formation reaction network consisting of the photoconversion of CH_3OH by two photocatalysts: (**a**) a $Cu/mpTiO_2$ [92], and (**b**) a M/DP25 (TiO₂) [90]. Note that the metal promotor, designated with "M", represents either Cu or Ni.

Furthermore, other important photocatalytic routes for hydrogen production involved other scavengers, such as glycerol ($C_3H_8O_3$). Fujita et al. [97] propose an overall stoichiometry using NiO_x/TiO₂ 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/TiO₂ photocatalyst.



Figure 14. Photocatalytic conversion scheme for H_2 production from glycerol and water, using two different photocatalysts: (a) NiO_x/TiO_2 [97], and (b) Pt/TiO_2 . Figure (b) is reproduced with the permission of the Elsevier journal, *Catalysis Today* [131].

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 TiO₂, at equilibrium [71,129,132,133]. This equation is represented as follows:

$$\theta_A = \frac{Q_{eq,ads}}{Q_{eq,max}} = \frac{K^A_{eq,i}C_{eq,i}}{\left(1 + K^A_{eq,i}C_{eq,i}\right)}$$
(2)

where θ_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_{cat}), respectively; $C_{eq,i}$ denotes "*i*", which is the species equilibrium concentration in the gas/liquid phase (mol/L); and $K_{eq,i}^A$ 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/TiO₂ 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_2H_5OH), with a regression coefficient (R^2) of 0.998. Rusinque et al. [126] also determined the adsorption isotherm parameter of hydrogen peroxide (H_2O_2) in the liquid phase, using a Pd/mpTiO₂ in the PCW-II reactor, with an R^2 of 0.995. Rivero et al. [95] calculated the adsorption parameter of CH₃OH for a Pt/rGO/DP25 photocatalyst, with an R^2 of 0.993. Table 3 presents the Langmuir parameters assessed in the different studies.

D (Adsorption Constants	- 2
Kei.	Photocatalyst	Adsorbate	$K^A_{eq,i}$ (L mol $^{-1}$)	R ²
[6,129]	1 wt.% Pt/DP25	C ₂ H ₅ OH	1.427	0.998
[126]	0.25 wt.% Pd/mpTiO ₂	H_2O_2	$31.633 imes 10^3$	0.995
[95]	0.5 wt.% Pt/(5 wt.%) rGO/DP25	CH ₃ OH	1.138	0.993
[52,95]	Pt/TiO ₂	C ₂ H ₅ OH	1.521	0.990
[97]	2 wt.% NiO/TiO ₂	C ₃ H ₈ O ₃	3.000	0.930

Table 3. Langmuir adsorption parameters obtained when using different sacrificial agents and photocatalysts for H_2 generation.

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., CH_3OH , C_2H_6OH , etc.) adsorption and conversion, as well as the formation of H_2 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:

$$r_{i} = LVRPA f[H^{+}] \frac{K_{i}^{A} k_{i}^{l} C_{i}}{1 + \sum_{j=1}^{n} K_{i}^{A} C_{j}} = \frac{K_{i}^{A} k^{*} C_{i}}{1 + \sum_{j=1}^{n} K_{i}^{A} C_{j}}$$
(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_i^A , which is the adsorption constant (L/mol); (d) k^* , which denotes the apparent reaction kinetic constant (mol/g_{cat} 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 (g_{cat}); 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_i^{app} , for the "*i*" chemical species, one can obtain Equation (5):

$$r_i = \frac{dC_i}{dt} = \frac{k_i^{app}C_i}{1 + \sum_{i=1}^n K_i^A C_i}$$
(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 $\sum_{j=1}^{n} K_{j}^{A}C_{j} \approx K_{EtOH}^{A}C_{EtOH}$

(1) Ethanol (EtOH)

$$r_{EtOh} = \frac{dN_{EtOH}}{dt} = \frac{-VC_{EtOH}(k_1 + k_2 + k_4 + k_5)}{1 + K^A_{EtOH}C_{EtOH}}$$
(6)

(2) Acetic Acid (AA)

$$\frac{dN_{AA}}{dt} = \frac{VC_{EtOH}(k_2C_{EtOH} - k_3C_{AA})}{1 + K^A_{EtOH}C_{EtOH}}$$
(7)

(3) Carbon Dioxide (CD)

$$\frac{dN_{CD}}{dt} = \frac{V[C_{EtOH}(k_1 + k_4) + k_3C_{AA}]}{1 + K^A_{EtOH}C_{EtOH}}$$
(8)

(4) Ethane (E)

$$\frac{dN_E}{dt} = \frac{VC_{EtOH}\left(\frac{1}{2}k_4 + k_5\right)}{1 + K^A_{EtOH}C_{EtOH}} \tag{9}$$

(5) Methane
$$(M)$$

(6) Hydrogen (H)

$$\frac{dN_M}{dt} = \frac{V(k_1 C_{EtOH} + k_3 C_{AA})}{1 + K^A_{EtOH} C_{EtOH}}$$
(10)

$$\frac{dN_H}{dt} = \frac{VC_{EtOH}(2k_1 + 2k_2 + 2.5k_4)}{1 + K_{EtOH}^A C_{EtOH}}$$
(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 (\pm 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 H₂ generation [129].

Parameter	Value (h^{-1})	95% CI (%)	±SD (%)
<i>k</i> ₁	$2.01 imes 10^{-6}$	21.6	11.5
<i>k</i> ₂	$2.23 imes10^{-6}$	23.5	10.4
k_3	$1.63 imes10^{-2}$	4.6	83.0
k_4	$5.18 imes10^{-6}$	3.9	2.3
k_5	$6.63 imes10^{-6}$	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:

$$\frac{dN_H}{dt} = \frac{k_{H_2} K^A_{MeOH} C_{MeOH}}{1 + K^A_{MeOH} C_{MeOH}}$$
(12)

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 1.37×10^{-4} mol/h, and that of K^A_{MeOH} 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 φ), 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 TiO₂-based photocatalysts, as well as heterojunction photocatalysts, for photocatalytic H₂ 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 $(K_{eq,i}^A)$; and (4) The intrinsic kinetic constants (k_i) .

5.1. Quantum Yields (QYs or φ)

The quantum yield (QY or φ) 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:

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

$$QY_{Overall} = \frac{moles \ of \ pollutant \ degraded \ via \ primary \ and \ a \ secundary \ process/s}{moles \ of \ photons \ absorbed/s}$$
(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:

$$QY_{app} = \frac{moles \ of \ pollutant \ degraded \ via \ a \ primary \ process/s}{moles \ of \ incident \ photons \ entering \ the \ photoreactor/s}$$
(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 spectrophotoradiometers 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 OH[•] radicals consumed over the rate of photons absorbed by TiO₂ ($\lambda \le 388$ 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].

$$QY = \frac{\text{rate of } H^{\bullet} \text{ produced}}{\text{rates of photons absorbed}} = \frac{\left[\frac{dN_{H^{\bullet}}}{dt}\right]}{P_{a}} = \frac{2\left[\frac{dN_{H_{2}}}{dt}\right]}{P_{a}}$$
(16)

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

$$QY_{theor} = \frac{moles \ of \ H^{\bullet}}{moles \ of \ photons} \tag{17}$$

The QY_{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_{theor} in Table 5. These values assume that ethanol was fully mineralized with an 80% efficiency.

Table 5. Theoretical QYs for the different steps involved in the photoconversion of ethanol during H_2 Generation [65], as shown in the "In-Series-Parallel Model" in Figure 9, Section 4.1.

Reaction Path	Reactant	Product	# Photons	H ₂ Generated	QY _{theor}
1		CH ₄ , CO ₂	5	2	0.80
2	C ₂ H ₅ OH	C ₂ H ₄ O	2	1	1
3	-	C II OOU	4	2	1
4	C ₂ H ₄ O	C ₂ H ₃ OOH	2	1	1
5	C ₂ H ₃ OOH	CU CO	1	0	0
6	C_2H_4O	CH_4, CO_2	3	1	0.66
7	2 C ₂ H ₃ OOH	C ₂ H ₆ , CO ₂	2	2	1

While the assessment of the QY_{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_{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 H₂ 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.



Figure 15. Quantum yields obtained for H₂ generation in 2 vol.% of ethanol: (**a**) using various Pt loadings on TiO₂ (DP25), with pH conditions of acidity, alkalinity, and neutrality; and (**b**) using different DP25 or mpTiO₂ photocatalysts loaded with Pt or Pd, at acidic pH conditions of 4.

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 mpTiO₂-550 °C and a 2.5 wt.% Pt/mpTiO₂-550 °C, respectively. Similarly, Rusinque et al. [66,88] determined QYs of 5% and 10.9% for a mpTiO₂-500 °C and for a 1 wt.% Pd/mpTiO₂-550 °C, respectively. Furthermore, a 1.13% QY for 0.25 wt.% Pd/mpTiO₂-500 °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 TiO₂ 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 -mpTiO₂ 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 ($n_{[OH^{\bullet}]}$) to form OH[•] radicals. The maximum value of $n_{[OH^{\bullet}]}$, 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[•] and OH[•], resulting in the fraction of photon energy $(n_{[H^{\bullet}+OH^{\bullet}]})$, as follows [39]:

$$PTEF = QY_{Exp} * n_{[H^{\bullet} + OH^{\bullet}]}$$
(18)

$$n_{[H^{\bullet}+OH^{\bullet}]} = \frac{\Delta H_{[H^{\bullet}+OH^{\bullet}]}}{(E_{av})}$$
(19)

where $\Delta H_{[H^{\bullet}+OH^{\bullet}]}$ is the enthalpy of the formation of the H[•] and OH[•] 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[•] radical and one OH[•] 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 TiO₂ under near-UV light, was near to seven times larger for the mpTiO₂-550 °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 mpTiO₂ 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 TiO₂, 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).

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].

Estabbanati 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:

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

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

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

$$MAE = \frac{\sum_{i=1}^{n} |x_{i,cal} - x_{i,exp}|}{n}$$
(23)

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

where *n* is the number of data points; *K* represents the number of input variables; and $x_{i,cal}$, $x_{i,exp}$, and $x_{ave,exp}$ 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 H₂.

Establanati 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) 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 H₂ 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. (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 H₂. 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.



Figure 18. Changes in hydrogen production as a function of (**a**) the particle volume fraction; (**b**) the inlet velocity; and (**c**) the particle diameter. Reproduced with the permission of the *Energy Conversion and Management* journal [77].



Figure 19. Overall process of the discovery of new photocatalysts by the integration of a photocatalysis domain database in an ML framework. Figure is reproduced with the permission of *ACS Catalysis* [146].

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 (C₂H₅OH) concentration, in the proposed modeling process. On this basis, Alyaa K. Mageed [150] observed that the ANNs have a superior ability to predict H₂ 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 TiO₂-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 TiO₂based 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" H₂ 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" H₂ Production

While the implementation of photocatalytic H2 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 H2 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.

Author Contributions: Investigating scientific literature, drafting figures and tables, preparation, writing and editing of the original-draft review article, S.E.; writing, editing, and reviewing final version of the original manuscript, H.d.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science and Engineering Research Council of Canada (NSERC), through the Hugo de Lasa's NSERC Discovery Grant.

Acknowledgments: The authors would like to thank Florencia de Lasa, who assisted with the editing and proofreading of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

- A Uniformly irradiated mesh area holding an optimum loading of TiO_2 (m²)
- Ag Silver
- Ar Argon
- Au Gold
- c Speed of light $(3 \times 10^8 \text{ m/s})$
- C Carbon

CH ₄	Methane
CH ₃ COOH	Acetic Acid
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
C_2H_4	Ethylene
C_2H_4O	Acetaldehyde
C_2H_6	Ethane
$C_3H_8O_3$	Glycerol
Cu	Copper
Co	Cobalt
C_A	Acetone concentration (kg/m^3)
C_i	Concentration of chemical species, "i", in the liquid phase (mol/L)
D _{p-BIH}	Pore diameter (nm)
e^{-1}	Electron
E_{av}	Average photon energy (kJ/mol photon).
EBC	Energy band gap (eV)
eV	Electron volts
f [H+]	Influence of pH
h	Planck's constant (6.63 \times 10 ⁻³⁴ L/s))
h^+	Hole
и Н+	Hydrogen ions
П П•	Hydrogen radicala
П Ц.	Hydrogen in gas phase
	Hydrogen in gas phase
HCI	
H ₂ O	
K_i^{+}	Apparent reaction kinetic constant of species, "1" (mol/ g_{cat} h)
K _i	Overall apparent reaction kinetic constant
K_j^A	Adsorption equilibrium constant (L/mol)
L	Liters
$n_{[H^{\bullet}+OH^{\bullet}]}$	Fraction of photon energy
Na ₂ S	Sodium sulfide
Na ₂ SO ₃	Sodium sulfite
Ni	Nickel
Ni(NO ₃) ₂	Nickel Nitrate (II)
OH•	Hydroxyl radicals
P_a	Rate of absorbed photons (mol of photons/s).
P_i	Incident radiation
\dot{P}_r	Reflected radiation
P_t	Transmitted radiation
Pd	Palladium
Pt	Platinum
$a(\theta,z,\lambda)$	Radiation measured (W/cm^2 nm)
$\int \int dx $	Existing equilibrium adsorption surface concentration (mol/g_{ret})
\mathcal{Q}_{eq} , ads	Maximum equilibrium adsorption surface concentration (mol/ g_{cat})
Qeq, max	Langmuir maximum equilibrium adsorption surface concentration (mol/ g_{cat})
Qeq, max-1	Eaughtun maximum equilibrium adsorption surface concentrations (mol/ g_{cat})
Qeq, max-2 P+	Preduced
K ¹	Reduced $C_{\rm eff}(x) = C_{\rm eff}(x)^2 (x)$
SBET	Surface Area (m^{-}/g)
t T	lime (s, min, or n)
11Cl ₄	
11O ₂	litanium dioxide
V	Iotal volume of the PCW-II reactors (L)
V _{p-BJH}	Pore volume (cm^3/g)
wt.%	Weight percent (%)
W _{irr,cat}	Irradiated photocatalyst mass (g _{cat})

Acronyms	
А	Anatase
AAD	Absolute Average Deviation
AI	Artificial Intelligence
ANN	Artificial Neural Network
BET	Brunauer–Emmett–Teller
BIH	Barrett–Joyner–Halenda
BTX	Benzene-Toluene-Xylene
CB	Conduction Band
CED	Computational Eluid Dynamics
CREC	Chamical Reactor Engineer Contro
CVD	Chemical Vapor Deposition
	Disthe Hithing house to Tribe house
DDIC	
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 Absolut Error
MIEB	Macroscopic Irradiation Energy Balances
mp	Mesoporous
NLM	Nonlinear Regression Model
PAHs	Polycyclic Aromatic Hydrocarbons
PCW-II	Photo-CREC Water-II Reactor
PTFFe	Photocatalytic Thermodynamic Efficiency Factors
OV_{c}	Quantum Vields
Q13	Apparent Quantum Vield
	Overall Overstum Vield
Q ¹ _{overall}	The sensitive low
Q ¹ theor	Participal Q1S
K P ²	
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	
θ	Angular position ($^{\circ}$)
θ_A	Dimensionless surface species concentration
r;	Rate of photoconversion of the model pollutant "i" (mol/t g_{cat})
$\Lambda H_{\Omega H}$	Enthalpy invested in the formation of the OH^{\bullet} radicals (I/mol)
λ	Radiation wavelength (nm)
0	Fluid density (kg/m ³)
г 1/	Stoichiometric coefficient
r	Radial position (cm)
1	Eraction of photon energy used to form OH [•] radicals
••ОН•	raction of photon energy used to tottil Off Taulcais

Appendix A

This Appendix shows a list of different ${\rm TiO}_2\mbox{-}based$ photocatalyst for ${\rm H}_2$ production and their most relevant features.

No.	Ref.	Year	Photocatalyst	Dopant (wt.%)	Load (g L ⁻¹)	Crystalline Phase (%)	S _{BET} (m²/g)	E _{BG} (eV)	e ⁻ /h ⁺ Scavenger	рН	Source of Light	λ (nm)	H ₂ Production (µmol h ⁻¹)	QYs%	PTEFs %
1		2012	TiO ₂ (DP25)	-		A . D		3.20					34	0.7	0.57
2	[39,65]	2013	Pt/TiO ₂ (DP25)	1		87: 13	54	2.73					256	7.9	6.05
3			mpTiO ₂ -550°C	-			168	3.10					229	9.3	-
4	[27]	2017	Pt/mpTiO ₂₋ 550 °C	2.5	0.15		150	2.34	C ₂ H ₃ OH	$4\pm$ 0.05	Near UV	340– 410	629	22.6	17.1
5	[20.66]	2010	mpTiO ₂ -500 °C	-		A 100	140	3.0					269	5	3.85
6	[39,66]	2019		1			123	2.55					943	10.9	8.39
7	[39,88]	2020	Pd/mp1iO ₂ - 500 °C	0.25			131	2.51			Visible	300– 700	54	1.13	1.04
8			Cu/TiO ₂ (DP25)			Δ· R							85	7 ^α	
9	[90]	2018	Ni/TiO ₂ (DP25)	1	2	80: 20	45	3.1	-	UV	-	34	2.8 α	-	
10			mpTiO ₂				188		CH ₃ OH				0	0 α	
11	[92]	2017	Cu/TiO ₂ (DP25)	3	6	A 100	-	-		-	Sunlight	-	67	4.1 α	-
12			Cu/mpTiO ₂	-			75						167	11.4 ~	
13	[94]	2014	CdS-ZnS/DP25	-	0.5	A: R 70: 30	55	2.88	Na ₂ S Na ₂ SO ₃	11.3	Visible UV	400– 700 365	1035	2.2 ~	-
14	[95]	2019	Pt/rGO/DP25	0.5/5/5	1	A: R 75: 25	48	-	CH ₃ OH	4	Near- UV	315– 400	505	1.57 °	-
15	[97]	2016	NiO/TiO ₂	2	1.67	A: R 70:3 0	54	2.4		6.6	Near- UV	340- 460	2054	-	-
16	[98]	2013	Co/DP25	1	2	A: R 80: 20	50	2.9	$C_3H_8O_3$	6	Visible	300– 700	1102	-	-

,	Table A1. Characterization of different TiO ₂ -based photocatalysts, and evaluation of hydrogen production using these
	photocatalysts, as reported in recent research literature.

Note: Acronyms are also provided in the "Nomenclature" section. S_{BET} = Brunauer–Emmett–Teller surface area; E_{BG} = energy band gap; A = anatase; R = rutile; B = brookite; λ = wavelength; α = QY_{app}.

Appendix B

This Appendix shows a list of different non TiO_2 -based photocatalyst for H_2 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)	S _{BET} (m²/g)	E _{BG} (eV)	e−/h+ Scavenger	рН	Source of Light	λ (nm)	H_2 Production (µmol h ⁻¹)	QYs%
17	[60]	2017	$Zn_{0.5}Cd_{0.5}S$	-	0.2	-	-	Na ₂ S/ Na ₂ SO ₃	~13	Xe Lamp	$420 \leq \lambda$	47	-
18		-	g-C ₃ N ₄	-					~11		<u> 2420</u>	5.6	-
19	[114]	2010	CdS	_	0.5	-	-	TEAO	12	Xe arc	Simulated	47	-
20	[114]	2019 -	g-C ₃ N ₄	-	0.5			11.10	12	Lamp	Solar light	41	-
21	[105]	2014	$WO_3/g-C_3N_4$	10	1	-	2.81	-	-	Xe Lamp	>420	110	0.9 ^α
22	[106]	2014	Ag ₂ S/g-C ₃ N ₄	5	0.625	13.02	2.58	CH ₃ OH	-	Low power UV-LEDs	≥420	10	-
23	[103]	2006	NiO/NaTaO2:	-	2.56	_	4.1	-	_	High	_	16	-
24	[105]	2006	La	0.2	2.36		~4.1			pressure Hg lamp		2180	-
25	[107]	2012	MoO ₃ /CdS	~9	0.5	25.82	2.65	Na ₂ SO ₃ /Na ₂ S	-	-	>420	2100	28.86 ^α
26	[108]	2014	TiS ₂ /CdS	- 42	0.05	48.2	_	Benzyl	_		> 200	742	-
27	[100]	2014 -	TaS ₂ /CdS	- 42	0.05	20.8	_	alcohol/ CH ₃ COOH		Xe Lamp		1758	-
28	[109]	2021	CuNi@C=O/g-	8	0.2	_	-	TEOA	_		340.780	47.2	21.51 ^α
20	[107]	2021	C ₃ N ₄	0	0.2			TEOA			540-700	47.2	10.22 ^α
29	[110]	2011	Fe/Al ₂ O ₃ - MCM-41	5	2	834	1.9	CH ₃ OH	-	High pressure Hg lamp	≥400	146	6.1 ^α
30	[112]	2012	In ₂ O ₃ /Ta ₂ O ₅	5	1.5	-	~2.75		-	Xe Lamp	320< λ <780	78	-

Note: Acronyms are also provided in the "Nomenclature" section. S_{BET} = Brunauer–Emmett–Teller surface area; E_{BG} = energy band gap; λ = wavelength; α = QY_{app}.

References

- 1. Dincer, I.; Acar, C. Smart energy solutions with hydrogen options. Int. J. Hydrog. Energy 2018, 43, 8579–8599. [CrossRef]
- 2. Acar, C.; Dincer, I. Energy and exergy analyses of a novel photoelectrochemical hydrogen production system. *Int. J. Hydrog. Energy* **2017**, *42*, 30550–30558. [CrossRef]
- 3. Watts, N.; Adger, W.N.; Agnolucci, P.; Blackstock, J.; Byass, P.; Cai, W.; Chaytor, S.; Colbourn, T.; Collins, M.; Cooper, A.; et al. Health and climate change: Policy responses to protect public health. *Lancet Comm.* **2015**, *386*, 1861–1914. [CrossRef]
- 4. Reza Gholipour, M.; Dinh, C.T.; Beland, F.; Do, T.O. Nanocomposite heterojunctions as sunlight-driven photocatalysts for hydrogen production from water splitting. *Nanoscale* **2015**, *7*, 8187–8208. [CrossRef]
- 5. Haines, A.; Kovats, R.S.; Campbell-lendrum, D.; Corvalan, C. Climate change and human health: Impacts, vulnerability and public health. *Public Health* **2006**, *120*, 585–596. [CrossRef]
- 6. Escobedo, S. Photocatalytic Water Splitting using a Modified Pt- TiO₂. Kinetic Modeling and Hydrogen Production Efficiency. Ph.D. Thesis, The University of Western Ontario, London, ON, Canada, 2013.
- 7. Kayfeci, M.; Kecebas, A.; Bayat, M. Hydrogen production. In *Solar Hydrogen Production: Processes, Systems and Technologies;* Academic Press: Cambridge, MA, USA, 2019; pp. 45–83, ISBN 9780128148532.
- Mazloomi, K.; Gomes, C. Hydrogen as an energy carrier: Prospects and challenges. *Renew. Sustain. Energy Rev.* 2012, 16, 3024–3033. [CrossRef]
- 9. Guo, S.; Li, X.; Li, J.; Wei, B. Boosting photocatalytic hydrogen production from water by photothermally induced biphase systems. *Nat. Commun.* **2021**, *12*, 1343. [CrossRef]
- Nikolaidis, P.; Poullikkas, A. A comparative overview of hydrogen production processes. *Renew. Sustain. Energy Rev.* 2017, 67, 597–611. [CrossRef]
- 11. Lee, D.H.; Hung, C.P. Toward a clean energy economy: With discussion on role of hydrogen sectors. *Int. J. Hydrog. Energy* **2012**, 37, 15753–15765. [CrossRef]
- 12. Rafal, Ł.; Holowacz, I.; Kucharska, K.; Glinka, M.; Rybarczyk, P.; Przyjazny, A.; Kaminski, M. Hydrogen production from biomass using dark fermentation. *Renew. Sustain. Energy Rev.* **2018**, *91*, 665–694. [CrossRef]
- The 4th Generation | Life Cycle Emissions of Hydrogen. Available online: https://4thgeneration.energy/life-cycles-emissions-ofhydrogen/ (accessed on 12 May 2021).
- 14. Muradov, N.Z.; Veziroğlu, T.N. "Green" path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies. *Int. J. Hydrog. Energy* **2008**, *33*, 6804–6839. [CrossRef]
- 15. Solar Panel Splits Water to Produce Hydrogen—IEEE Spectrum. Available online: https://spectrum.ieee.org/energywise/green-tech/fuel-cells/solar-panel-prototype-splits-water-to-produce-hydrogen (accessed on 12 May 2021).
- 16. Producing Green Hydrogen through the Exposure of Nanomaterials to Sunlight | INRS. Available online: https://inrs.ca/en/ news/producing-green-hydrogen-through-the-exposure-of-nanomaterials-to-sunlight (accessed on 12 May 2021).
- 17. Torres-martínez, L.M.; Gómez, R.; Vázquez-cuchillo, O.; Juárez-ramírez, I. Enhanced photocatalytic water splitting hydrogen production on RuO₂/La:NaTaO₃ prepared by sol—Gel method. *Catal. Commun.* **2010**, *12*, 268–272. [CrossRef]
- Rawool, S.A.; Pai, M.R.; Banerjee, A.M.; Bapat, R.D.; Nayak, C.; Tripathi, A.K. Lab scale optimization of various factors for photocatalytic hydrogen generation over low cost Cu 0.02 Ti 0.98 O2-S photocatalyst under UV/Visible irradiation and sunlight. *Int. J. Hydrog. Energy* 2018, 43, 1271–1284. [CrossRef]
- 19. Vamathevan, V.; Amal, R.; Beydoun, D.; Low, G.; McEvoy, S. Silver metallisation of titania particles: Effects on photoactivity for the oxidation of organics. *Chem. Eng. J.* 2004, *98*, 127–139. [CrossRef]
- 20. Dupont, V. Steam Reforming of Sunflower Oil for Hydrogen Gas Production. Helia 2007, 30, 103–132. [CrossRef]
- 21. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38. [CrossRef] [PubMed]
- 22. Licht, S. Multiple Band Gap Semiconductor/Electrolyte Solar Energy Conversion. J. Phys. Chem. B 2001, 105, 6281–6294. [CrossRef]
- 23. Rusinque, B. Hydrogen Production by Photocatalytic Water Splitting Under Near-UV and Visible Light Using Doped Pt and Pd TiO₂. Master's Thesis, The University of Western Ontario, London, ON, Canada, 2018.
- 24. Leung, D.Y.C.; Fu, X.; Wang, C.; Ni, M.; Leung, M.K.H.; Wang, X.; Xianzhi, F. Hydrogen Production over Titania-Based Photocatalysts. *ChemSusChem* 2010, 350002, 681–694. [CrossRef]
- 25. Ray, A.K. A new photocatalytic reactor for destruction of toxic water pollutants by advanced oxidation process. *Catal. Today* **1998**, 44, 357–368. [CrossRef]
- 26. Akach, J.; Ochieng, A. Monte Carlo simulation of the light distribution in an annular slurry bubble column photocatalytic reactor. *Chem. Eng. Res. Des.* **2017**, *129*, 248–258. [CrossRef]
- 27. Guayaquil-Sosa, J.F.; Serrano-Rosales, B.; Valadés-Pelayo, P.J.; de Lasa, H. Photocatalytic hydrogen production using mesoporous TiO₂ doped with Pt. *Appl. Catal. B Environ.* **2017**, *211*, 337–348. [CrossRef]
- 28. Sirivallop, A.; Escobedo, S.; Areerob, T.; de Lasa, H.; Chiarakorn, S. Photocatalytic Conversion of Organic Pollutants in Air: Quantum Yields Using a Silver/Nitrogen/TiO₂ Mesoporous Semiconductor under Visible Light. *Catalysts* **2021**, *11*, 529. [CrossRef]

- 29. Yang, J.; Yan, H.; Wang, X.; Wen, F.; Wang, Z.; Fan, D.; Shi, J. Roles of cocatalysts in Pt–PdS/CdS with exceptionally high quantum efficiency for photocatalytic hydrogen production. *J. Catal.* 2012, 290, 151–157. [CrossRef]
- Chen, H.; Matsumoto, A.; Nishimiya, N.; Tsutsumi, K. Preparation and characterization of TiO₂ incorporated Y-zeolite. *Colloids Surfaces A Physicochem. Eng. Asp.* 1999, 157, 295–305. [CrossRef]
- Rusinque, B. Hydrogen Production Via Photocatalytic Water Splitting Under Near-UV and Visible Light Using Doped Pd TiO₂. Ph.D. Thesis, The University of Western Ontario, London, ON, Canada, 2021.
- 32. Dubey, N.; Rayalu, S.; Labhsetwar, N.; Devotta, S. Visible light active zeolite-based photocatalysts for hydrogen evolution from water. *Int. J. Hydrog. Energy* **2008**, *33*, 5958–5966. [CrossRef]
- 33. Sreethawong, T.; Junbua, C.; Chavadej, S. Photocatalytic H₂ production from water splitting under visible light irradiation using Eosin Y-sensitized mesoporous-assembled Pt/TiO₂ nanocrystal photocatalyst. *J. Power Sources* **2009**, *190*, 513–524. [CrossRef]
- 34. Kim, S.; Hwang, S.-J.; Choi, W. Visible light active platinum-ion-doped TiO₂ photocatalyst. *J. Phys. Chem. B* **2005**, *109*, 24260–24267. [CrossRef] [PubMed]
- 35. Lin, C.; Lee, C.; Chao, J.; Kuo, C.; Cheng, Y.; Huang, W.; Chang, H.; Huang, Y. Photocatalytic generation of H₂ gas from neat ethanol over Pt/TiO2 nanotube catalysts. *Catal. Lett.* **2004**, *98*, 61–66. [CrossRef]
- 36. Bahruji, H.; Bowker, M.; Davies, P.R.; Morgan, D.J.; Morton, C.A.; Egerton, T.A.; Kennedy, J.; Jones, W. Rutile TiO₂—Pd Photocatalysts for Hydrogen Gas Production from Methanol Reforming. *Top. Catal.* **2015**, 70–76. [CrossRef]
- Yu, J.; Hai, Y.; Jaroniec, M. Photocatalytic hydrogen production over CuO-modified titania. J. Colloid Interface Sci. 2011, 357, 223–228. [CrossRef]
- Choudhury, B.; Choudhury, A. Luminescence characteristics of cobalt doped TiO₂ nanoparticles. J. Lumin. 2012, 132, 178–184.
 [CrossRef]
- 39. Escobedo, S.; Rusinque, B.; de Lasa, H. Photochemical Thermodynamic Efficiency Factors (PTEFs) for Hydrogen Production Using Different TiO₂ Photocatalysts. *Ind. Eng. Chem. Res.* **2019**, *58*, 22225. [CrossRef]
- 40. Ning, X.; Lu, G. Photocorrosion inhibition of CdS-based catalysts for photocatalytic overall water splitting. *Nanoscale* **2020**, *12*, 1213–1223. [CrossRef] [PubMed]
- Ilie, M.; Cojocaru, B.; Parvulescu, V.I.; Garcia, H. Improving TiO₂ activity in photo-production of hydrogen from sugar industry wastewaters. *Int. J. Hydrog. Energy* 2011, *36*, 15509–15518. [CrossRef]
- 42. Draz, M.A.; El-maghrabi, H.H.; Soliman, F.S.; Selim, H. Large scale hybrid magnetic ZnFe₂O₄/TiO₂ nanocomposite with highly photocatalytic activity for water splitting. *J. Nanoparticle Res.* **2021**, *23*, 10. [CrossRef]
- Castañeda, C.; Tzompantzi, F.; Rodríguez-Rodríguez, A.; Sánchez-dominguez, M.; Gómez, R. Improved photocatalytic hydrogen production from methanol/water solution using CuO supported on fluorinated TiO₂. *J. Chem. Technol. Biotechnol.* 2018, 93, 1113–1120. [CrossRef]
- Wysmulek, K.; Sar, J.; Osewski, P.; Orlinski, K.; Kolodziejak, K.; Trenczek-zajac, A.; Radecka, M.; Pawlak, D.A. A SrTiO₃ -TiO₂ eutectic composite as a stable photoanode material for photoelectrochemical hydrogen production. *Appl. Catal. B Environ.* 2017, 206, 538–546. [CrossRef]
- 45. Fan, W.; Zhang, Q.; Wang, Y. Semiconductor-based nanocomposites for photocatalytic H₂ production and CO₂ conversion. *Phys. Chem. Chem. Phys.* **2013**, 2632–2649. [CrossRef] [PubMed]
- 46. Reisner, E.; Powell, D.J.; Cavazza, C.; Fontecilla-camps, J.C.; Armstrong, F.A. Visible Light-Driven H₂ Production by Hydrogenases Attached to Dye-Sensitized TiO₂ Nanoparticles. *JACS* **2009**, *131*, 18457–18466. [CrossRef] [PubMed]
- 47. Willkomm, J.; Orchard, K.L.; Reynal, A.; Pastor, E.; Durrant, J.R.; Reisner, E. Chem Soc Rev Dye-sensitised semiconductors modified with molecular catalysts for light-driven H₂ production. *Chem. Soc. Rev.* **2016**, *45*, 9–23. [CrossRef]
- Ranwaha, T.; Elegbeleye, I.; Maluta, N.; Maphanga, R. Optical and electronic properties of croconates dye molecules adsorbed on TiO₂ brookite nanocluster for dye sensitized solar cells application. *Mater. Express* 2020, 10, 1917–1924. [CrossRef]
- Barrios, C.E.; Albiter, E.; Gracia y Jimenez, J.M.; Tiznado, H.; Romo-Herrera, J.; Zanella, R. Photocatalytic hydrogen production over titania modified by gold – Metal (palladium, nickel and cobalt) catalysts. *Int. J. Hydrog. Energy* 2016, 41, 23287–23300. [CrossRef]
- 50. Caudillo-Flores, U.; Muñoz-Batista, M.J.; Cortés, J.A.; Fernández-García, M.; Kubacka, A. UV and visible light driven H₂ photo-production using Nb-doped TiO₂: Comparing Pt and Pd co-catalysts. *Mol. Catal.* **2017**, 437, 1–10. [CrossRef]
- 51. Navarro, R.M.; Arenales, J.; Vaquero, F.; González, I.D.; Fierro, J.L.G. The effect of Pt characteristics on the photoactivity of Pt/TiO₂ for hydrogen production from ethanol. *Catal. Today* **2013**, *210*, 33–38. [CrossRef]
- 52. Strataki, N.; Bekiari, V.; Kondarides, D.I.; Lianos, P. Hydrogen production by photocatalytic alcohol reforming employing highly efficient nanocrystalline titania films. *Appl. Catal. B Environ.* **2007**, *77*, 184–189. [CrossRef]
- Asal, S.; Saif, M.; Hafez, H.; Mozia, S.; Heciak, a.; Moszyński, D.; Abdel-Mottaleb, M.S.A. Photocatalytic generation of useful hydrocarbons and hydrogen from acetic acid in the presence of lanthanide modified TiO₂. *Int. J. Hydrog. Energy* 2011, 36, 6529–6537. [CrossRef]
- 54. Min, S.; Lu, G. Dye-cosensitized graphene/Pt photocatalyst for high efficient visible light hydrogen evolution. *Int. J. Hydrog. Energy* **2012**, *37*, 10564–10574. [CrossRef]
- 55. Srta, N.O.; Adhikari, S.P.; Hood, Z.D.; Wang, H.; Peng, R.; Krall, A.; Li, H.; Chen, V.W.; More, K.L.; Wu, Z.; et al. Environmental Enhanced visible light photocatalytic water reduction from a g-C₃N₄/SrTa₂O₆ heterojunction. *Appl. Catal. B Environ.* 2017, 217, 448–458. [CrossRef]

- Lin, B.; An, H.; Yan, X.; Zhang, T.; Wei, J.; Yang, G. Environmental Fish-scale structured g-C₃N₄ nanosheet with unusual spatial electron transfer property for high-efficiency photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* 2017, 210, 173–183. [CrossRef]
- 57. Cai, X.; Zhang, J.; Fujitsuka, M.; Majima, T. Environmental layered composites as efficient visible-light-driven photocatalyst. *Appl. Catal. B Environ.* **2017**, 202, 191–198. [CrossRef]
- 58. Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* 2009, *38*, 253–278. [CrossRef] [PubMed]
- 59. Schneider, J.; Bahnemann, D.W. Undesired Role of Sacri fi cial Reagents in Photocatalysis. J. Phys. Chem. Lett. 2013, 4, 3479–3483. [CrossRef]
- 60. Wang, M.; Shen, S.; Li, L.; Tang, Z.; Yang, J. Effects of sacrificial reagents on photocatalytic hydrogen evolution over different photocatalysts. *J. Mater. Sci.* 2017, *52*, 5155–5164. [CrossRef]
- 61. Alkaim, A.F.; Kandiel, T.A.; Dillert, R.; Bahnemann, D.W. Photocatalytic hydrogen production from biomass-derived compounds: A case study of citric acid. *Environ. Technol.* **2016**, *37*, 2687–2693. [CrossRef] [PubMed]
- Speltini, A.; Sturini, M.; Maraschi, F.; Dondi, D.; Fisogni, G.; Annovazzi, E.; Profumo, A.; Buttafava, A. ScienceDirect Evaluation of UV-A and solar light photocatalytic hydrogen gas evolution from olive mill wastewater. *Int. J. Hydrog. Energy* 2015, 40, 4303–4310. [CrossRef]
- 63. Villa, K.; Domenec, X.; Malato, S.; Maldonado, M.I.; Peral, J. Heterogeneous photocatalytic hydrogen generation in a solar pilot plant. *Int. J. Hydrog. Energy* **2013**, *8*, 12718–12724. [CrossRef]
- 64. Sakata, T.; Kawai, T. Heterogeneous photocatalytic production of hydrogen and methane from ethanol and water. *Chem. Phys. Lett.* **1981**, *80*, 341–344. [CrossRef]
- 65. Escobedo, S.; Serrano, B.; de Lasa, H. Quantum yield with platinum modified TiO₂ photocatalyst for hydrogen production. *Appl. Catal. B Environ.* **2013**, *140*, 523–536. [CrossRef]
- 66. Rusinque, B.; Escobedo, S.; de Lasa, H. Photocatalytic Hydrogen Production Under Near-UV Using Pd-Doped Mesoporous TiO₂ and Ethanol as Organic Scavenger. *Catalysts* **2019**, *19*, 33. [CrossRef]
- 67. Salaices, M.; Serrano, B.; de Lasa, H. Photocatalytic Conversion of Organic Pollutants Extinction Coefficients and Quantum Efficiencies. *Ind. Eng. Chem. Res.* 2001, 40, 5455–5464. [CrossRef]
- Salaices, M.; Serrano, B.; de Lasa, H. Experimental evaluation of photon absorption in an aqueous TiO₂ slurry reactor. *Chem. Eng. J.* 2002, 90, 219–229. [CrossRef]
- 69. Moreira, J.; Serrano, B.; Ortiz, A.; de Lasa, H. Evaluation of Photon Absorption in an Aqueous TiO₂ Slurry Reactor Using Monte Carlo Simulations and Macroscopic Balance. *Ind. Eng. Chem. Res.* **2010**, *49*, 10524–10534. [CrossRef]
- Serrano, B.; Ortíz, A.; Moreira, J.; de Lasa, H. Photocatalytic Thermodynamic Efficiency Factors. Practical Limits in Photocatalytic Reactors. Ind. Eng. Chem. Res. 2010, 49, 6824–6833. [CrossRef]
- 71. De Lasa, H.; Serrano, B.; Salaices, M. *Photocatalytic Reaction Engineering*, 1st ed.; Springer: Berlin/Heidelberg, Germany, 2005; ISBN 978-0-387-27591-8.
- 72. Serrano, B.; Ortíz, A.; Moreira, J.; de Lasa, H. Energy efficiency in photocatalytic reactors for the full span of reaction times. *Ind. Eng. Chem. Res.* **2009**, *48*, 9864–9876. [CrossRef]
- 73. Hernandez, J.M.G.; Rosales, B.S.; de Lasa, H. The photochemical thermodynamic efficiency factor (PTEF) in photocatalytic reactors for air treatment. *Chem. Eng. J.* 2010, *165*, 891–901. [CrossRef]
- 74. Lugo-Vega, C.S.; Serrano-Rosales, B.; de Lasa, H. Energy efficiency limits in Photo-CREC-Air photocatalytic reactors. *Chem. Eng. Sci.* **2016**, *156*, 77–88. [CrossRef]
- 75. Estahbanati, M.R.K.; Feilizadeh, M.; Iliuta, M.C. Photocatalytic valorization of glycerol to hydrogen: Optimization of operating parameters by artificial neural network. *Appl. Catal. B Environ.* **2017**, *209*, 483–492. [CrossRef]
- 76. Farsi, A.; Dincer, I.; Naterer, G.F. Multi-objective optimization of an experimental integrated thermochemical cycle of hydrogen production with an artificial neural network. *Int. J. Hydrog. Energy* **2020**, *45*, 24355–24369. [CrossRef]
- Ren, T.; Wang, L.; Chang, C.; Li, X. Machine learning-assisted multiphysics coupling performance optimization in a photocatalytic hydrogen production system. *Energy Convers. Manag.* 2020, 216, 112935. [CrossRef]
- Nurul, M.; Podder, J.; Saadat, K.; Sagadevan, S. Band gap tuning of p-type al-doped TiO₂ thin films for gas sensing applications. *Thin Solid Film.* 2020, 714, 138382. [CrossRef]
- 79. Moctezuma, E.; Leyva, E.; Aguilar, C.A.; Luna, R.A.; Montalvo, C. Photocatalytic degradation of paracetamol: Intermediates and total reaction mechanism. *J. Hazard. Mater.* **2012**, *243*, 130–138. [CrossRef] [PubMed]
- 80. Kiyama, M.; Akita, T.; Tsutsumi, Y.; Takada, T. Formation of Titanic Oxides of Anatase, Brookite, and Rutiles Types by Aerial Oxidation of Titanous Solutions. *Chem. Lett.* **1972**, *1*, 21–24. [CrossRef]
- 81. Freyria, F.S.; Blangetti, N.; Esposito, S.; Nasi, R. Effects of the Brookite Phase on the Properties of Different Nanostructured TiO₂ Phases Photocatalytically Active Towards the Degradation of N-Phenylurea. *Chem. Open* **2020**, *9*, 903–912. [CrossRef]
- Zu, M.; Zhou, X.; Zhang, S.; Qian, S.; Li, D. Sustainable engineering of TiO₂ -based advanced oxidation technologies: From photocatalyst to application devices. J. Mater. Sci. Technol. 2021, 78, 202–222. [CrossRef]
- Li, R.; Hu, B.; Yu, T.; Shao, Z.; Wang, Y.; Song, S. New TiO₂-Based Oxide for Catalyzing Alkaline Hydrogen Evolution Reaction with Noble Metal-Like Performance. *Small Methods* 2021, *5*, 2100246. [CrossRef]

- 84. Sescu, A.M.; Favier, L.; Lutic, D.; Soto-donoso, N.; Ciobanu, G.; Harja, M. TiO2 Doped with Noble Metals as an Efficient Solution for the Photodegradation of Hazardous Organic Water Pollutants at Ambient Conditions. *Water* **2021**, *13*, 19. [CrossRef]
- 85. Bellamkonda, S.; Thangavel, N.; Yusuf, H.; Neppolian, B. Highly active and stable multi-walled carbon nanotubes-graphene-TiO₂ nanohybrid: An e ffiicient non-noble metal photocatalyst for water splitting. *Catal. Today* **2019**, *321–322*, 120–127. [CrossRef]
- Mishra, A.; Mehta, A.; Kainth, S.; Basu, S. A comparative study on the effect of different precursors for synthesis and efficient photocatalytic activity of g-C₃N₄/TiO₂/bentonite nanocomposites. *J. Mater. Sci.* 2018, *53*, 13126–13142. [CrossRef]
- 87. Kapilashrami, M.; Zhang, Y.; Liu, Y.; Hagfeldt, A.; Guo, J. Probing the Optical Property and Electronic Structure of TiO₂ Nanomaterials for Renewable Energy Applications. *Chem. Rev.* **2014**, *114*, 9662–9707. [CrossRef]
- Rusinque, B.; Escobedo, S.; de Lasa, H. Photoreduction of a Pd-Doped Mesoporous TiO₂ Photocatalyst for Hydrogen Production under Visible Light. *Catalysts* 2020, 74, 74. [CrossRef]
- 89. Mehta, A.; Sharma, M.; Kumar, A.; Basu, S. Effect of Au content on the enhanced photocatalytic efficiency of mesoporous Au/TiO₂ nanocomposites in UV and sunlight. *Gold Bull.* **2017**, *50*, 33–41. [CrossRef]
- Tio, S.; Montoya, A.T.; Gillan, E.G. Enhanced Photocatalytic Hydrogen Evolution from Transition-Metal Surface-Modi fi ed TiO₂. ACS Omega 2018, 3, 2947–2955. [CrossRef]
- 91. Bahruji, H.; Bowker, M.; Brookes, C.; Davies, P.R.; Wawata, I. The adsorption and reaction of alcohols on TiO₂ and Pd/TiO₂ catalysts. *Appl. Catal. A Gen.* **2013**, 454, 66–73. [CrossRef]
- Rather, R.A.; Singh, S.; Pal, B. A Cu⁺¹/Cu⁰-TiO₂ mesoporous nanocomposite exhibits improved H₂ production from H₂O under direct solar irradiation. *J. Catal.* 2017, 346, 1–9. [CrossRef]
- 93. Choi, H.J.; Kang, M. Hydrogen production from methanol/water decomposition in a liquid photosystem using the anatase structure of Cu loaded TiO₂. *Int. J. Hydrog. Energy* **2007**, *32*, 3841–3848. [CrossRef]
- 94. Ruban, P.; Sellappa, K. Development and performance of bench-scale reactor for the photocatalytic generation of hydrogen. *Energy* **2014**, *73*, 926–932. [CrossRef]
- 95. Rivero, M.J.; Iglesias, O.; Ribao, P.; Ortiz, I. Kinetic performance of TiO₂/Pt/reduced graphene oxide composites in the photocatalytic hydrogen production. *Int. J. Hydrog. Energy* **2018**, *44*, 101–109. [CrossRef]
- 96. Liu, R.; Yoshida, H.; Fujita, S.; Arai, M. Environmental Photocatalytic hydrogen production from glycerol and water with NiO_x/TiO₂ catalysts. *Appl. Catal. B Environ.* **2014**, *144*, 41–45. [CrossRef]
- Fujita, S.; Kawamori, H.; Honda, D.; Yoshida, H.; Arai, M. Environmental Photocatalytic hydrogen production from aqueous glycerol solution using NiO/TiO₂ catalysts: Effects of preparation and reaction conditions. *Appl. Catal. B Environ.* 2016, 181, 818–824. [CrossRef]
- 98. Sadanandam, G.; Lalitha, K.; Durga, V. Cobalt doped TiO₂: A stable and efficient photocatalyst for continuous hydrogen production from glycerol: Water mixtures under solar light irradiation. *Int. J. Hydrog. Energy* **2013**, *38*, 9655–9664. [CrossRef]
- Li, Y.; Jin, Z.; Zhang, L.; Fan, K. Controllable design of Zn-Ni-P on g-C₃N₄ for efficient photocatalytic hydrogen production. *Chin. J. Catal.* 2019, 40, 390–402. [CrossRef]
- Singla, S.; Sharma, S.; Basu, S.; Shetti, N.P.; Raghava, K. Graphene/graphitic carbon nitride-based ternary nanohybrids: Synthesis methods, properties, and applications for photocatalytic hydrogen production. *FlatChem* 2020, 24, 100200. [CrossRef]
- Xiong, J.; Li, X.; Huang, J.; Gao, X.; Chen, Z.; Liu, J.; Li, H.; Kang, B.; Yao, W.; Zhu, Y. CN/rGO@BPQDs high-low junctions with stretching spatial charge separation ability for photocatalytic degradation and H₂O₂ production. *Appl. Catal. B Environ.* 2020, 266, 118602. [CrossRef]
- 102. Cheng, L.; Xiang, Q.; Liao, Y. CdS-Based Photocatalysts. Energy Environ. Sci. 2018, 11, 1362–1391. [CrossRef]
- 103. Kudo, A. Development of photocatalyst materials for water splitting. Int. J. Hydrog. Energy 2006, 31, 197–202. [CrossRef]
- 104. Jing, X.; Lu, N.; Huang, J.; Zhang, P.; Zhang, Z. One-step hydrothermal synthesis of S-defect-controlled ZnIn₂S₄ microflowers with improved kinetics process of charge-carriers for photocatalytic H₂ evolution. J. Energy Chem. 2021, 58, 397–407. [CrossRef]
- Katsumata, H.; Tachi, Y.; Suzuki, T.; Kaneco, S. Z-scheme photocatalytic hydrogen production over WO₃/g-C₃N₄ composite photocatalysts. *RSC Adv.* 2014, 21405–21409. [CrossRef]
- 106. Jiang, D.; Chen, L.; Xie, J.; Chen, M. Ag2S/g-C3N4 composite photocatalysts for efficient Pt-free hydrogen production. The co-catalyst function of Ag/Ag2S formed by simultaneous photodeposition. *Dalt. Trans.* 2014, 43, 4878–4885. [CrossRef]
- 107. Shen, Z.; Chen, G.; Yu, Y.; Wang, Q.; Zhou, C.; Hao, L.; Li, Y.; Heb, L.; Mu, R. Sonochemistry synthesis of nanocrystals embedded in a MoO₃–CdS core–shell photocatalyst with enhanced hydrogen production and photodegradation. *J. Mater. Sci.* 2012, 19646–19651. [CrossRef]
- Gupta, U.; Rao, B.G.; Maitra, U.; Prasad, B.E.; Rao, C.N.R. Visible-Light-Induced Generation of H₂ by Nanocomposites of Few-Layer. *Chem. Asian J.* 2014, 1311–1315. [CrossRef]
- Chen, S.; Liao, J.; Zhou, Z.; Yang, S.; Gao, Q.; Cai, X.; Peng, F.; Fang, Y.; Zhang, S. Boosting photocatalytic hydrogen evolution using a noble-metal-free co-catalyst: CuNi@C with oxygen-containing functional groups. *Appl. Catal. B Environ.* 2021, 291, 120139. [CrossRef]
- Pradhan, A.C.; Martha, S.; Mahanta, S.K.; Parida, K.M. Mesoporous nanocomposite Fe/Al₂O₃ -MCM-41: An efficient photocatalyst for hydrogen production under visible light. *Int. J. Hydrog. Energy* 2011, 36, 12753–12760. [CrossRef]
- 111. Trens, P.; Russell, M.L.; Spjuth, L.; Hudson, M.J.; Liljenzin, J.; Normale, Ä.; Cedex, M. Preparation of Malonamide-MCM-41 Materials for the Heterogeneous Extraction of Radionuclides. *Ind. Eng. Chem. Res.* 2002, 5220–5225. [CrossRef]

- 112. Leilei, X.U.; Lei, N.I.; Weidong, S.H.I.; Jianguo, G. Photocatalytic Activity for Hydrogen Evolution over Well-Dispersed Heterostructured In2O3/Ta2O 5 Composites. *Chin. J. Catal.* **2012**, *33*, 1101–1108. [CrossRef]
- 113. Escobedo, S.; de Lasa, H. Photocatalysis for Air Treatment Processes: Current Technologies and Future Applications for the Removal of Organic Pollutants and Viruses. *Catalysts* **2020**, *10*, 966. [CrossRef]
- 114. Kumaravel, V.; Imam, M.D.; Badreldin, A.; Chava, R.K.; Do, J.Y.; Kang, M.; Abdel-Wahab, A. Photocatalytic hydrogen production: Role of sacrificial reagents on the activity of oxide, carbon, and sulfide catalysts. *Catalysts* **2019**, *9*, 276. [CrossRef]
- 115. Imoberdorf, G.E.; Cassano, A.E.; Irazoqui, H.A.; Alfano, O.M. Optimal design and modeling of annular photocatalytic wall reactors. *Catal. Today* **2007**, *129*, 118–126. [CrossRef]
- Lugo-Vega, C.S.; Moreira, J.; Serrano-Rosales, B.; de Lasa, H. Kinetics of the pollutant photocatalytic conversion in a Photo-CREC-Air Reactor. Chem. Eng. J. 2017, 317, 1069–1082. [CrossRef]
- 117. Lugo-Vega, C.S.; Serrano-Rosales, B.; de Lasa, H. Immobilized particle coating for optimum photon and TiO₂ utilization in scaled air treatment photo reactors. *Appl. Catal. B Environ.* **2016**, *198*, 211–223. [CrossRef]
- Imoberdorf, G.E.; Irazoqui, H.A.; Cassano, A.E.; Alfano, O.M. Photocatalytic Degradation of Tetrachloroethylene in Gas Phase on TiO₂ Films: A Kinetic Study. *Ind. Eng. Chem. Res.* 2005, 44, 6075–6085. [CrossRef]
- Héquet, V.; Batault, F.; Raillard, C.; Thévenet, F.; Le Coq, L.; Dumont, É. Determination of the clean air delivery rate (CADR) of photocatalytic oxidation (PCO) purifiers for indoor air pollutants using a closed-loop reactor. Part II: Experimental results. *Molecules* 2017, 22, 408. [CrossRef]
- 120. Xu, T.; Zheng, H.; Zhang, P. Performance of an innovative VUV-PCO purifier with nanoporous TiO₂ film for simultaneous elimination of VOCs and by-product ozone in indoor air. *Build. Environ.* **2018**, 142, 379–387. [CrossRef]
- Debono, O.; Thévenet, F.; Gravejat, P.; Héquet, V.; Raillard, C.; Le Coq, L.; Locoge, N. Gas phase photocatalytic oxidation of decane at ppb levels: Removal kinetics, reaction intermediates and carbon mass balance. *J. Photochem. Photobiol. A Chem.* 2013, 258, 17–29. [CrossRef]
- 122. Sirivallop, A.; Areerob, T.; Chiarakorn, S. Enhanced Visible Light Photocatalytic Activity of N and Ag Doped and Co-Doped TiO₂ Synthesized by Using an In-Sity Solvothermal Method for Gas Phase Ammonia Removal. *Catalysts* **2020**, *10*, 251. [CrossRef]
- 123. Zhong, L.; Haghighat, F.; Lee, C.S.; Lakdawala, N. Performance of ultraviolet photocatalytic oxidation for indoor air applications: Systematic experimental evaluation. *J. Hazard. Mater.* **2013**, *261*, 130–138. [CrossRef] [PubMed]
- 124. Dong, F.; Wang, Z.; Li, Y.; Ho, W.K.; Lee, S.C. Immobilization of polymeric g-C₃N₄ on structured ceramic foam for efficient visible light photocatalytic air purification with real indoor illumination. *Environ. Sci. Technol.* 2014, 48, 10345–10353. [CrossRef] [PubMed]
- 125. Esterkin, C.R.; Negro, A.C.; Alfano, O.M.; Cassano, A.E. Air pollution remediation in a fixed bed photocatalytic reactor coated with TiO₂. *AIChE J.* 2003, *51*, 2298–2310. [CrossRef]
- 126. Rusinque, B.; Escobedo, S.; de Lasa, H. Hydrogen Production via Pd-TiO₂ Photocatalytic Water Splitting under Near-UV and Visible Light: Analysis of the Reaction Mechanism. *Catalysts* **2021**, *11*, 405. [CrossRef]
- 127. Lugo-Vega, C.S. Evaluation of VOC Degradation in Photo- Catalytic Air Reactors: TiO₂ Immobilization, Energy Efficiency and Kinetic Modeling. Ph.D. Thesis, The University of Western Ontario, London, ON, Canada, 2016.
- 128. Dey, G.R.; Pushpa, K.K. Methane generated during photocatalytic redox reaction of alcohols on TiO₂ suspension in aqueous solutions. *Res. Chem. Intermed.* **2006**, *32*, 725–736. [CrossRef]
- 129. Escobedo, S.; Serrano, B.; Calzada, A.; Moreira, J.; de Lasa, H. Hydrogen production using a platinum modified TiO₂ photocatalyst and an organic scavenger. Kinetic modeling. *Fuel* **2016**, *181*, 438–449. [CrossRef]
- 130. Guayaquil, J.F.; Escobedo, S.; Calzada, A.; Serrano, B.; de Lasa, H. Hydrogen Production via Water Dissociation Using Pt–TiO₂ Photocatalysts: An Oxidation–Reduction Network. *Catalysts* **2017**, *7*, 324. [CrossRef]
- 131. Panagiotopoulou, P.; Karamerou, E.E.; Kondarides, D.I. Kinetics and mechanism of glycerol photo-oxidation and photo-reforming reactions in aqueous TiO₂ and Pt/ TiO₂ suspensions. *Catal. Today* **2013**, *209*, 91–98. [CrossRef]
- 132. Besov, A.S.; Vorontsov, A.V.; Parmon, V.N. Fast adsorptive and photocatalytic purification of air from acetone and dimethyl methylphosphonate by TiO₂ aerosol. *Appl. Catal. B Environ.* **2009**, *89*, 602–612. [CrossRef]
- Boulamanti, A.K.; Philippopoulos, C.J. Photocatalytic degradation of C₅-C₇ alkanes in the gas-phase. *Atmos. Environ.* 2009, 43, 3168–3174. [CrossRef]
- 134. Weibel, a.; Bouchet, R.; Knauth, P. Electrical properties and defect chemistry of anatase (TiO₂). *Solid State Ionics* **2006**, 177, 229–236. [CrossRef]
- 135. Sauer, L.M.; Ollis, F.D. Acetone Oxidation in Photocatalytic Monolith Reactor. J. Catal. 1994, 149, 81–94. [CrossRef]
- Trong On, D.; Desplantier-Giscard, D.; Danumah, C.; Kaliaguine, S. ChemInform Abstract: Perspectives in Catalytic Applications of Mesostructured Materials. *ChemInform* 2010, 33, 299–357. [CrossRef]
- 137. Hoffmann, M.R.; Martin, S.T.; Choi, W.; Bahnemannt, D.W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95*, 69–96. [CrossRef]
- Cassano, A.E.; Martín, C.A.; Brandi, R.J.; Alfano, O.M. Photoreactor Analysis and Design: Fundamentals and Applications. *Ind. Eng. Chem. Res.* 1995, 34, 2155–2201. [CrossRef]
- Davydov, L.; Smirniotis, P.G.; Pratsinis, S.E. Novel differential reactor for the measurement of overall quantum yields. *Ind. Eng. Chem. Res.* 1999, 38, 1376–1383. [CrossRef]

- 140. Yamazaki-Nishida, S.; Nagano, K.; Phillips, L.A.; Cervera-March, S.; Anderson, M.A. Photocatalytic degradation of trichloroethylene in the gas phase using titanium dioxide pelle. *J. Photochem. Photobiol. A Chem.* **1993**, *70*, 95–99. [CrossRef]
- 141. Ibrahim, H.; de Lasa, H. Novel photocatalytic reactor for the destruction of airborne pollutants reaction kinetics and quantum yields. *Ind. Eng. Chem. Res.* **1999**, *38*, 3211–3217. [CrossRef]
- 142. Ibrahim, H.; de Lasa, H. Photo-catalytic degradation of air borne pollutants apparent quantum efficiencies in a novel photo-CREC-air reactor. *Chem. Eng. Sci.* 2003, *58*, 943–949. [CrossRef]
- 143. Valadés-Pelayo, P.J.; Moreira del Rio, J.; Solano-Flores, P.; Serrano, B.; de Lasa, H. Establishing photon absorption fields in a Photo-CREC Water II Reactor using a CREC-spectroradiometric probe. *Chem. Eng. Sci.* 2014, *116*, 406–417. [CrossRef]
- 144. Garcia-Hernandez, J.M.; Serrano-Rosales, B.; de Lasa, H. Energy efficiencies in a photo-CREC-air reactor: Conversion of model organic pollutants in air. *Ind. Eng. Chem. Res.* 2012, *51*, 5715–5727. [CrossRef]
- 145. Serrano, B.; de Lasa, H. Photocatalytic Degradation of Water Organic Pollutants. Kinetic. *Ind. Eng. Chem. Res.* **1997**, *36*, 4705–4711. [CrossRef]
- 146. Masood, H.; Toe, C.Y.; Teoh, W.Y.; Sethu, V.; Amal, R. Machine Learning for Accelerated Discovery of Solar Photocatalysts. *ACS Catal.* 2019, 11774–11787. [CrossRef]
- Eskandarloo, H.; Badiei, A.; Behnajady, M.A. Study of the Effect of Additives on the Photocatalytic Degradation of a Triphenylmethane Dye in the Presence of Immobilized TiO₂/NiO Nanoparticles: Artificial Neural Network Modeling. *Ind. Eng. Chem. Res.* 2014, 53, 6881–6895. [CrossRef]
- 148. Ardabili, S.F.; Najafi, B.; Shamshirband, S.; Bidgoli, B.M.; Deo, R.C.; Chau, K. Computational intelligence approach for modeling hydrogen production: A review. *Eng. Appl. Comput. Fluid Mech.* **2018**, *12*, 438–458. [CrossRef]
- 149. Tabatabai-yazdi, F.; Ebrahimian, A.; Khalil, F.E.; Gilani, N. Construction of graphene based photocatalysts for photocatalytic degradation of organic pollutant and modeling using artificial intelligence techniques. *Phys. B Phys. Condens. Matter* **2021**, 608, 412869–412887. [CrossRef]
- 150. Mageed, A.K. Modeling photocatalytic hydrogen production from ethanol over copper oxide nanoparticles: A comparative analysis of various machine learning techniques. *Biomass Convers. Biorefinery* **2021**, 1–9. [CrossRef]