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# Advances in Photocatalytic Hydrogen Production for a Sustainable Future

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Received: 5 August 2025; Revised: 20 December 2025; Accepted: 23 December 2025; Published: 29 December 2025

**Abstract:** The pursuit of sustainable and clean energy has highlighted hydrogen as a key alternative to traditional fossil fuels due to its high energy content and zero-emission characteristics. Among various hydrogen production methods, photocatalytic water splitting, which utilizes solar energy, emerges as a particularly promising approach for generating renewable and environmentally friendly hydrogen. This review examines recent progress in the field of photocatalysis, focusing on significant advancements in photocatalytic materials, system designs, and reactor configurations that have improved the efficiency of hydrogen production. The discussion includes traditional photocatalysts like titanium dioxide ( $TiO_2$ ) and explores new materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and perovskites, highlighting innovations in material development and surface modification. Additionally, the integration of photocatalytic systems with solar energy technologies and artificial photosynthesis is explored, showcasing progress towards scalable and cost-effective solutions. Despite these advancements, challenges such as material stability, economic feasibility, and environmental impacts persist and are critically assessed. The review concludes by outlining future research directions and opportunities, emphasizing that ongoing interdisciplinary efforts and supportive policies are crucial for overcoming current obstacles and achieving broad adoption of photocatalytic hydrogen production. This comprehensive review aims to provide a detailed understanding of the current status and potential future of photocatalytic hydrogen production as a cornerstone of sustainable energy solutions.

**Keywords:** green energy; photocatalyst; hydrogen; sustainability; net zero

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## 1. Introduction

The increasing global energy demand, coupled with the urgent need to mitigate climate change, has driven the search for sustainable and renewable energy solutions. Traditional fossil fuels, while historically reliable, contribute significantly to greenhouse gas emissions and environmental degradation. As a result, the transition towards cleaner energy sources is not only desirable but imperative for ensuring long-term ecological and economic stability. Hydrogen has emerged as a promising clean fuel due to its high energy density and its ability to produce water as the only byproduct when used in fuel cells [1]. Unlike fossil fuels, hydrogen combustion does not release carbon dioxide, making it an attractive option for reducing the carbon footprint of various industries, including transportation, power generation, and manufacturing [2]. Moreover, hydrogen can be stored and transported efficiently, offering flexibility in its application across different sectors [3]. There are several methods for hydrogen production, each with its own advantages and challenges (Figure 1). The most common methods include:

**Steam Methane Reforming (SMR):** This process involves reacting methane with steam under high pressure to produce hydrogen, carbon monoxide, and a small amount of carbon dioxide [4]. While this method is currently the most economical, it relies on natural gas, a fossil fuel, and results in significant  $CO_2$  emissions.

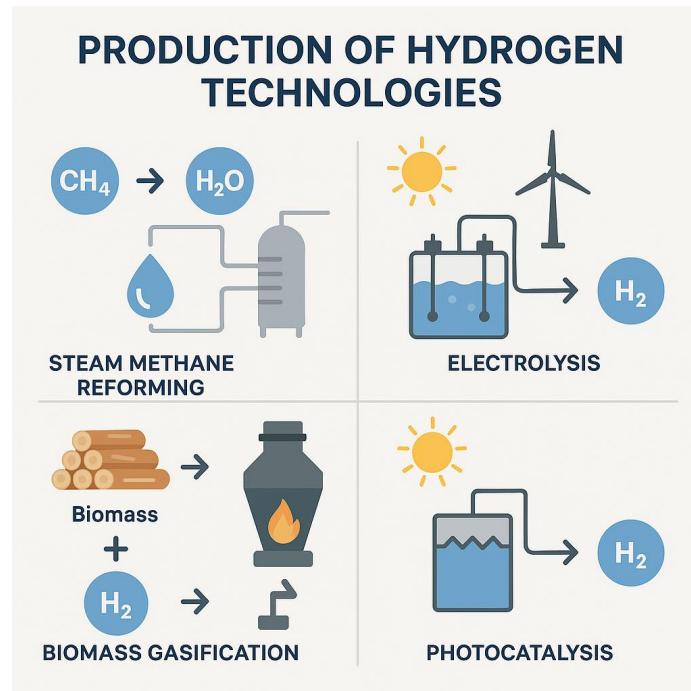
**Electrolysis:** This method uses electricity to split water into hydrogen and oxygen [5]. When powered by renewable energy sources such as wind or solar, electrolysis can produce green hydrogen with zero emissions. However, the high cost of electricity and the need for efficient electrolyzers remain challenges.

**Biomass Gasification:** This process converts organic materials into hydrogen, carbon monoxide, and carbon dioxide through high-temperature reactions [6]. It offers the potential to use waste materials and biomass, but the technology is still developing and requires further optimization.



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**Figure 1.** Overview of hydrogen production technologies.

Among these methods, photocatalytic hydrogen production stands out due to its potential for harnessing solar energy to drive the water-splitting reaction [7]. Photocatalysis involves the use of semiconductor materials that absorb sunlight and generate electron-hole pairs, which then participate in redox reactions to produce hydrogen and oxygen from water. This method is particularly appealing because it directly converts solar energy into chemical energy, offering a sustainable and renewable pathway for hydrogen production. Photocatalytic hydrogen production leverages abundant solar energy, which is a clean and inexhaustible resource [7]. The process can be conducted under mild conditions, reducing the need for high temperatures and pressures associated with other hydrogen production methods. Additionally, advances in material science have led to the development of more efficient and robust photocatalysts, enhancing the feasibility of this approach.

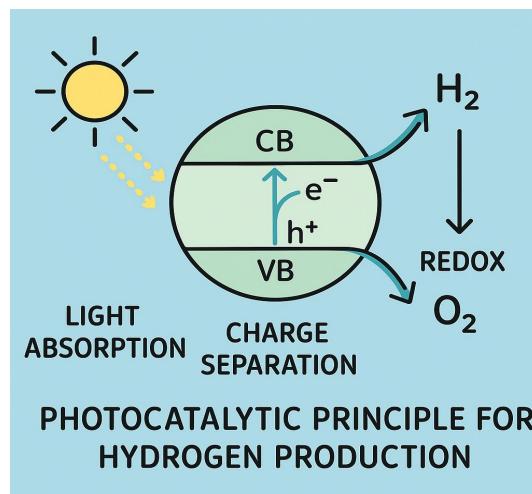
Recent advancements in photocatalytic water splitting have focused on developing efficient and cost-effective materials, including traditional options like titanium dioxide ( $\text{TiO}_2$ ) and innovative alternatives such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and perovskites. Progress in system designs and reactor configurations has further improved the efficiency of hydrogen production. Despite these advancements, significant challenges remain, including material stability, scalability, and economic feasibility, which hinder widespread adoption. This review distinguishes itself from existing literature by providing a comprehensive examination of interdisciplinary approaches that integrate photocatalytic systems with solar energy technologies and artificial photosynthesis. It critically assesses current challenges and explores future research directions, emphasizing the importance of collaborative efforts and supportive policies to overcome obstacles.

## 2. Fundamentals of Photocatalysis

### 2.1. Definition and Basic Principles of Photocatalysis

Photocatalysis is a process in which light energy, typically from the sun, is used to accelerate a chemical reaction via a photocatalyst [8]. A photocatalyst is a specialized material capable of absorbing light and generating electron-hole pairs, which subsequently drive redox reactions. This process is inspired by natural photosynthesis, the mechanism by which plants convert sunlight into chemical energy. However, unlike photosynthesis, which primarily produces biomass for energy storage, photocatalysis is designed to produce valuable chemicals, such as hydrogen gas, offering a promising pathway for renewable energy production and environmental remediation.

The mechanism of photocatalytic reactions can be broken down into three fundamental steps, each of which is critical to the overall efficiency of the process (Figure 2) [9]. The first step is light absorption, where the photocatalyst absorbs photons with energy equal to or greater than its band gap. The absorption of energy excites electrons from the valence band to the conduction band, leaving behind positively charged holes in the valence band and generating electron-hole pairs that drive subsequent chemical transformations.



**Figure 2.** Photocatalytic principle for hydrogen production.

The second step is charge separation, a crucial phase in ensuring the effectiveness of the photocatalytic reaction. Once electron-hole pairs are generated, they must be efficiently separated to prevent recombination, a process where electrons and holes annihilate each other, releasing energy as heat and significantly reducing photocatalytic efficiency. Effective charge separation is essential for maintaining high photocatalytic activity, as it ensures that the excited electrons and holes remain available to participate in chemical reactions.

The final step involves redox reactions, where the separated electrons and holes migrate to the surface of the photocatalyst and engage in oxidation and reduction processes. For example, in hydrogen production, the excited electrons reduce protons ( $H^+$ ) to generate hydrogen gas ( $H_2$ ), a clean and renewable energy source. Simultaneously, the holes oxidize water ( $H_2O$ ) to produce oxygen gas ( $O_2$ ), completing the reaction cycle. This dual functionality of the photocatalyst in facilitating both reduction and oxidation reactions underscores its importance in driving sustainable chemical transformations.

## 2.2. Key Materials Used in Photocatalysis

A variety of materials have been explored as photocatalysts, each offering unique properties that make them suitable for specific applications. These materials play a pivotal role in determining the efficiency, selectivity, and applicability of the photocatalytic process. Below is an expanded discussion of the key materials commonly used in photocatalysis, along with their advantages and limitations.

**Titanium Dioxide ( $TiO_2$ ):**  $TiO_2$  is the most widely studied photocatalyst due to its high stability, non-toxicity, and strong oxidative power [10].  $TiO_2$  is particularly valued for its robustness under harsh chemical conditions and its low environmental impact, making it a popular choice for environmental remediation and energy applications. However, one significant limitation of  $TiO_2$  is its wide band gap (~3.2 eV), which restricts its photocatalytic activity to ultraviolet (UV) light. Since UV light constitutes only a small fraction (around 5%) of the solar spectrum, this limits the material's efficiency under natural sunlight. Efforts to overcome this limitation include doping with metals or non-metals to narrow the band gap and enable visible-light absorption. For instance, nitrogen-doped  $TiO_2$  has shown improved visible-light photocatalytic activity, making it suitable for applications like  $H_2$  production [11].

**Zinc Oxide ( $ZnO$ ):**  $ZnO$  is another popular photocatalyst with a similar band gap to  $TiO_2$  [12].  $ZnO$  is notable for its high electron mobility, which enhances charge transport and reduces electron-hole recombination, thereby improving photocatalytic efficiency. Additionally,  $ZnO$  exhibits good chemical stability and is relatively cost-effective. However, like  $TiO_2$ ,  $ZnO$  is primarily active under UV light, limiting its application under visible-light conditions. Moreover,  $ZnO$  is prone to photocorrosion under prolonged light exposure, which can degrade its performance over time. Strategies like surface modification and composite formation are being explored to enhance its stability and light absorption. An example is  $ZnO$  nanoparticles coated with graphene oxide, which exhibit improved photocatalytic performance under visible light [13].

**Metal-Organic Frameworks (MOFs):** MOFs represent a newer class of photocatalytic materials that have garnered attention for their unique structural and functional properties [14]. MOFs are porous, crystalline materials composed of metal ions coordinated to organic ligands, resulting in high surface areas and tunable band gaps. These properties make MOFs highly versatile for a range of photocatalytic applications, including visible-light-driven processes. Furthermore, the modular nature of MOFs allows for the design of materials tailored to specific

reactions, such as CO<sub>2</sub> reduction or hydrogen production. For example, MIL-125(Ti), a titanium-based MOF, has demonstrated excellent photocatalytic activity for the degradation of organic pollutants under UV light, while NH<sub>2</sub>-MIL-125(Ti), a functionalized derivative, has shown enhanced performance under visible light [15]. However, challenges such as limited thermal and chemical stability, as well as the complexity of synthesis, need to be addressed to fully realize the potential of MOFs in practical applications. Ongoing research focuses on improving the stability of MOFs through post-synthetic modifications, incorporating robust linkers, and developing cost-effective synthesis methods [16].

**Perovskites:** Perovskites have emerged as a promising material for photocatalysis due to their excellent light absorption and superior charge transport properties [17]. Unlike TiO<sub>2</sub> and ZnO, perovskites can be engineered to absorb a broader spectrum of light, including visible and near-infrared wavelengths, significantly enhancing their efficiency under sunlight. They also exhibit lower electron-hole recombination rates, which further boosts their photocatalytic performance. For example, methylammonium lead iodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) has been widely studied for photocatalytic water splitting, demonstrating high hydrogen production rates under visible light [18]. Despite these advantages, perovskites face challenges related to stability, as they are often sensitive to moisture, oxygen, and high temperatures. Advances in material engineering, such as encapsulation and compositional tuning, are being pursued to improve the durability of perovskites for long-term applications. For instance, the incorporation of hydrophobic organic cations, such as phenylethylammonium (PEA), has been shown to enhance stability by protecting the perovskite layers from moisture [19].

Each of these materials—TiO<sub>2</sub>, ZnO, MOFs, and perovskites—offers distinct advantages and faces unique challenges, underscoring the importance of material selection and optimization in photocatalysis. While TiO<sub>2</sub> and ZnO are well-established and cost-effective options for UV-driven reactions, MOFs and perovskites represent the forefront of innovation, offering solutions for visible-light-driven processes [20,21]. By combining the strengths of these materials, such as through hybrid systems or composites, researchers aim to develop photocatalysts that are not only efficient but also versatile and durable, paving the way for advancements in sustainable energy and environmental technologies.

### 2.3. Factors Affecting Photocatalytic Efficiency

The efficiency of photocatalytic processes is determined by a combination of factors that influence the material's ability to absorb light, separate charges, and sustain chemical reactions over time. These factors are interdependent, and optimizing them is crucial for achieving high-performance photocatalytic systems. Below is an expanded and interconnected discussion of the key factors affecting photocatalytic efficiency.

**Light Absorption:** The foundation of photocatalysis lies in the photocatalyst's ability to absorb light and utilize its energy to drive chemical reactions. Materials with a narrow band gap are particularly advantageous because they can absorb light across a broader spectrum, including visible light, which constitutes the majority of solar radiation. For example, while traditional materials like TiO<sub>2</sub> and ZnO are primarily active under UV light due to their wide band gaps, emerging materials such as perovskites and modified metal-organic frameworks (MOFs) are engineered to harness visible and near-infrared light [20,21]. Enhancing light absorption not only improves the utilization of solar energy but also directly impacts the generation of electron-hole pairs, which are crucial for initiating photocatalytic reactions.

**Electron-Hole Separation:** Once light is absorbed, the generation of electron-hole pairs occurs, but their effective separation and migration are critical to sustaining the photocatalytic process. Recombination of these pairs leads to energy loss, significantly reducing photocatalytic activity [22]. To address this challenge, various strategies have been developed. For instance, doping the photocatalyst with metals or non-metals can introduce defect sites that improve charge separation [23]. Similarly, forming heterojunctions—interfaces between two materials with different band structures—facilitates the transfer of electrons and holes, reducing recombination rates [24]. The use of co-catalysts, such as noble metals or transition metal oxides, further enhances charge separation by acting as electron sinks or hole scavengers, thereby prolonging the lifetime of charge carriers. These approaches collectively improve the efficiency of photocatalytic systems.

**Surface area and morphology:** The surface area and morphology of the photocatalyst play a pivotal role in determining its catalytic performance. Photocatalysts with high surface areas provide more active sites for chemical reactions, thereby increasing the overall reaction rate. Nanostructured materials, such as nanoparticles, nanorods, and nanosheets, are particularly effective in this regard due to their large surface-to-volume ratios [25]. Additionally, the morphology of the photocatalyst can influence light scattering and absorption, further enhancing photocatalytic efficiency. For example, hierarchical structures and porous materials can facilitate light trapping,

while also improving the diffusion of reactants and products to and from the active sites [26]. Thus, tailoring the surface area and morphology is a key strategy for optimizing photocatalysis.

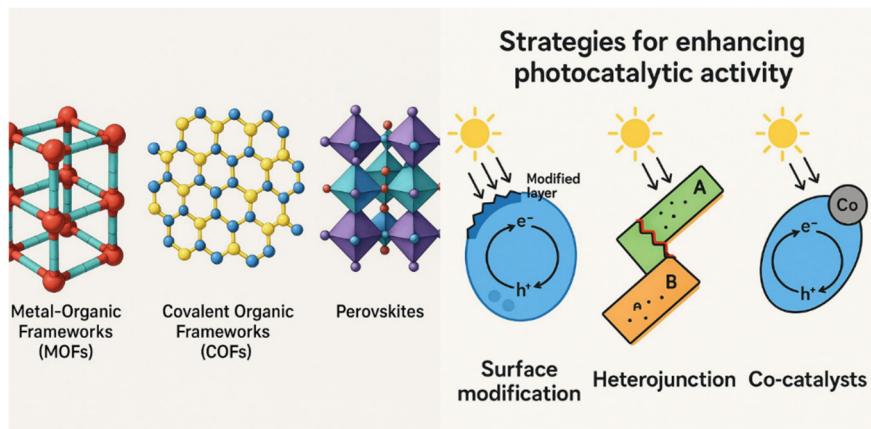
**Stability and Durability:** For photocatalysis to be viable in practical applications, the photocatalyst must demonstrate long-term stability under reaction conditions. Stability involves resistance to photo-corrosion, chemical degradation, and structural changes that could impair performance over time. Materials like  $\text{TiO}_2$  and  $\text{ZnO}$  are known for their chemical stability, but they may still suffer from issues such as photocorrosion under prolonged light exposure [27]. Emerging materials, such as perovskites and MOFs, often face challenges related to moisture and thermal stability, which limit their durability [28]. To address these issues, researchers are exploring strategies such as surface passivation, encapsulation, and the development of composite materials that combine the strengths of different components. Ensuring stability not only extends the lifespan of the photocatalyst but also reduces operational costs, making photocatalysis more sustainable and economically feasible.

### 3. Photocatalytic Materials and Their Development

Photocatalytic materials have garnered significant attention due to their immense potential in addressing global challenges, such as environmental remediation, renewable energy generation, and sustainable chemical synthesis [29]. The field has evolved remarkably, driven by advancements in materials science and engineering, which have enabled the development of innovative materials with enhanced performance and functionality.

For decades,  $\text{TiO}_2$  has been the cornerstone of photocatalytic research. Its remarkable stability, non-toxicity, and strong oxidative power have made it a widely studied material for various applications. However, despite these advantages,  $\text{TiO}_2$  suffers from inherent limitations that restrict its efficiency. The wide bandgap of anatase  $\text{TiO}_2$  (~3.2 eV) limits its activation to ultraviolet (UV) light, which accounts for only a small fraction of the solar spectrum [27]. This means that the majority of visible light, a more abundant energy source, remains unutilized. Additionally, the rapid recombination of photo-generated electron-hole pairs further diminishes its photocatalytic efficiency, posing a significant barrier to its practical use. To address these challenges, researchers have explored modifications to  $\text{TiO}_2$ , such as doping with metal or non-metal elements, surface functionalization, and constructing heterojunctions. While these strategies have yielded improvements, they are often insufficient to fully overcome  $\text{TiO}_2$ 's limitations, prompting a shift toward the exploration of alternative materials with superior properties.

Beyond traditional and modified  $\text{TiO}_2$ , several emerging materials have demonstrated significant promise in photocatalysis (Figure 3). These materials offer unique structural and electronic properties, enabling enhanced light absorption, charge separation, and catalytic activity.



**Figure 3.** Developed materials and strategies for enhancing photocatalytic activity.

**Metal-Organic Frameworks (MOFs):** MOFs are a class of porous crystalline materials composed of metal ions coordinated with organic ligands. Their highly tunable porosity, large surface area, and customizable chemical functionality make them excellent candidates for photocatalysis. By incorporating photoactive components, researchers can design MOFs to enhance light absorption and facilitate efficient charge separation. For example, MOFs have been utilized in applications such as  $\text{CO}_2$  reduction, water splitting, and pollutant degradation, demonstrating their versatility and potential for addressing diverse challenges in photocatalysis.

**Covalent Organic Frameworks (COFs):** COFs share structural similarities with MOFs but are composed entirely of light elements such as carbon, hydrogen, oxygen, nitrogen, and boron [30]. These crystalline, porous materials exhibit high thermal and chemical stability, making them suitable for demanding photocatalytic applications. A key advantage of COFs lies in their extended  $\pi$ -conjugated systems, which facilitate efficient

charge transport and light harvesting. By tailoring the molecular structure of COFs, researchers can optimize their photocatalytic properties for specific applications, including hydrogen evolution, organic transformations, and environmental remediation.

**Perovskites:** Metal halide perovskites, particularly those based on lead halides, have emerged as highly efficient photocatalysts due to their exceptional optoelectronic properties. These materials exhibit tunable bandgaps, high absorption coefficients, and long carrier lifetimes, making them suitable for a wide range of photocatalytic processes. However, their practical application is hindered by challenges such as instability under environmental conditions and the toxicity of lead-based compounds. Addressing these issues through material engineering and the development of lead-free perovskites is a critical area of ongoing research.

To further enhance the photocatalytic activity of both traditional and emerging materials, researchers have employed several innovative strategies (Figure 3). These approaches aim to maximize light absorption, improve charge separation, and increase the availability of active sites for catalytic reactions.

**Surface Modification:** Surface modification is a widely used technique to enhance the photocatalytic performance of materials. By modifying the surface with functional groups, noble metals (e.g., Pt, Au), or other active species, researchers can improve light absorption, provide additional active sites, and facilitate efficient charge separation [31]. For instance, the deposition of noble metal nanoparticles on  $\text{TiO}_2$  has been shown to enhance its catalytic activity by creating surface plasmon resonance effects, which extend light absorption into the visible range [32].

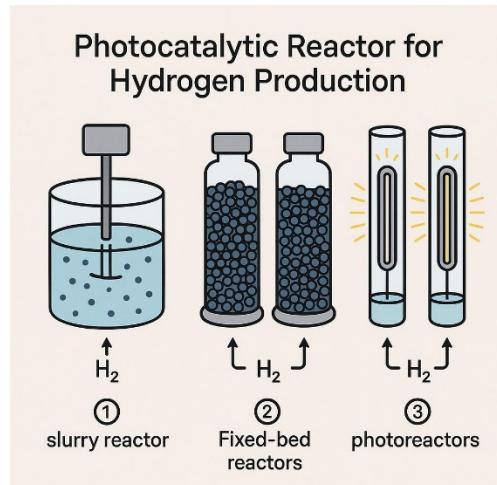
**Heterojunctions:** The construction of heterojunctions by combining two or more semiconductors with complementary band structures is another effective strategy for improving photocatalytic efficiency [24]. Heterojunctions create an internal electric field at the interface of the semiconductors, promoting the separation of photo-generated electron-hole pairs and reducing recombination rates. Examples of successful heterojunction systems include  $\text{TiO}_2/\text{CdS}$ ,  $\text{ZnO}/\text{WO}_3$ , and  $\text{g-C}_3\text{N}_4/\text{TiO}_2$ , which have demonstrated enhanced performance in applications such as hydrogen production and pollutant degradation [33].

**Co-Catalysts:** Incorporating co-catalysts into photocatalytic systems has proven to be an effective way to boost their activity. Co-catalysts, such as transition metal oxides, sulfides, or noble metals, can provide additional active sites, facilitate charge transfer, and participate in redox reactions. For example, the addition of platinum (Pt) nanoparticles to  $\text{TiO}_2$  has been shown to significantly enhance hydrogen production during water splitting [34]. Similarly, the use of co-catalysts in emerging materials like MOFs and COFs has expanded their applicability and improved their catalytic performance.

#### 4. Photocatalytic Systems and Reactor Design

Hydrogen production through photocatalytic water splitting has gained significant attention as a clean and sustainable energy solution. The efficiency and scalability of this process are heavily dependent on the design and operation of photocatalytic systems and reactors [35]. These systems must optimize light utilization, catalyst performance, and hydrogen collection while addressing challenges associated with large-scale implementation. This section explores the various types of photocatalytic reactors, key design considerations, and recent innovations aimed at improving their performance for hydrogen production.

Types of Photocatalytic Reactors for Hydrogen Production (Figure 4):



**Figure 4.** Type of photoreactor for hydrogen production.

**Slurry Reactors:** Slurry reactors are one of the most common reactor designs for photocatalytic hydrogen production. In these systems, photocatalytic nanoparticles are dispersed in a liquid medium, typically water containing a sacrificial agent (e.g., methanol or ethanol) to enhance hydrogen evolution [35]. The suspended photocatalysts provide a large surface area for light absorption and reaction, making slurry reactors highly efficient for hydrogen production in laboratory-scale experiments. The high surface area of dispersed photocatalysts allows for efficient light harvesting and interaction with reactants, leading to enhanced hydrogen generation rates. However, a major drawback of slurry reactors is the difficulty in separating the photocatalyst from the liquid after the reaction. This separation process can be energy-intensive and impractical for large-scale applications. Additionally, photocatalyst agglomeration over time can reduce the effective surface area and light absorption, impacting hydrogen production efficiency. Despite these challenges, slurry reactors remain a vital tool for studying photocatalytic hydrogen production processes, particularly in research settings focused on developing new photocatalytic materials.

**Fixed-Bed Reactors:** Fixed-bed reactors address many of the limitations of slurry reactors by immobilizing the photocatalyst on a solid substrate, such as glass beads, metal meshes, or ceramic plates [36]. This configuration eliminates the need for post-reaction separation of the photocatalyst, making fixed-bed reactors more practical for continuous hydrogen production processes. Fixed-bed reactors are particularly suited for industrial-scale hydrogen production, where continuous flow operations are required. In this setup, water or a water-sacrificial agent mixture flows over the immobilized photocatalyst, and hydrogen gas is collected as it evolves. However, fixed-bed reactors often face challenges related to limited mass transfer and lower surface area compared to slurry systems [36]. The immobilized photocatalyst may not interact with reactants as effectively, and light penetration through the reactor may be hindered by uneven illumination. To overcome these challenges, researchers are exploring advanced designs, such as structured catalyst supports (e.g., honeycomb or foam structures) and improved flow geometries, to enhance mass transfer, light distribution, and overall hydrogen production efficiency.

**Photoreactors:** Photoreactors are specialized reactor systems designed to maximize light exposure to the photocatalyst, which is critical for driving hydrogen production via photocatalytic water splitting. These reactors come in various configurations, including tubular, flat-plate, and annular designs, each optimized for specific operational conditions.

A key feature of photoreactors is the integration of light sources, such as UV lamps, visible light LEDs, or solar concentrators, to activate the photocatalyst. For hydrogen production, photoreactors are often designed to ensure uniform illumination of the photocatalytic material, minimizing shadowing and maximizing light absorption. Advanced photoreactor designs may include reflective surfaces, optical fibers, or light guides to enhance light utilization and improve the efficiency of the water-splitting process [37]. Solar-driven photoreactors, which harness natural sunlight as the energy source, are particularly promising for sustainable hydrogen production. These systems often incorporate solar concentrators or tracking mechanisms to optimize sunlight capture and focus it onto the photocatalyst, reducing energy costs while enhancing hydrogen yield.

Effective reactor design plays a pivotal role in maximizing light absorption, material utilization, and overall performance in photocatalytic systems. By addressing critical design considerations and integrating recent advancements, researchers can significantly enhance the efficiency, scalability, and sustainability of photocatalytic processes. Below, we explore key factors in reactor design and highlight recent innovations that are shaping the future of photocatalytic systems.

**Light Source and Distribution:** Uniform and sufficient light distribution across the photocatalyst surface is essential to maximize photocatalytic activity. Uneven light exposure can lead to inefficient utilization of the photocatalyst and suboptimal reaction rates. To address this, careful selection of light sources (e.g., LEDs, mercury lamps, or solar light) is critical. Reactor geometries should be designed to promote even light penetration, such as by using reflective surfaces, transparent reactor walls, or light guides. Advanced optical systems, such as lenses or mirrors, can further enhance light intensity and distribution, ensuring that the photocatalyst receives adequate illumination.

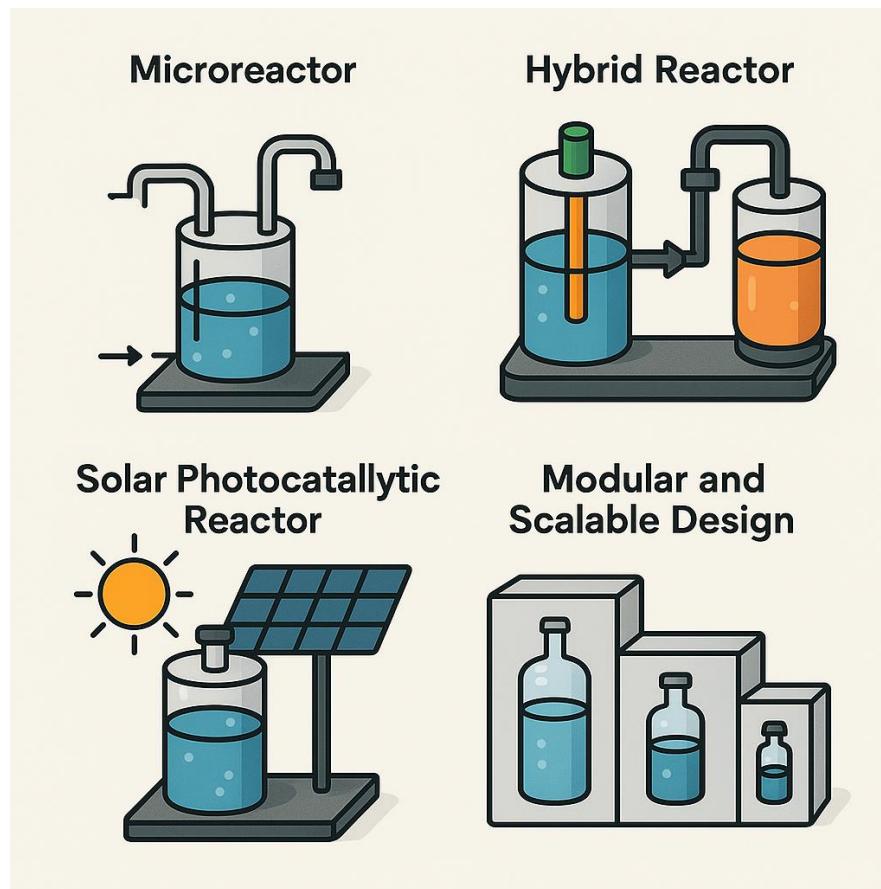
**Photocatalyst Configuration:** The configuration and placement of the photocatalyst within the reactor significantly influence its performance. Immobilizing the photocatalyst onto transparent or light-permeable substrates can enhance light penetration and reduce issues related to catalyst recovery. Alternatively, highly porous materials or nanostructured photocatalysts can increase the active surface area, improving both light absorption and reaction efficiency. Innovative designs, such as 3D-printed structures or hierarchical porous materials, are increasingly being employed to optimize photocatalyst placement and performance.

**Mass Transfer Efficiency:** Efficient mass transfer of reactants to the photocatalytic sites is crucial for maintaining high reaction rates and preventing the formation of concentration gradients. Reactor designs that promote turbulent flow, such as those incorporating baffles or stirrers, can enhance mixing and improve reactant delivery to

the photocatalyst surface. Microfluidic channels, which provide precise control over fluid flow and reduce diffusion limitations, are also gaining attention for their ability to improve mass transfer in small-scale systems.

**Thermal Management:** Photocatalytic reactions often generate heat, which can impact the stability and efficiency of the photocatalyst. Excessive heat may lead to photocatalyst degradation or undesirable side reactions. To address this, reactors can be equipped with cooling systems, such as water jackets or heat exchangers, to dissipate heat effectively. Additionally, materials with high thermal conductivity, such as metal-based reactor components, can be used to ensure efficient thermal management and maintain optimal reaction conditions.

To overcome challenges related to efficiency, scalability, and sustainability, researchers have developed innovative reactor designs tailored to specific applications. Some of the most promising advancements include (Figure 5):



**Figure 5.** Innovative reactor design for photocatalytic hydrogen production.

**Microreactors:** Microreactors, which utilize microchannels to enhance mass transfer and light absorption, represent a cutting-edge approach in photocatalytic reactor design. Their small size allows for precise control over reaction conditions, including temperature, flow rate, and light intensity. Microreactors are particularly well-suited for high-throughput screening, enabling rapid testing of photocatalysts under various conditions. Additionally, their compact design facilitates the integration of multiple reaction steps within a single device, making them ideal for small-scale applications and specialized processes. An optofluidic planar microreactor was fabricated using a Pt/TiO<sub>2</sub> film-coated glass substrate as the bottom plate and an uncoated glass substrate with a planar reaction chamber as the cover plate, with the Pt/TiO<sub>2</sub> film achieving the highest hydrogen production rate of 16.35 mmol h<sup>-1</sup> g<sup>-1</sup> (4.7 µmol h<sup>-1</sup> cm<sup>-2</sup>) at an optimal reactant flow rate of 0.3 mL min<sup>-1</sup> under visible light irradiation from a 400 W metal halide lamp [38].

**Hybrid Reactors:** Hybrid reactors combine the advantages of different reactor types, such as slurry reactors and fixed-bed reactors, to achieve superior performance. For instance, slurry reactors offer high surface area and efficient mass transfer, while fixed-bed reactors simplify photocatalyst recovery and separation. By integrating these features, hybrid reactors provide a versatile solution for diverse applications, ranging from water treatment to chemical synthesis. Recent advancements in hybrid reactor design include the use of magnetic photocatalysts, which can be easily separated using external magnetic field. For example, an optimized Ru-doped LaFeO<sub>3</sub> photocatalyst (Ru-LaFeO<sub>3</sub>) coupled with Fe<sub>2</sub>O<sub>3</sub> magnetic particles achieved total glucose degradation and

produced 5460  $\mu\text{mol/L}$  of hydrogen from glucose aqueous solutions and food industry wastewater after 4 h under visible light, demonstrating its stability and reusability through external magnetic field recovery [39].

**Solar Photocatalytic Reactors:** Harnessing solar energy directly in photocatalytic processes is a key step toward sustainability and cost-effectiveness [40]. Solar photocatalytic reactors are specifically designed to maximize the utilization of natural sunlight. Innovations such as solar concentrators, which focus sunlight onto the photocatalyst, and advanced light-harvesting materials, such as plasmonic nanoparticles, have significantly improved the efficiency of these systems. Additionally, reactor geometries optimized for outdoor use, such as parabolic troughs or flat-panel designs, enhance light capture and enable large-scale solar photocatalysis.

**Modular and Scalable Designs:** Developing modular reactor systems is essential for transitioning photocatalytic technologies from laboratory-scale experiments to industrial applications. Modular designs allow for flexible adjustment of reactor capacity, enabling researchers to scale up or down based on specific requirements [41]. These systems also facilitate the parallel operation of multiple reactors, improving productivity and reliability. Scalable designs often incorporate standardized components, making them easier to assemble, maintain, and expand for large-scale production [41].

The design and development of photocatalytic reactors are critical to advancing the field of photocatalysis [42]. By addressing key design considerations—such as light distribution, photocatalyst configuration, mass transfer, and thermal management—and leveraging recent innovations, researchers can create more efficient, versatile, and sustainable systems. Future efforts will likely focus on integrating smart technologies, such as real-time monitoring and automation, to further optimize reactor performance and enable the widespread adoption of photocatalytic processes in various industries.

## 5. Challenges and Limitations

Photocatalytic hydrogen production holds immense promise as a sustainable and environmentally friendly energy solution. However, several challenges and limitations hinder its widespread adoption and commercialization. These challenges can be broadly categorized into technical, economic, and environmental/safety concerns. Addressing these issues is critical to advancing photocatalytic technologies and achieving large-scale implementation.

### 5.1. Technical Challenges: Material Stability, Efficiency Under Visible Light, and Scalability

One of the primary technical challenges in photocatalytic hydrogen production is the stability of photocatalytic materials under operational conditions. Photocatalysts are often exposed to prolonged light irradiation, aqueous environments, and oxidative or reductive reactions, all of which can lead to material degradation. For example, metal oxide photocatalysts such as  $\text{TiO}_2$ , while stable under UV light, may suffer from surface deactivation or leaching of active sites over time. Similarly, perovskite-based materials, which show excellent photocatalytic performance, are highly sensitive to moisture, oxygen, and high temperatures, causing rapid degradation. This instability reduces the efficiency and lifespan of photocatalytic systems, necessitating the development of robust materials capable of maintaining activity under harsh operational conditions. Strategies such as surface passivation, encapsulation, and the incorporation of protective coatings are being explored to improve material durability.

Another critical technical challenge is achieving high efficiency under visible light. While ultraviolet (UV) light is highly effective in driving photocatalytic reactions, it constitutes only about 4–5% of the solar spectrum. Visible light, which makes up approximately 43% of sunlight, is far more abundant and must be efficiently utilized for practical applications. Traditional photocatalysts like  $\text{TiO}_2$  have a wide bandgap (~3.2 eV), limiting their absorption to the UV region. To address this, researchers are exploring various strategies to extend the light absorption range of photocatalysts into the visible spectrum. These strategies include doping with metal or non-metal elements, creating heterojunctions with narrow-bandgap semiconductors, and developing novel materials such as MOFs and COFs. For instance, nitrogen-doped  $\text{TiO}_2$  has shown enhanced visible-light absorption due to the narrowing of its bandgap, while bismuth-based materials like  $\text{BiVO}_4$  have emerged as promising visible-light-responsive photocatalysts.

Scalability remains a significant hurdle in translating laboratory-scale successes to industrial-scale applications. Many photocatalytic systems demonstrate impressive efficiency in small-scale experiments but face significant challenges when scaled up. Uniform light distribution, mass transfer limitations, and the need for large quantities of high-purity materials are key issues that arise during scale-up. For example, in large-scale reactors, ensuring that all photocatalyst particles receive adequate light exposure can be challenging, leading to uneven reaction rates. Additionally, the synthesis of advanced photocatalytic materials often requires precise control over parameters such as particle size, morphology, and composition, which becomes more difficult at larger scales. To

address these challenges, researchers are focusing on the development of scalable synthesis techniques, such as sol-gel processes, and innovative reactor designs, including fluidized bed reactors and photoreactors with optimized light-harvesting geometries. These advancements are essential for maintaining high performance and efficiency in large-scale applications.

### 5.2. Economic Challenges: Cost of Materials and Production Processes

The economic feasibility of photocatalytic hydrogen production is another significant challenge that must be addressed to enable widespread adoption. Many high-performance photocatalysts rely on expensive and scarce materials, such as noble metals (e.g., platinum, gold) and certain metal oxides (e.g., ruthenium oxide). These materials, while highly effective in enhancing photocatalytic activity, contribute to the high cost of hydrogen production, making it less competitive compared to conventional methods like steam methane reforming. For instance, platinum is one of the most effective co-catalysts for hydrogen evolution but is prohibitively expensive for large-scale applications. Moreover, the synthesis processes for advanced photocatalytic materials often involve complex and energy-intensive methods. Techniques such as high-temperature calcination, hydrothermal synthesis, and chemical vapor deposition require significant energy input and specialized equipment, further driving up costs. For example, the synthesis of MOFs and COFs, which are promising photocatalytic materials, often involves multi-step procedures and the use of expensive organic linkers. To overcome these economic barriers, researchers are exploring the development of cost-effective materials, such as earth-abundant metal oxides (e.g.,  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ) and carbon-based materials like graphene. Additionally, efforts are being made to simplify synthesis methods, such as using low-temperature processes, green chemistry approaches, and scalable techniques like spray pyrolysis and solution-phase synthesis.

### 5.3. Environmental and Safety Concerns Associated with Photocatalytic Materials

The environmental and safety implications of photocatalytic materials are crucial considerations for ensuring the sustainability of hydrogen production. These concerns span the entire lifecycle of photocatalytic materials, from raw material extraction and synthesis to operational use and end-of-life disposal. For instance, the extraction of rare or precious metals used in photocatalysts, such as platinum or cadmium, often involves environmentally harmful mining practices that contribute to habitat destruction and pollution. During synthesis, the use of organic solvents, strong acids, and energy-intensive processes can generate hazardous waste, further adding to environmental degradation. To address these issues, researchers are exploring green synthesis methods that utilize renewable precursors, water-based solvents, and energy-efficient techniques to minimize the environmental impact. Lifecycle assessments (LCAs) are also being conducted to evaluate the environmental footprint of photocatalytic materials at each stage, providing critical insights into areas where improvements can be made.

Material toxicity and disposal remain significant challenges. Certain photocatalysts, such as cadmium-based semiconductors (e.g.,  $\text{CdS}$ ,  $\text{CdSe}$ ), are highly effective for hydrogen production but are also toxic and pose risks to human health and the environment. The leaching of heavy metals during material degradation or improper disposal can lead to long-term ecological damage. To mitigate these risks, researchers are focusing on developing earth-abundant, non-toxic alternatives, such as iron-based photocatalysts (e.g.,  $\text{Fe}_2\text{O}_3$ ) and carbon-based materials like graphene. Additionally, efforts are being made to recycle and reuse spent photocatalytic materials to reduce waste and minimize the demand for raw material extraction, further enhancing the sustainability of the process.

Safety concerns during the operational phase are also critical, particularly regarding the generation and handling of hydrogen gas. Hydrogen is highly flammable, and its accumulation in confined spaces can result in significant explosion risks if not properly managed. This is especially important in large-scale industrial applications, where hydrogen is produced in greater volumes. To address these challenges, advanced reactor designs are being developed with built-in safety features, such as effective ventilation systems, hydrogen sensors, and gas separation membranes, to ensure safe collection and storage of hydrogen. Furthermore, optimizing operating conditions, such as reducing the need for high-pressure systems, can further minimize safety risks. For instance, designing photocatalysts that operate efficiently under ambient conditions can significantly reduce the potential for accidents.

Addressing these lifecycle and safety concerns requires a comprehensive approach that combines material science, engineering, and environmental policy. Future research should prioritize the development of non-toxic and biodegradable photocatalysts, along with green and energy-efficient synthesis methods. Conducting detailed lifecycle assessments will help identify and mitigate environmental impacts at each stage of the material lifecycle. Additionally, designing scalable and safe reactor systems with robust safety measures for hydrogen handling and

storage is crucial. By overcoming these challenges, the photocatalytic hydrogen production process can become a viable and sustainable energy solution, paving the way for a cleaner and safer energy future.

## 6. Future Directions and Research Opportunities

### 6.1. Potential for Novel Materials and Hybrid Systems

The future of photocatalytic hydrogen production lies in the discovery and development of novel materials and hybrid systems. Researchers are exploring a wide range of materials, including perovskites, carbon-based nanomaterials, and covalent organic frameworks, which offer unique properties that can enhance photocatalytic performance. These materials can be engineered to have better light absorption, charge separation, and stability, addressing some of the current limitations in the field.

Hybrid systems, which combine different types of photocatalysts or integrate photocatalysts with other functional materials, are also showing great promise [43]. For instance, combining semiconductor materials with plasmonic nanoparticles can enhance light absorption through localized surface plasmon resonance, while integrating photocatalysts with co-catalysts can improve the efficiency of hydrogen evolution and oxygen evolution reactions. These hybrid approaches can lead to synergistic effects that significantly boost overall photocatalytic efficiency.

### 6.2. Role of Computational Modeling and AI in Material Discovery

Computational modeling and artificial intelligence (AI) are revolutionizing the way new photocatalytic materials are discovered and optimized. Advanced computational techniques, such as density functional theory (DFT) and machine learning algorithms, can predict the properties and performance of potential photocatalysts before they are synthesized. This accelerates the discovery process by allowing researchers to screen a vast number of materials and identify the most promising candidates for experimental validation.

AI can also be used to optimize synthesis processes and operational conditions, leading to more efficient and cost-effective production methods. By analyzing large datasets from experimental results, AI algorithms can uncover patterns and correlations that might not be apparent through traditional analysis, guiding the design of next-generation photocatalytic systems.

### 6.3. Integration with Other Renewable Energy Technologies

Integrating photocatalytic hydrogen production with other renewable energy technologies can create synergistic systems that maximize overall energy efficiency and sustainability. For example, combining photocatalytic systems with photovoltaic cells can enhance solar energy utilization, where excess electricity generated by photovoltaics can be used to drive supplementary electrolysis processes, thereby increasing hydrogen production rates. Additionally, integrating photocatalytic hydrogen production with wind or biomass energy systems can provide a continuous and reliable hydrogen supply, even when solar irradiance is low. These hybrid renewable energy systems can contribute to a more resilient and diversified energy infrastructure, reducing dependence on fossil fuels and lowering greenhouse gas emissions.

### 6.4. Policy and Funding Support for Research and Development

The advancement of photocatalytic hydrogen production technologies requires robust policy and funding support. Governments and international organizations play a crucial role in providing the necessary resources and creating an enabling environment for research and development. Policies that promote renewable energy adoption, provide subsidies or tax incentives for clean energy technologies, and support collaborative research initiatives can significantly accelerate progress in this field.

Increased funding for fundamental and applied research is essential to overcome the technical and economic challenges associated with photocatalytic hydrogen production. Public-private partnerships, grants, and investment in research infrastructure can facilitate the development of innovative solutions and their transition from the laboratory to commercial applications. Furthermore, international cooperation and knowledge-sharing can help address global energy challenges and drive the widespread adoption of sustainable hydrogen production technologies.

By focusing on these future directions and leveraging emerging research opportunities, the field of photocatalytic hydrogen production can make substantial contributions to the global transition towards clean and renewable energy sources.

## 7. Conclusions

In this review, we have explored the fundamentals and advancements in photocatalytic hydrogen production, emphasizing its potential as a sustainable and renewable energy solution. We began by discussing the need for clean energy alternatives and the significance of hydrogen as a zero-emission fuel. Various hydrogen production methods were introduced, with a particular focus on the photocatalytic approach, which harnesses solar energy to drive the water-splitting reaction. The core principles of photocatalysis were outlined, including the mechanisms of light absorption, charge separation, and redox reactions. Key materials such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , MOFs, and perovskites were highlighted for their roles in enhancing photocatalytic efficiency. Additionally, factors affecting the performance of photocatalysts, such as light absorption, electron-hole separation, surface area, and stability, were examined in detail. Photocatalytic hydrogen production holds significant promise for contributing to global sustainability efforts. By utilizing abundant and clean solar energy, this technology offers a pathway to produce hydrogen without the associated carbon emissions of traditional methods like steam methane reforming. The integration of advanced photocatalytic materials and innovative system designs continues to improve the efficiency and scalability of this approach, bringing it closer to practical and widespread application. The potential impact of photocatalytic hydrogen production on sustainability is profound. It provides a renewable and environmentally friendly alternative to fossil fuels, contributing to the reduction of greenhouse gas emissions and the mitigation of climate change. Moreover, the development of efficient photocatalytic systems can support the transition to a hydrogen economy, fostering energy security and reducing dependence on non-renewable resources. Looking ahead, the future of photocatalytic hydrogen production is promising but requires ongoing research and development to overcome existing challenges. Enhancing the efficiency, stability, and cost-effectiveness of photocatalysts remains a critical focus. Interdisciplinary efforts, combining advances in material science, nanotechnology, and chemical engineering, are essential to drive innovation in this field. Additionally, supportive policies and investment in renewable energy infrastructure will play a crucial role in facilitating the adoption of photocatalytic hydrogen production on a larger scale.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The author declares no conflict of interest.

**Use of AI and AI-Assisted Technologies:** No AI tools were utilized for this paper.

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