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Review

Advanced TiO₂ Based Photocatalytic Systems for Water Splitting: A Comprehensive Review from Fundamentals to Manufacturing

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Abstract: The global imperative for clean energy solutions has positioned photocatalytic water splitting as a promising pathway for sustainable hydrogen production. This review comprehensively analyzes recent advances in TiO₂-based photocatalytic systems, focusing on materials engineering, water source effects, and scale-up strategies. We recognize the advancement in nanoscale architectural design, engineered heterojunction of the catalyst, and cocatalyst integration that have significantly enhanced photocatalytic efficiency. Particular emphasis is placed on the crucial role of water chemistry in photocatalytic system performance, analyzing how different water sources—from wastewater to seawater—impact hydrogen evolution rates and system stability. Additionally, the review addresses key challenges in scaling up these systems, including optimization of reactor design, light distribution, and mass transfer. Recent developments in artificial intelligence-driven materials discovery and process optimization are discussed, along with emerging opportunities in bio-hybrid systems and CO₂ reduction coupling. Through critical analysis, we identify fundamental challenges and propose strategic research directions for advancing TiO₂-based photocatalytic technology toward practical implementation. This work will provide a comprehensive framework for researchers to explore advanced TiO₂-based composite materials to develop efficient and scalable photocatalytic systems for multifunctional simultaneous hydrogen production.

Keywords: photocatalytic water splitting; hydrogen evolution; heterojunction engineering; water chemistry; scale-up engineering; reactor design; artificial intelligence in catalysis; sustainable energy

1. Introduction

Energy is becoming an increasingly critical factor in global socio-economic development and environmental sustainability [1–3]. The global energy infrastructure continues to be overwhelmingly reliant on fossil fuels, with oil being the predominant source, followed closely by coal, while natural gas constitutes approximately one-fourth of power generation (Figure 1) [4,5]. The predominant reliance on non-renewable energy sources has precipitated substantial environmental deterioration through carbon dioxide emissions (CO₂), exacerbating both concerns in climate change and challenges inherited with global energy security [6–8]. These global challenges represent two of humanity's most pressing concerns, particularly in light of the IPCC's recommendation to achieve substantial CO₂ emissions reductions by 2050 and limit global average temperature increase below 1.5°C [9–12]. To meet these ambitious zero-emission targets while ensuring energy security, a transition toward clean, sustainable energy alternatives is imperative [13,14]. Among various renewable energy sources, hydrogen has emerged as a promising energy carrier due to its zero greenhouse gas emissions, superior energy capacity, and ecological sustainability [15–18]. However, the current hydrogen production methods, dominated by steam methane reforming, contribute significantly to greenhouse gas emissions, accounting for approximately 530 million tons of CO₂ annually [19–21]. While hydrogen can be produced through multiple pathways, photocatalytic water

splitting using natural light has recently gained attention as a sustainable approach that harnesses abundant renewable resources such as water and solar energy [22–24].

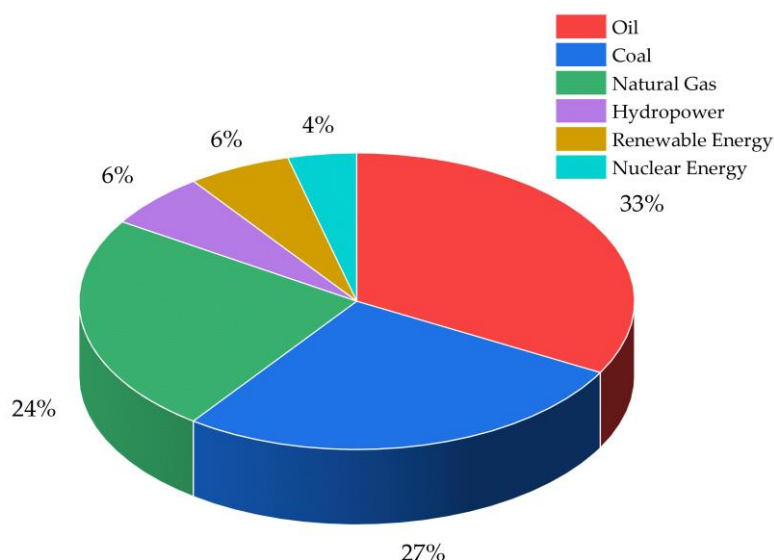


Figure 1. Global Energy Resource Distribution by Percentage [25].

Photocatalytic water splitting represents a transformative approach to hydrogen production, offering the possibility of harnessing abundant solar energy to generate clean hydrogen fuel [26–28]. Among various photocatalytic materials, titanium dioxide (TiO_2) has maintained its position as a cornerstone material since Fujishima and Honda's seminal work in 1972 [29,30]. The enduring interest in TiO_2 -based systems stems from their unique combination of chemical stability, cost-effectiveness, low toxicity, and favorable band edge positions for water splitting reactions [31–34].

Recent years have witnessed remarkable advances in TiO_2 -based photocatalytic and photo-reforming systems [35–41]. The emergence of precise nanoscale engineering techniques has enabled unprecedented control over material properties, leading to significant improvements in hydrogen evolution rates [42–44]. Notable achievements include the development of black TiO_2 with engineered oxygen vacancies showing exceptional hydrogen evolution performance under visible light irradiation, and the creation of Z-scheme $\text{TiO}_2/\text{g-C}_3\text{N}_4$ heterojunction systems demonstrating promising photocatalytic activity with superior quantum efficiency under solar illumination [45–49]. Additionally, noble metal-decorated TiO_2 nanomaterials with optimized morphology have exhibited remarkable stability over extended periods while maintaining outstanding hydrogen production rates [50–52].

Despite these significant advances, several fundamental challenges continue to impede the widespread implementation of TiO_2 -based photocatalytic systems for practical hydrogen production. The primary limitations include the wide bandgap of TiO_2 (3.2 eV), which restricts light absorption to the UV region, representing only about 4% of the solar spectrum [35,53–55]. Therefore, the pristine TiO_2 exhibits minimal hydrogen production under natural light conditions due to the low intensity of UV light in the solar spectrum. While various bandgap engineering strategies have been explored, achieving both efficient visible light absorption and maintaining appropriate band positions for water splitting remains a significant challenge, as visible light, which constitutes a larger portion of the solar spectrum than UV, offers more practical and sustainable energy for photocatalytic processes [56,57]. Another critical barrier is the rapid recombination of photogenerated electron-hole pairs, which substantially reduces quantum efficiency [58–60]. Although heterojunction engineering and cocatalyst incorporation have shown promise in charge carrier separation, the fundamental

understanding of interfacial charge transfer dynamics and the precise role of cocatalysts in multi-component systems requires further investigation [61–63]. The stability of these complex architectures under prolonged photocatalytic conditions, particularly in terms of maintaining interfacial contacts and preventing photocorrosion, presents additional challenges [64–66]. Water chemistry also emerges as a critical yet often overlooked factor in photocatalytic hydrogen production efficiency. The pH, ionic strength, and dissolved species in the reaction medium significantly influence the surface chemistry of TiO₂ and the kinetics of water splitting reactions [67–71]. Moreover, the hardness and impurities in the water can lead to surface poisoning or competitive reactions that diminish hydrogen evolution rates [72,73]. These challenges become particularly pronounced when considering alternative water sources such as municipal wastewater, seawater, and produced water from industrial processes [74–77]. While these non-traditional water sources present an attractive opportunity for sustainable hydrogen production, their complex chemical matrices (such as total dissolved solids concentrations ranged from ~500 mg/L of municipal wastewater to 260,000 mg/L in oil field produced water) introduce additional complications, including enhanced catalyst deactivation, and selective ion interference [78–80]. Understanding the intricate relationships between water source characteristics and photocatalytic performance is crucial for advancing the field toward practical applications.

This comprehensive review analyzes the state-of-the-art advances in TiO₂-based photocatalytic systems for sustainable hydrogen production, addressing challenges from fundamental science to practical implementation. Beginning with photocatalytic water splitting mechanisms, we examine recent breakthroughs in materials design, including nanoscale engineering, crystal phase control, and advanced heterojunction systems. Special attention is given to the critical yet often overlooked influence of water chemistry on photocatalytic performance, providing insights into how various water sources—from municipal wastewater to seawater—affect system efficiency and stability. We address engineering challenges for scaling up these systems, incorporating developments in reactor design, process integration, and artificial intelligence approaches for optimization. Through this analysis, we identify current knowledge gaps and propose strategic directions for advancing TiO₂-based photocatalytic systems toward feasible large-scale hydrogen production, aiming to serve as a comprehensive reference for researchers working at the intersection of materials science, catalysis, and sustainable energy technologies.

2. Mechanism of Photocatalytic Water Splitting

The energetically-driven process of water splitting facilitates the dissociation of water molecules into their fundamental elements: hydrogen and oxygen [81]. Photocatalytic water splitting represents a sophisticated approach for converting light energy into chemical energy through water decomposition into stoichiometric hydrogen and oxygen using photocatalysts [82,83]. The process fundamentally relies on semiconductor photocatalysts with distinct valence band (VB) and conduction band (CB) in the electronic structures, where incident photons generate electron-hole pairs by exciting the electron when the light energy equals or exceeds the photocatalyst's bandgap energy [84,85]. The VB and CB distinguish semiconductors from conductors, with the bandgap representing the energy difference between these two bands [86]. The mechanism follows thermodynamic constraints, requiring a Gibbs free energy change of 237 kJ/mol ($\Delta G = +237$ kJ/mol) and an energy barrier of 1.23 eV for the complete water-splitting redox process [87,88].

Two distinct mechanisms have emerged for photocatalytic water splitting: the one-step and two-step (Z-scheme) photo-excitation processes [89]. In the one-step mechanism, the photocatalytic activity in single-semiconductor systems occurs when incident photons exceeding the material's bandgap energy trigger electronic transitions. This photoexcitation process generates electron-hole pairs through the promotion of electrons to the CB, simultaneously creating positive holes in the VB structure [90]. The efficacy of photocatalytic water splitting hinges on precise energetic alignment: the semiconductor's CB minimum must maintain a more negative potential than the H⁺/H₂ reduction potential (0 V vs. Normal Hydrogen Electrode (NHE) at pH = 0), while its VB maximum must exceed

the $\text{O}_2/\text{H}_2\text{O}$ oxidation potential (+1.23 V vs. NHE at pH = 0). These thermodynamic constraints enable photogenerated charge carriers to facilitate the requisite redox reactions - electrons driving proton reduction and holes mediating water oxidation [91]. Therefore, the one-step excitation mechanism necessitates a minimum theoretical photon energy of 1.23 eV to overcome the thermodynamic barrier for water splitting, corresponding to the standard potential difference between water oxidation and proton reduction [92]. The efficiency of one-step photocatalytic water splitting is governed by three fundamental processes: photon absorption, charge carrier dynamics (separation and transport), and surface-mediated catalytic reactions of adsorbed species (Figure 2) [93]. In one step mechanism, a single photocatalyst directly facilitates water splitting through the following sequential reactions [89]:

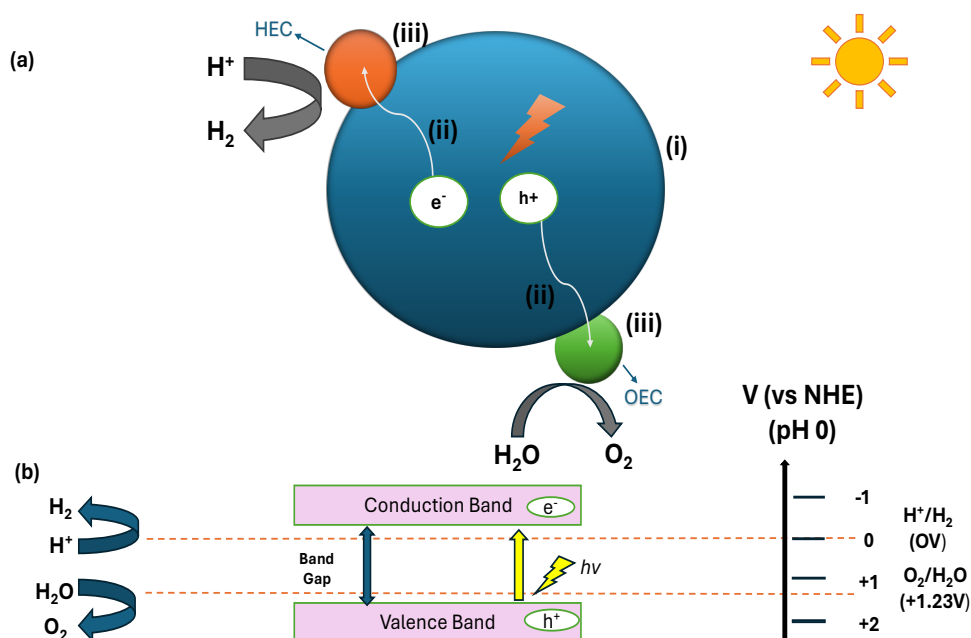
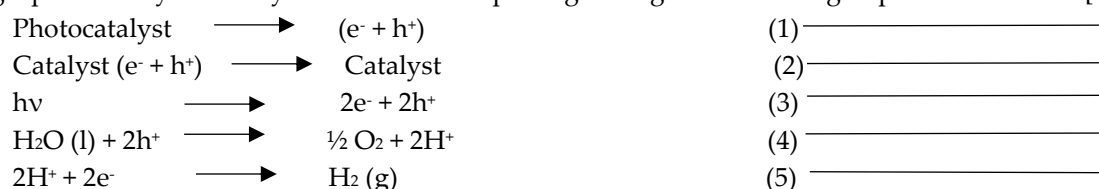


Figure 2. a) Schematic representing the key steps of photocatalytic water splitting: light absorption, charge carrier separation, and surface redox reactions. b) Energy band diagram illustrating the thermodynamic requirements for water splitting using semiconductor photocatalysts [88].

In two-step water splitting mechanism, the Z-scheme approach employs dual photocatalysts – customized for hydrogen and oxygen production, respectively - linked by electron-shuttling redox mediators, which provides more photocatalyst options than single-step excitation systems with their constraints [94]. In this process, the CB electrons of the hydrogen evolution photocatalyst reduce protons, while the VB holes convert reduced mediators to their oxidized form, generating H_2 gas and oxidized mediator molecules, respectively [95,96]. At the oxygen evolution photocatalyst, light-excited electrons restore the oxidized mediators to their reduced form, while holes facilitate water oxidation to generate molecular oxygen [97,98]. A material qualifies as a hydrogen evolution photocatalyst in Z-scheme systems when its CB minimum lies above the proton reduction potential, while its VB maximum exceeds the mediator's redox potential [99]. A material can function as an oxygen evolution photocatalyst when its VB maximum surpasses water's oxidation potential, with its CB minimum positioned above the mediator's redox potential [100–102]. The more flexible thermodynamic criteria for Z-scheme systems enable redox reactions between the mediator species and significantly expand the selection of suitable photocatalysts for overall water splitting [103–108].

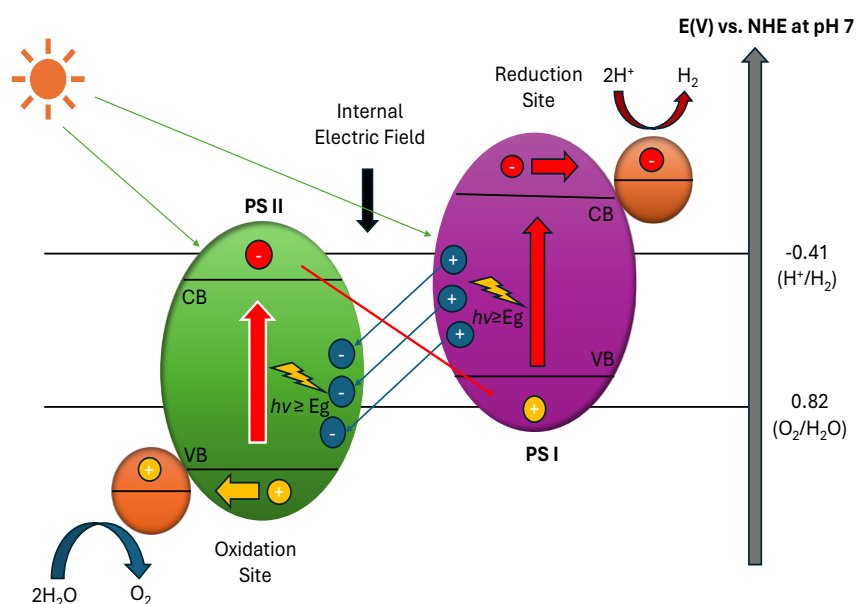


Figure 3. Diagram illustrating the energy band in a two-step photocatalytic water splitting system [109].

While significant advances have been made in understanding photocatalytic water splitting mechanisms, several fundamental challenges remain unresolved. The widely accepted one-step excitation mechanism, though elegant in its simplicity, faces severe limitations in practical applications. The requirement for semiconductors with both suitable band positions and a minimum bandgap of 1.23 eV significantly restricts material selection [110], with current materials achieving efficiencies well below their theoretical maximum due to rapid charge carrier recombination [111]. The Z-scheme approach, while promising in its ability to utilize a broader range of materials, introduces additional complexity through interfacial charge transfer resistance, which can impact the overall efficiency of the photocatalytic system [112–114]. Recent attempts to enhance charge separation through cocatalyst integration have shown limited success, with noble metal cocatalysts improving efficiency by only 2–3 fold while significantly increasing system costs [115,116]. Surface modification strategies, particularly the creation of oxygen vacancies, have demonstrated enhanced visible light absorption but often face stability challenges, as these defects tend to be filled by water/oxygen from the air or blocked by reaction intermediates, leading to gradual performance decline unless specific stabilization strategies are employed [117,118]. This inherent trade-off necessitates a more holistic approach to mechanism design, potentially incorporating dynamic response elements that can adapt to changing reaction conditions [119]. These challenges are particularly evident in TiO_2 -based systems, where the wide bandgap of 3.2 eV limits visible light absorption, while rapid electron-hole recombination and surface stability issues continue to constrain the hydrogen evolution rates.

3. Advanced Engineering of TiO_2 for Photocatalytic Water Splitting

Recent advances in materials science and nanotechnology have enabled unprecedented control over the structural and electronic properties of TiO_2 -based photocatalysts, leading to significant improvements in water splitting efficiency. These developments encompass multiple engineering strategies, ranging from precise architectural design to sophisticated surface modifications and interface engineering. The following sections will detail these key advances, beginning with fundamental architectural considerations and crystal phase engineering, followed by surface chemistry modifications, heterojunction development, and cocatalyst integration strategies. Each of

these approaches contributes uniquely to addressing the inherent limitations of TiO₂-based systems, particularly in terms of light absorption, charge separation, and catalytic activity.

3.1. Architectural Design and Crystal Phase Engineering

The evolution of nanoscale material engineering has fundamentally transformed TiO₂-based photocatalyst design, introducing sophisticated approaches that have revolutionized photocatalytic water splitting efficiency [120–127]. This transformation encompasses multiple critical advances in materials design and engineering, ranging from novel nanostructure architectures to advanced interface engineering strategies, each contributing uniquely to enhanced photocatalytic performance [128–130]. Hierarchical nanostructures have emerged as a groundbreaking development, integrating multiple morphological elements such as nanotubes, nanosheets, and nanoparticles into cohesive architectures [131–133]. These sophisticated structures demonstrate remarkable improvements in light harvesting efficiency through enhanced light scattering and trapping mechanisms [134,135]. When combined with carefully engineered macro/mesoporous structures, these systems facilitate superior mass transport while maximizing reactive surface area, leading to significant improvements in photocatalytic activity [136–138]. The integration of ordered arrays and self-assembled structures has particularly advanced directional charge transport, addressing one of the fundamental limitations in traditional photocatalyst designs [139–141]. Crystal phase engineering has emerged as a critical strategy in photocatalyst development, with mixed-phase TiO₂ (anatase/rutile) junctions exhibiting exceptional charge separation properties. The controlled synthesis of these phase junctions has enabled precise manipulation of electron-hole pair dynamics, significantly reducing recombination rates [142–147]. Table 1 summarizes these key advancements in TiO₂-based photocatalysts, highlighting their features and specific impacts on hydrogen production efficiency via water splitting.

Table 1. Key Advancements in TiO₂-Based Photocatalysts.

Advancement	Key Features	Impact on Efficiency	References
Hierarchical Nanostructures	Integration of nanotubes, nanosheets, and nanoparticles into cohesive architectures.	Enhanced light scattering and trapping mechanisms, leading to improved photocatalytic hydrogen production.	[148]
Macro/Mesoporous Structures	Engineered pores facilitating superior mass transport and maximizing reactive surface area.	Significant improvements in photocatalytic hydrogen production due to enhanced surface area and reaction kinetics. Addressed limitations in	[149]
Ordered Arrays and Self-Assembly	Formation of ordered arrays and self-assembled structures for directional charge transport.	traditional designs by enhancing charge separation and reducing recombination rates, leading to improved hydrogen evolution.	[150]
Crystal Phase Engineering	Controlled synthesis of mixed-phase TiO ₂ (anatase/rutile) junctions.	Exceptional charge separation properties, significantly reducing recombination rates and enhancing hydrogen production efficiency.	[151]

Nanoscale Engineering	Precise control over TiO ₂ nanostructures, including size, shape, and surface properties.	Enhanced light absorption, charge separation, and surface reaction kinetics, leading to improved hydrogen production efficiency. [152]
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3.2. Surface Chemistry and Defect Engineering

Notably, the development of black TiO₂ through controlled oxygen vacancy engineering has revolutionized visible light absorption capabilities. These modified materials demonstrate photocatalytic activity well beyond traditional UV-restricted domains, with some systems showing remarkable quantum efficiencies under visible light irradiation [153,154]. Surface modification and defect engineering have advanced significantly, with atomic-level control over surface chemistry becoming increasingly precise [155,156]. The strategic introduction of oxygen vacancies and Ti³⁺ states, coupled with non-metal doping, has enabled targeted band structure modifications [157–159]. These modifications have substantially improved visible light absorption and charge separation efficiency, with some systems demonstrating marked increase in photocatalytic hydrogen evolution rates compared to unmodified TiO₂ [160,161]. Advanced characterization techniques, including in-situ X-ray absorption spectroscopy and electron paramagnetic resonance, have provided unprecedented insights into the role of surface defects in photocatalytic processes [162–165]. Table 2 outlines the major advancements in modifying TiO₂ photocatalysts for visible light-driven hydrogen production, focusing on defect engineering, doping strategies, and surface modifications.

Table 2. Advances in Surface Chemistry and Defect Engineering.

Advancement	Key Features	Impact on Efficiency	References
Black TiO ₂ via Oxygen Vacancy Engineering	Controlled introduction of oxygen vacancies to create black TiO ₂ with enhanced visible light absorption.	Extends photocatalytic activity into the visible spectrum, significantly improving hydrogen production rates.	[153]
Surface Modification and Defect Engineering	Atomic-level control over surface defects, including Ti ³⁺ states and non-metal doping.	Improves charge separation and extends light absorption, leading to higher hydrogen evolution rates.	[166]
Co-doping with Transition Metals and Non-Metals	Incorporation of both metal and non-metal dopants into TiO ₂ lattice.	Synergistic effect leading to enhanced visible light absorption and improved hydrogen production rates.	[167]

To provide a quantitative comparison of different TiO₂-based photocatalysts and their hydrogen production efficiencies, Table 3 summarizes various modified TiO₂ photocatalysts, their fabrication methods, testing conditions, and corresponding hydrogen evolution rates.

Table 3. Summary of Modified TiO₂-Based Photocatalysts and Hydrogen Production Efficiencies.

Photocatalyst Composition	Fabrication Method	Hydrogen Production Rate	Light Source	References
Ag/TiO ₂	Chemical Reduction	23.5 mmol g ⁻¹ h ⁻¹	UV lamp (254 nm Wavelength)	[168]

Co ₃ O ₄ @C/TiO ₂	Carbonization	11,400 μmol g ⁻¹ h ⁻¹	UV-LED lamp (365 nm Wavelength)	[169]
CuO/TiO ₂	Hydrothermal	2,000 μmol g ⁻¹ h ⁻¹	300 W Xe lamp	[170]
Co ₃ O ₄ QDs/TiO ₂	Hydrothermal	1735 μmol g ⁻¹ h ⁻¹	Solar light	[171]
Co ₃ O ₄ @TiO ₂ / Pt	Hydrothermal	5280 μmol g ⁻¹ h ⁻¹	300 W Xe lamp	[172]
CoOx-TiO ₂ / CdS	Solvothermal	660 μmol g ⁻¹ h ⁻¹	Visible light (> 400 nm Wavelength)	[173]
Pt/TiO ₂	Hydrothermal	334 μmol h ⁻¹	350 W Xe lamp	[149]
FP-Pt/TiO ₂	Pyrolysis	19.25 mmol g ⁻¹ h ⁻¹	300 W Xe lamp	[174]
FP-Cu/TiO ₂	Pyrolysis	5.02 mmol g ⁻¹ h ⁻¹	300W Xenon lamp	[174]
Cr-TiO ₂	Magnetron sputt ering and Sol- gel	5.3 μmol h ⁻¹	Visible light	[175]
Fe-TiO ₂	Magnetron sputt ering and Sol-gel	15.5 μmol h ⁻¹	Visible light	[175]
Cu-TiO ₂ (P25)	Photoassisted Deposition	8.47 mmol g ⁻¹ h ⁻¹	450 W Hg lamp	[176]
Co-TiO ₂	Photoassisted Deposition	2.48 mmol g ⁻¹ h ⁻¹	450 W Hg lamp	[176]
Fe-TiO ₂	Microwave- Hydrothermal	11 μmol g ⁻¹ h ⁻¹	Xe lamp	[177]
Fe-TiO ₂	Impregnation	230 μmol g ⁻¹ h ⁻¹	UV light	[178]
Ru-TiO ₂	Micro-emulsion	0.80 mmol g ⁻¹ h ⁻¹	500 W Xe lamp	[179]
Au-TiO ₂	Photodeposition	1.1 mmol g ⁻¹ h ⁻¹	UV lamp	[180]
Pd/N-TiO ₂	Chemical vapor deposition	6.3 mmol g ⁻¹ h ⁻¹	White LED	[181]
Fe-Ni-/Ag/TiO ₂	Solvothermal	794 μmol g ⁻¹ h ⁻¹	500 W Xe lamp	[182]
Pt/Mg-TiO ₂	Hydrothermal	850 μmol g ⁻¹ h ⁻¹	300 W Xe lamp	[183]
Pt SA/Def-s-TiO ₂	Deposition- Precipitation	13.5 mmol g ⁻¹ h ⁻¹	300 W Xe lamp	[184]
Cu-TiO ₂	Ball Milling	9.5 mmol g ⁻¹ h ⁻¹	300 W Xe lamp	[185]
Ni-TiO ₂	Molten Salt	1.9 mmol g ⁻¹ h ⁻¹	300 W Xe lamp	[186]
Sn/TiO ₂	Photoinduced Deposition	553 μmol g ⁻¹ h ⁻¹	3 W UV lamp	[187]
N-TiO ₂	Sol-gel and Electrospinning	28 μmol h ⁻¹	150 W Xe lamp	[188]
N-TiO ₂	RF Magnetron Sputtering Deposition	4.5 mmol cm ⁻² h ⁻¹	300 W Xe lamp	[189]
N-TiO ₂ with VO	Solvothermal	1.04 mmol g ⁻¹ h ⁻¹	Solar Simulator	[190]
S-TiO ₂	Thermal Protection	164 μmol g ⁻¹ h ⁻¹	Visible light	[191]
TiC@C-TiO ₂	Situ Thermal Growth	558 μmol g ⁻¹ h ⁻¹	300 W Xe lamp	[192]
N/F-TiO ₂	Calcination	11.5 μmol g ⁻¹ h ⁻¹	300 W Xe lamp	[193]
C/N self-doped TiO ₂	Hydrothermal	332.3 μmol g ⁻¹ h ⁻¹	300 W Xe lamp	[157]
Br/N-TiO ₂	Hydrothermal	2.3 mmol g ⁻¹ h ⁻¹	300 W Xe lamp	[194]

3.3. Advanced Heterojunction Systems and Z-scheme Design

Heterojunction engineering has witnessed significant progress, particularly in Z-scheme systems, where the integration of 2D materials such as g-C₃N₄ and MXenes has established new paradigms for electron transfer [195–199]. Direct Z-scheme systems, eliminating the need for electron mediators, have demonstrated unprecedented charge separation efficiency while maintaining robust stability under prolonged operation [200–202]. The development of atomically sharp interfaces and implementation of strain engineering at heterojunctions has led to significant improvements in charge transfer efficiency, with some systems approaching theoretical maximum quantum yields [203].

3.4. Cocatalyst Integration and Interface Optimization

Cocatalyst integration has evolved substantially, with single-atom catalysts and bimetallic systems showing exceptional hydrogen evolution performance. The development of core-shell structures and protective layers has addressed long-standing stability challenges, while interface engineering has optimized charge transfer dynamics [204–206]. Recent advances in synthetic methods have enabled precise control over cocatalyst size, distribution, and electronic structure, leading to significant improvements in catalytic activity and stability [83,207].

3.5. Current Challenges and Future Perspectives

Despite remarkable advances in nanoscale engineering of TiO₂-based photocatalysts, several critical challenges impede widespread implementation. While hierarchical nanostructures have demonstrated enhanced light harvesting through increased surface area and improved charge transport pathways, their complex synthesis often results in inconsistent reproducibility between research batches [208]. The integration of ordered arrays and self-assembled structures, though promising for directional charge transport, faces significant scalability challenges, with production costs typically 5-10 times higher than conventional materials [27,209]. Crystal phase engineering, particularly in mixed-phase TiO₂ systems namely anatase-rutile heterojunction has shown enhanced charge separation efficiency but often suffers from phase instability under prolonged operation, with anatase-to-rutile transformation accelerated by reaction conditions [210,211]. The introduction of surface defects and oxygen vacancies, while effective for visible light absorption, frequently leads to reduced photocatalytic stability due to their metastable nature, with surface defects being particularly susceptible to repair through water and oxygen adsorption [212]. These limitations highlight the critical need for balanced material design approaches that consider not only performance metrics but also practical aspects of scalability, stability, and cost-effectiveness.

Future directions in advanced materials design point toward several promising avenues. The exploration of earth-abundant cocatalysts with high activity and stability remains a priority, as does the investigation of dynamic interface phenomena under reaction conditions [213–215]. Integration of design principles across multiple time and length scales, coupled with advanced in-situ characterization techniques, is expected to provide deeper insights into reaction mechanisms and degradation pathways [216,217]. Additionally, the development of scalable synthesis methods for complex nanostructures and the optimization of interface engineering strategies continue to be active areas of research [218,219]. This evolution in materials design represents a significant step toward practical, large-scale implementation of photocatalytic water splitting systems. However, continued research is essential to address the remaining challenges in stability, efficiency, and cost-effectiveness. The integration of multiple design strategies, coupled with advanced characterization and theoretical modeling, provides a promising pathway toward achieving commercially viable photocatalytic water splitting systems [119,220].

4. Hydrogen Production from Different Water Sources: Effects and Applications

The development of efficient and sustainable photocatalytic water splitting systems requires careful consideration of water source characteristics. While significant advancements have been

made in photocatalytic technologies, the transition from laboratory conditions to real-world water sources presents distinct challenges. Different water sources, such as seawater, municipal wastewater, and industrial wastewater introduce unique complexities that affect both the performance and stability of TiO₂-based photocatalysts. Understanding these effects and developing appropriate solutions is crucial for practical applications. Figure 4 provides an overview of the challenges associated with seawater and different wastewater sources such as municipal wastewater and industrial wastewater in TiO₂ photocatalytic systems.

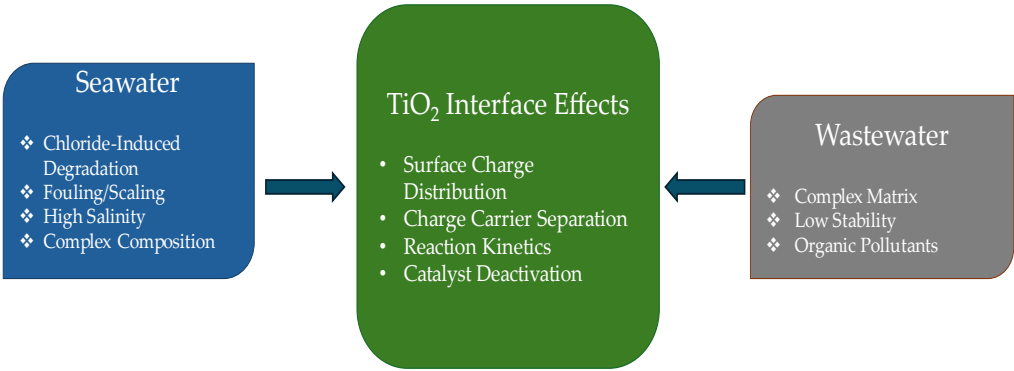


Figure 4. Challenges of Seawater and Wastewater in TiO₂-Based Photocatalytic Systems.

4.1. Influence of Water Chemistry on Photocatalytic Performance

The efficiency of TiO₂-based photocatalytic water splitting is profoundly influenced by water chemistry, which plays a crucial role in determining both reaction kinetics through pH-dependent charge distribution and ionic interactions, and catalyst stability [221,222]. Some investigations have revealed that pH, ionic strength, and dissolved species significantly impact the surface chemistry of TiO₂ and the kinetics of water splitting reactions [70,223–228]. Modulating pH not only affects the band edge positions of TiO₂ but also influences the surface charge distribution, which in turn alters the adsorption-desorption equilibrium of reactive species like water and protons [229,230]. The presence of common ions such as Na⁺, Cl⁻, SO₄²⁻ etc., in natural water sources modifies the local electric field at the semiconductor-electrolyte interface, affecting charge carrier separation and transport efficiency [231,232]. In addition, dissolved organic matter (DOM) can serve as both electron donors and acceptors, introducing competing reaction pathways that may either enhance or inhibit hydrogen evolution rates [233,234]. Specifically, while some ions (e.g., sulfate ions) stabilize charge carriers and enhance photocatalytic activity, others (e.g., chloride ions) may cause catalyst degradation [235–237]. Moreover, dissolved oxygen can act as an electron acceptor, competing with hydrogen evolution and thus reducing the overall photocatalytic performance [238]. The intricate interplay of these water chemistry factors underscores the complexity of optimizing TiO₂-based photocatalysts for practical hydrogen production. The key water chemistry parameters and their specific effects on photocatalytic performance in TiO₂-based systems are summarized in Table 4.

Table 4. Water Chemistry Influence.

Factors	Effect of Photocatalytic Performance	References
pH	Modulates band edge positions, surface charge, and adsorption/desorption equilibrium of reactive species.	[229,230]
	Affects hydrogen evolution rates depending on the pH range.	
Ionic Strength	Influences the electric double layer and charge carrier separation. High ionic strength can improve conductivity [69,239] but may increase recombination.	

DOM	Acts as electron donors and acceptors; competing pathways can either enhance or inhibit hydrogen evolution rates.	[233]
Common Ions (e.g., Na ⁺ , Cl ⁻ , SO ₄ ²⁻)	Alters the electric field at the semiconductor-electrolyte interface and influences charge carrier separation. Some ions stabilize the catalyst, while others lead to degradation.	[235,236]
Dissolved Oxygen	Competes with hydrogen evolution by capturing electrons, reducing overall photocatalytic efficiency.	[238]

4.2. Impact of Dissolve Species and Impurities

The presence of dissolved species and impurities in water presents both challenges and opportunities for photocatalytic water splitting. Certain ionic species such as Ca²⁺, Zn²⁺, Fe²⁺, Fe³⁺ can adversely affect catalyst performance by causing surface poisoning through competitive adsorption or the formation of inactive surface complexes, as observed with multivalent metal ions that induce surface precipitation and alter the electric double layer structure [240,241]. These interactions can reduce the availability of active sites and disrupt charge carrier dynamics, thereby diminishing overall efficiency [242]. Conversely, some dissolved species such as triethylamine and potassium iodide offer advantageous effects, acting as hole scavengers or facilitating charge separation by forming beneficial surface complexes [243–245].

4.3. Advanced Strategies for Seawater Splitting

Seawater splitting offers a sustainable pathway for large-scale hydrogen production yet present distinct challenges due to its complex chemical composition and high salinity. The primary issues include chloride-induced catalyst degradation, fouling, and scaling through the formation of Ca(OH)₂ and Mg(OH)₂ deposits [246–248]. To address these challenges, recent advancements have focused on developing chloride-resistant photocatalysts through surface modifications and protective layer integration [249–251]. Strategies such as selective membranes and buffer layers have been shown to mitigate the corrosive effects of chloride ions while preserving high photocatalytic activity [252,253]. Additionally, the incorporation of engineered cocatalyst systems has demonstrated the ability to sustain stability in high-salt environments, achieving hydrogen evolution rates comparable to those observed in pure water systems [254,255]. The performance metrics of various TiO₂-based photocatalysts designed for seawater splitting, along with their corresponding strategies, are presented in Table 5.

Table 5. Strategies Employed in Seawater Splitting.

Photocatalyst	Hydrogen Production Rate	Key Strategy/Condition Addressed	References
Mesoporous brookite/anatase TiO ₂	6.59 mmolg ⁻¹ h ⁻¹	Mitigated chloride-induced degradation	[256]
Brookite TiO ₂	1,476 μmolg ⁻¹ h ⁻¹	Improved stability in saline environments	[257]
Phosphorus and Nickel co-doped TiO ₂	149 μmolg ⁻¹ h ⁻¹	Improved stability by preventing photo-corrosion	[258]
TiO ₂ (NT)/Pt/Cd _{0.8} Zn _{0.2} S	21.7 mmolg ⁻¹ h ⁻¹	Increased active sites and hydrogen production rate	[259]
Granular Pt/TiO ₂	23.6 μmolh ⁻¹	Catalyst deflocculation and oxygen inhibition	[260]

WS ₂ /C-TiO ₂ /g-C ₃ N ₄	986 μmolg ⁻¹ h ⁻¹	Enhanced electron-hole pair separation [261]
MoS ₂ @TiO ₂	580 mmolg ⁻¹ h ⁻¹	Enhanced plasmonic effect [262]
SiO ₂ /Ag@TiO ₂	816 μmolg ⁻¹ h ⁻¹	Photothermal interfacial heating synergy [263]

4.4. Integration with Wastewater Treatment Systems

The integration of photocatalytic hydrogen production with wastewater treatment offers a transformative approach to addressing energy and environmental challenges concurrently. TiO₂-based photocatalysts have demonstrated promising potential for simultaneous hydrogen evolution and the degradation of organic pollutants [35,264,265]. Advanced reactor configurations, including membrane separation and continuous flow systems, have been developed to maintain stable hydrogen production while achieving substantial reductions in organic contaminant concentrations [266,267]. Organic pollutants present in wastewater effectively serve as sacrificial electron donors, thereby enhancing hydrogen evolution rates and enabling efficient water purification [268]. Despite these advancements, key challenges, such as catalyst deactivation and ensuring long-term stability within the chemically complex matrices of wastewater remain [269,270]. Future research should focus on optimizing catalyst designs and reactor configurations to address these limitations and enhance the scalability of these integrated systems. To illustrate the current state of technology, Table 6 presents the simultaneous hydrogen production and wastewater treatment performance of selected TiO₂-based catalysts.

Table 6. Simultaneous Wastewater treatment and Hydrogen Production.

Photocatalyst	Hydrogen Production Rate	Pollutant Treated	Light Source	References
CuO/TiO ₂ NT	3.43 μmolg ⁻¹ h ⁻¹	Phenol	Visible light	[271]
Ag-G-TiO ₂	191 μmolg ⁻¹ h ⁻¹	Methylene Blue	Visible light	[35]
BiVO ₄ /TiO ₂	14.3 mmolg ⁻¹ h ⁻¹	Rhodamine B	Visible light	[272]
NiPc@GO/TiO ₂	1.38 mmolh ⁻¹	Formic Acid	Visible light	[273]
7CuO-TiNTA	910 mmol/m ²	Ammonia	UV light	[274]
Ag/TiO ₂	1729 μmolg ⁻¹ h ⁻¹	Paracetamol	Natural sunlight	[275]
MoS _{2-x} @TiO ₂ -OV	42 μmolg ⁻¹ h ⁻¹	Pharmaceutical Wastewater	300W Xenon lamp	[276]
MoS _{2-x} @TiO ₂ -OV	103 μmolg ⁻¹ h ⁻¹	Coking wastewater	300W Xenon lamp	[276]
PtCo ₃ O ₄ TiO ₂	2200 μmolg ⁻¹ h ⁻¹	Enrofloxacin	300W Xenon lamp	[277]
Fe-doped TiO ₂	2423 μmolh ⁻¹	Methyl Orange	Visible light	[278]
Mixed TiO ₂ nanosphere and nanosheet	19.4 μmolg ⁻¹ h ⁻¹	Glycerol	300W Xenon arc lamp	[279]
Pt/TiO ₂	101 μmolg ⁻¹ h ⁻¹	Oxalic Acid	450W Xenon Arc lamp	[280]
Carbon-doped TiO ₂	374 μmolg ⁻¹ h ⁻¹	Lactic Acid	Visible light	[281]
Cr ₂ O ₃ /Rh/SrTiO ₃	590 μmolg ⁻¹ h ⁻¹	4-chlorophenol	300W Xe Arc lamp	[282]
Nanostructure mesoporous TiO ₂	19 mmolh ⁻¹	Olive mill wastewater	UV light	[283]

4.5. Future Prospectives and Challenges

The translation of laboratory-scale success to real-world water sources reveals significant performance gaps in TiO₂-based photocatalytic systems. While impressive results have been achieved in controlled laboratory conditions, performance typically decreases when applied to actual environmental waters [84]. Common ionic species present in natural waters, particularly chloride and carbonate ions, can significantly reduce photocatalytic efficiency through competitive adsorption and radical scavenging effects [284,285]. The deposition of carbonaceous compounds on the catalyst surface, known as fouling or coking, is a common cause of deactivation that can block active sites and pores, often necessitating frequent regeneration cycles which impact the long-term operational costs and viability of the process [286]. Moreover, the synergistic effects of multiple ions and organic compounds in real water sources create complex interaction patterns that current theoretical models fail to fully predict [287]. Standard testing protocols often overlook these crucial matrix effects, leading to overoptimistic performance projections that rarely translate to practical applications [288]. This disconnect between idealized laboratory conditions and real-world performance necessitates a fundamental shift in how we evaluate and design photocatalytic systems for practical water splitting applications [289].

Despite notable advancements, significant challenges remain in the practical implementation of photocatalytic water splitting systems, particularly when using non-traditional water sources such as seawater or wastewater. One critical issue is ensuring long-term stability under variable and often harsh water chemistry conditions [290]. The development of robust and scalable catalyst systems capable of maintaining activity and selectivity in such environments is imperative [291]. Furthermore, optimizing integrated treatment processes to handle complex water matrices without compromising hydrogen production efficiency is essential for widespread application [292].

Future research should prioritize the development of smart, self-healing materials that can adapt dynamically to fluctuating water chemistry, such as changes in pH, ionic strength, or contaminant levels [293]. Advancements in in-situ and operando characterization techniques are needed to provide real-time insights into reaction mechanisms and surface interactions, which are crucial for understanding and mitigating deactivation pathways [216,217,290]. Additionally, the establishment of standardized protocols for performance evaluation under realistic operating conditions is necessary to facilitate reliable comparisons and accelerate the translation of laboratory-scale findings to industrial applications [294]. The integration of artificial intelligence (AI) and machine learning approaches holds immense potential in optimizing system performance. These technologies can be leveraged to model complex reaction networks, predict catalyst behavior across diverse water sources, and design adaptive operational strategies [292,294]. By combining AI-driven insights with experimental advancements, researchers can streamline the development of next-generation water splitting systems [293].

5. Scale-Up and Engineering Challenges

5.1. Reactor Design Considerations and Optimization

The scaling of photocatalytic water splitting systems from laboratory to industrial scale presents significant engineering challenges that demand innovative reactor design solutions. Recent advances in reactor engineering have focused on optimizing light utilization efficiency, mass transfer, and reaction kinetics while maintaining economic viability [119,295,296]. Advanced reactor configurations, including suspended particle systems, fixed-bed reactors, and optical fiber reactors, have demonstrated varying degrees of success in addressing scale-up challenges [297]. Computational fluid dynamics modeling has emerged as a powerful tool for predicting flow patterns, light distribution, and reaction kinetics in large-scale reactors, enabling more efficient design optimization [298]. Furthermore, modular reactor systems have shown promise in addressing scalability issues, offering operational flexibility and ease of maintenance, which are critical for real-world applications [299]. The key characteristics, challenges, and engineering solutions for major photocatalytic reactor designs are summarized in Table 7.

Table 7. Overview of Photocatalytic Reactor Designs and Scale-up Challenges.

Reactor Type	Key Features	Scalability Challenges	Engineering Solutions	References
Suspended Particle	High light absorption, dynamic particle flow	Potential clogging, complex design	Optimization of particle dispersion and flow dynamics	[300]
Fixed-Bed Reactor	Stable, large-scale suitability	Low light utilization, heat management	Reactor designed for improved light penetration and mass transfer	[301]
Optical Fiber Reactor	Efficient light delivery through fibers, compact	Cost, complexity in large-scale integration	Optimization of fiber configuration for large-scale light distribution	[302]

5.2. Light Distribution and Mass Transfer Phenomena

The optimization of light distribution represents a critical challenge in large-scale photocatalytic systems. Non-uniform light distribution in scaled-up reactors has been shown to significantly affect overall system efficiency, leading to suboptimal photocatalytic performance [29,296]. Advanced light delivery systems, including internal illumination configurations and solar concentrators, have been developed to enhance light utilization efficiency in photocatalytic reactors [303,304]. Additionally, the integration of plasmonic materials and photonic crystals has demonstrated significant improvements in light harvesting and uniform light distribution throughout the reactor volume [305–309]. Addressing mass transfer limitations, particularly in gas-liquid-solid systems, remains a key focus of reactor design. Innovative solutions, such as enhanced mixing strategies and optimized flow patterns, have been implemented to improve mass transfer dynamics [310–312]. The incorporation of structured catalysts and membrane-integrated systems has further demonstrated enhanced mass transfer characteristics, ensuring high photocatalytic activity under operational conditions [313,314]. The major technical challenges encountered in large-scale photocatalytic reactor design and their corresponding solutions are presented in Table 8.

Table 8. Key Technical Challenges and Solutions in Large-Scale Photocatalytic Reactor Design.

Aspect	Challenges	Solutions	References
Light Distribution	- Non-uniform illumination in scaled reactors leading to efficiency loss.	- Advanced light delivery systems (e.g., internal illumination, solar concentrators). - Integration of plasmonic materials and photonic crystals to enhance light harvesting and uniformity	[298,315]
Mass Transfer	- Limitation in gas-liquid-solid interactions affecting reaction rates.	- Enhanced mixing strategies to improve contact between phases. - Structured catalysts and membrane-integrated systems	[316,317]

- Poor mixing leading to facilitate better mass to concentration transfer.
gradients

While various strategies have been proposed to address these challenges, a quantitative assessment of key scalability factors is essential to guide future advancements in photocatalytic hydrogen production. Table 9 summarizes the key engineering challenges in scaling up photocatalytic hydrogen production, providing quantitative data on efficiency losses, material limitations, and proposed solutions derived from recent advancements.

Table 9. Quantitative Assessment of Key Challenges Proposed Solutions in Scaling Up Photocatalytic Hydrogen Production.

Scaling-Up Factor	Challenges	Quantitative Metrics	Proposed Solutions	References
Light Delivery Efficiency	- Light Scattering. - Poor penetration in slurries. - Limited light absorption by photocatalyst.	- Single LED to optical fiber efficiency: ~91% evanescent wave utilization. - TiO ₂ -coated optical fibers enhance degradation by 32%.	- Optical fibers with reduced TiO ₂ patchiness (0.034 cm ² /cm ²). -Optimized interspace distance (114.3 nm) for evanescent waves.	[318,319]
Reactor Design and Photocatalyst Loading	- Low photocatalyst mass-loading. - Reactor inefficiencies. - Catalyst detachment.	- Mass-loading of g-C ₃ N ₄ -POFs up to 100-1000× higher than conventional reactors. - Photocatalyst coated optical fibers improved micropollutant degradation by 4×.	- Bundled 150 optical fibers for higher quantum efficiency and scalable production.	[320,321]
Surface Area Utilization	- Limited catalyst loading. - Light scattering losses. - Inefficient pollutant degradation. - Catalyst leaching. - High energy consumption.	- High mass-loading g-C ₃ N ₄ embedded in metamaterial porous polymer fibers (100-1000× higher than traditional coatings). - 4× higher degradation rates compared to slurry reactors. - Maintains photocatalytic activity for 20+ cycles. - No catalyst leaching. - Reduced energy-per-order (EEO) compared to slurry reactors	- Metamaterial porous polymer fibers for efficient light delivery and increased reaction sites. - Photocatalyst immobilization for long-term stability. - Energy-efficient fiber-based reactor designs	
Biofouling and Catalyst Stability	- Biofilm accumulation on photocatalytic surfaces reduces	- UV-C SEOFs (side-emitting optical fibers) inhibited biofilm	- Low-fluence UV-C SEOFs enable continuous	[323,324]

	efficiency and leads to fouling.	formation at $\geq 10 \mu\text{W}/\text{cm}^2$ (265-275 nm).	surface disinfection,
	- Controlling biofilm growth in enclosed water systems is challenging due to light delivery limitations.	- UV-A and UV-B SEOFs were ineffective and even increased EPS (Extracellular Polymeric Substances) accumulation, leading to more fouling.	preventing biofilm accumulation.
			- Subtractive engineering approach enhances UV-C side-emission, improving biofilm control in confined spaces.
		- Quantum yield increased by nearly 2 $\times$ when reactor length was doubled.	- Evanescent wave enhancement using optical fibers improves light utilization.
Hydrogen Evolution Reaction (HER) Efficiency	- Electron-hole recombination losses reduce reaction efficiency.	- Photocatalytic H_2O_2 production improved by 60 $\times$ compared to slurries, demonstrating superior light utilization.	- Dual optical-membrane fiber systems enable stable photocatalysis with enhanced oxygen delivery and light absorption.
	- Conventional systems suffer from low quantum yield due to inefficient light absorption.	- HER efficiency increased significantly using g- C_3N_4 and ITO-modified polymer optical fibers.	- Coupled adsorption-photocatalysis systems enhance contaminant capture and oxidation efficiency.
			- Porous electrospun fibers increase surface area, improving pollutant access to photocatalytic sites.
Water Source and Impurities	- Organic pollutants act as reactive species scavengers, reducing oxidation efficiency.	- Organic matter in secondary wastewater effluent (17 mg TOC/L) inhibited photocatalysis.	- TiO_2 immobilization mitigates organic interference, enhancing stability and reusability.
	- Background organic matter (e.g., WWTP effluent) significantly decreases photocatalytic degradation rates.	- In the presence of WWTP effluent, BPA removal rates decreased by 52% for electrospun TiO_2 fibers, compared to 91% for suspended TiO_2 .	[319,321,325]
			[322]

Chemical Stability of Photocatalysts	Potential long-term performance degradation	Photocatalytic performance sustained over 20 cycles, with no structural loss of optical fibers.	- High-mass-loading photocatalysts. - Roll-to-roll fabrication for scalable and stable production.	[320]
Photoelectrochemical (PEC) Integration	High energy cost due to inefficient PEC designs.	- Geometric space capacity: 2670 m ² /m ³ (>25× higher than flat PEC electrodes). - Photocurrent density: 0.2 mA/cm ² . - Hydrogen production rate: 15× higher than standard reactors.	ITO and g-C ₃ N ₄ coated polymer optical fiber optoelectrode improves electron transfer and efficiency.	[321]
Flexible Fiber-Based Reactor Designs	- Need for scalable and adaptable configurations for industrial applications. - Current reactor designs suffer from low energy efficiencies due to light attenuation.	- >6000% larger surface area than flat glass electrodes. - >300% better incident photon-to-current efficiency.	Flexible Perovskite-Nafion-ITO fiber optoelectrodes for efficient light-driven PEC water purification and hydrogen production.	[326]

5.3. Process Integration and System Optimization

The successful implementation of large-scale photocatalytic water splitting systems requires careful consideration of process integration and system optimization. Recent developments have focused on integrating hydrogen separation and purification systems, thermal management strategies, and control systems to achieve optimal performance [251,327]. Incorporating renewable energy sources, such as solar and wind power, for supplementary energy needs has emerged as a promising approach to enhance the sustainability of these systems. Hybrid systems that combine photocatalytic and conventional water splitting techniques have demonstrated improved overall system efficiency and adaptability under varying operational conditions [328].

Advanced process control strategies leveraging machine learning algorithms and real-time monitoring systems have been instrumental in enhancing system performance and reliability. These technologies enable the prediction and adjustment of operational parameters to maintain stable performance under fluctuating conditions [329]. Furthermore, the integration of heat recovery systems has been shown to improve energy efficiency by capturing and reusing waste heat generated during the process [330].

5.4. Economic Feasibility and Sustainability Analysis

Economic considerations play a pivotal role in determining the commercial viability of scaled-up photocatalytic water splitting systems. Recent techno-economic analyses have highlighted key cost drivers and potential strategies for optimization, including advancements in reactor construction, catalyst synthesis, and the development of auxiliary equipment [331,332]. Capital costs, particularly those related to the production and scalability of photocatalysts, remain a significant barrier to widespread adoption, while operating costs, encompassing maintenance, catalyst replacement, and energy consumption, have been systematically evaluated to identify areas for cost reduction and

efficiency improvements [333,334]. Life cycle assessment studies have underscored the importance of incorporating environmental and sustainability metrics into system design and optimization [335]. These assessments provide insights into the long-term environmental impacts, such as carbon emissions and resource utilization, associated with large-scale photocatalytic hydrogen production. Furthermore, the development of cost-effective methods for catalyst production, including scalable and sustainable synthesis techniques, has emerged as a critical area of research [336,337]. In addition, the integration of renewable energy sources for supplementary power, combined with strategies to minimize waste and recycle key materials, has shown promise in enhancing the economic feasibility and sustainability of these systems [35]. By addressing these economic and environmental challenges, future developments can pave the way for the commercialization of photocatalytic hydrogen production technologies.

5.5. Future Direction and Research Needs

The pilot and full scale TiO₂-based photocatalytic systems reveal fundamental limitations that are often masked in bench-scale studies. While bench-scale reactors demonstrate promising efficiencies, scaling to industrial volumes results in significant performance losses, primarily due to light distribution limitations and mass transfer constraints [298,338]. Current reactor designs struggle to maintain uniform light intensity throughout larger volumes, with light penetration depth rarely exceeding 5 cm in typical slurry systems [315,339]. While advanced light delivery systems like optical fibers and solar concentrators offer potential improvements, they present significant engineering challenges in maintaining uniform light distribution and thermal management [340,341]. Mass transfer limitations are a major challenge in scaled-up systems, with a recent survey showing 30% of scale-up failures were attributed to mass transfer issues, and reaction times potentially increasing 4-5 fold without proper controls [342]. The economic viability of large-scale implementation remains questionable, with techno-economic analyses indicating photocatalyst costs need to be below \$10/kg and solar-to-hydrogen efficiencies above 10% for commercial viability - targets that remain elusive with existing technologies [343].

Future advancements in the scale-up and engineering of photocatalytic water splitting systems must address several crucial areas to ensure both efficiency and commercial viability. Key research directions include:

- The development of advanced reactor designs that integrate improved light delivery systems and enhanced mass transfer characteristics, aiming to maximize the system's overall performance.
- The incorporation of artificial intelligence and machine learning approaches for the optimization of operational strategies, system control, and real-time monitoring [344].
- The implementation of sustainable and cost-effective manufacturing processes for catalyst production and system components, ensuring scalability and resource efficiency.
- The establishment of standardized methodologies for performance evaluation, including techno-economic and life cycle assessments, to streamline industry adoption and regulatory compliance.

Furthermore, addressing the challenges related to catalyst recovery and regeneration, system maintenance, and ensuring long-term stability under industrial conditions is essential for the practical application of photocatalytic water splitting technologies [345,346].

6. Advanced Applications and System Integration of TiO₂-Based Photocatalysts

Advanced integration of TiO₂-based photocatalysts encompasses multiple strategic approaches, including bio-hybrid systems, CO₂ reduction, and machine learning applications. These integration strategies present both opportunities and challenges in advancing photocatalytic technology.

6.1. Integration with Artificial Photosynthesis

The integration of photocatalytic water splitting with artificial photosynthesis offers a promising path for advancing sustainable energy solutions. Recent progress has demonstrated the successful incorporation of photocatalysts with synthetic biological components, resulting in enhanced energy conversion efficiency [347]. Novel bio-hybrid systems, which integrate engineered proteins and light-harvesting complexes, have shown significant improvements in solar-to-hydrogen conversion rates, outperforming traditional systems [348]. These hybrid systems combine the selectivity of biological catalysts with the robustness and stability of inorganic semiconductor materials, making them ideal candidates for large-scale energy production [349,350]. Moreover, advanced architectures that combine multiple photocatalytic centers with biomimetic electron transfer pathways have achieved remarkable stability and improved quantum efficiency under visible light irradiation, thereby enhancing overall system performance and longevity [351,352]. The major innovations in bio-hybrid photocatalytic systems and their corresponding significance in advancing sustainable energy solutions are detailed in Table 10.

Table 10. Key Innovations in Bio-Hybrid Photocatalytic Systems.

Category	Innovation	Significance	Example Applications	References
Material Integration	Combination of photocatalysts with engineered proteins and synthetic biological components	Enhanced synergy between biological selectivity and inorganic stability	Large-scale hydrogen production systems.	[353]
Hybrid System Design	Bio-hybrid architectures incorporating light-harvesting complexes with multiple catalytic sites	Increased efficiency and robustness under visible light conditions.	Artificial photosynthesis setups for clean energy.	[354]
Electron Transfer Pathways	Biomimetic electron transfer mechanisms inspired by natural processes	Improved quantum efficiency and system longevity	Sustainable solar-to-hydrogen energy conversion	[355]
Performance Optimization	Development of systems with high solar-to-hydrogen conversion rates and operational stability	Breakthrough in achieving industrial scale feasibility.	Scaled-up photocatalytic energy production plants.	[356]
Advanced Architectures	Architectures combining multiple photocatalytic centers for distributed light utilization.	Uniform energy conversion and improved system durability.	Decentralized renewable energy systems.	[357]

While bio-hybrid photocatalytic systems present an attractive pathway for mimicking natural photosynthesis, significant technical barriers impede their practical implementation. The integration of biological components with inorganic photocatalysts, though promising in principle, faces considerable challenges, including limited operational stability, low energy conversion efficiency, and poor sustainability of the catalytic system during continuous operation [358,359]. Current bio-hybrid photocatalytic systems for water splitting hydrogen production still face efficiency challenges. Although these systems show promise, their hydrogen evolution rates need further improvement for

practical applications [351,360]. The structural complexity and synthesis requirements of these bio-hybrid systems currently present challenges for large-scale production and practical implementation. While these systems show promising potential in mimicking natural photosynthesis and offer unique advantages in biomass conversion, their widespread adoption is limited by the need for:

- Improved photocatalytic efficiency and stability
- Enhanced charge separation and transfer
- Optimization of light harvesting capabilities
- Development of more cost-effective alternatives to noble metal co-catalysts

These limitations suggest that while bio-hybrid systems represent an innovative approach, continued advances in materials design, synthesis methods, and interface engineering are necessary to make them commercially competitive with conventional photocatalysts [361,362].

6.2. Coupling with CO₂ Reduction Systems

The integration of hydrogen production with CO₂ reduction in photocatalytic systems represents a transformative approach to sustainable energy and chemical synthesis. Recent advancements have centered on the development of dual-function catalysts capable of simultaneously facilitating water oxidation and CO₂ reduction [363]. The incorporation of selective cocatalysts, such as metal oxides and molecular complexes, has significantly improved reaction efficiency and product selectivity [364]. Z-scheme photocatalytic systems, which mimic natural photosynthesis, have demonstrated the ability to couple water splitting and CO₂ reduction with enhanced energy conversion efficiency [365]. Emerging approaches leveraging plasmonic effects and defect engineering have shown great promise in enhancing CO₂ activation while maintaining robust water-splitting performance [366,367].

6.3. Machine Learning Applications in Materials Discovery

The application of machine learning has significantly advanced the discovery and optimization of photocatalytic materials, enabling efficient identification of promising candidates and pathways. Advanced machine learning algorithms have been instrumental in rapidly screening vast material combinations and accurately predicting photocatalytic performance based on theoretical and experimental data [72,368]. Deep learning models have revealed intricate structure-property relationships, aiding in the prediction of optimal synthesis conditions for novel photocatalysts [369].

The integration of high-throughput experimentation with machine learning driven analysis has accelerated the pace of material discovery. These combined approaches allow researchers to evaluate numerous variables simultaneously, reducing the time and resources required for experimental validation [370–372]. Notably, interpretable machine learning models have emerged as a valuable tool, offering insights into fundamental mechanisms governing photocatalytic activity, stability, and efficiency. These models provide transparent and explainable predictions, bridging the gap between computational predictions and experimental realities [72,373–375]. Figure 5 provides an overview of these key integration approaches and their associated developments.

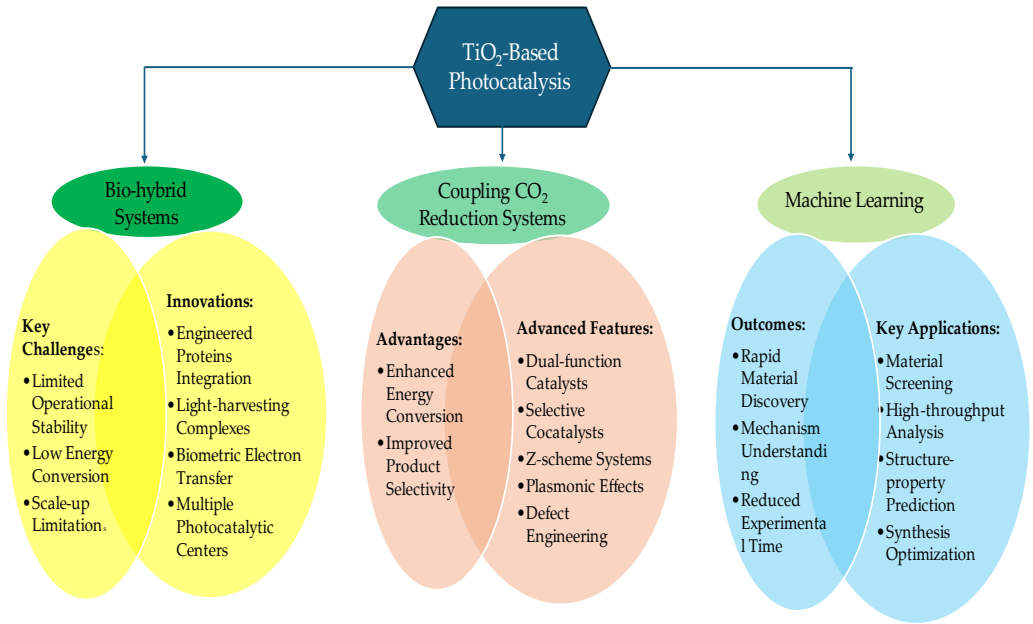


Figure 5. Integration Strategies for Advanced TiO₂ Systems.

7. Future Perspectives and Emerging Opportunities in Photocatalytic Water Splitting

The field of photocatalytic water splitting stands at a critical juncture, where despite significant scientific advances, practical implementation remains elusive. Current state-of-the-art systems achieve solar-to-hydrogen efficiencies of only 1-2% under real-world conditions, far below the 10% threshold considered necessary for commercial viability [334,376]. The cost of hydrogen production through photocatalytic water splitting remains 3-4 times higher than conventional methods, primarily due to expensive materials and complex system requirements [27,333]. Stability issues remain a critical challenge in photocatalytic devices, with the most advanced systems demonstrating limited operational lifetimes. Current research indicates that while a five-year lifetime (approximately 21,900 hours) is required for cost-competitive hydrogen production, most cutting-edge systems struggle to maintain performance beyond 100 hours [377]. These fundamental challenges suggest that revolutionary rather than evolutionary advances are needed across multiple fronts - from basic materials design to system engineering [378]. The field must address not only efficiency and stability but also scalability and economic viability to bridge the gap between laboratory success and commercial implementation [379]. Promising areas for future exploration include:

- **Efficient Visible-Light-Responsive Materials:** Advanced bandgap engineering has enabled the design of photocatalysts capable of harnessing a broader spectrum of sunlight, significantly enhancing overall efficiency [380,381].
- **Quantum Computing for Materials Optimization:** Quantum computing approaches are being explored for accelerated discovery and optimization of photocatalytic materials, offering potential breakthroughs in reaction efficiency and material design [382].
- **Autonomous Systems for Real-Time Optimization:** Autonomous systems equipped with real-time monitoring and adaptive control mechanisms are transforming operational efficiency and system reliability [383].
- **Sustainable Manufacturing Processes:** A focus on eco-friendly manufacturing of advanced photocatalytic materials ensures scalability and minimizes environmental impact [384].

- **Smart Photocatalytic Systems:** Systems capable of adapting to environmental changes (e.g., varying water quality or solar intensity) have potential for robust operation under diverse conditions [27,385].

Addressing challenges related to long-term stability, scalability, and cost-effectiveness is essential for commercial success. Recent trends also highlight the development of multifunctional systems capable of tackling multiple environmental issues concurrently, such as simultaneous water purification and hydrogen production [27,379].

In conclusion, while significant strides have been made in photocatalytic water splitting, achieving commercial viability demands transformative innovations that address critical challenges such as efficiency, stability, scalability, and cost-effectiveness. By advancing material design, leveraging emerging technologies like quantum computing and autonomous systems, and prioritizing sustainable manufacturing, the field can move closer to bridging the gap between laboratory success and real-world implementation. A multidisciplinary approach that integrates these solutions will be pivotal in unlocking the full potential of photocatalytic water splitting as a sustainable pathway for green hydrogen production.

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