

A Short Review of Recent Advances in Artificial Photosynthesis Chemistry

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ABSTRACT

Artificial photosynthesis has emerged as a promising strategy for sustainable solar-to-chemical energy conversion by mimicking natural photosynthetic processes to produce fuels from water and carbon dioxide. In recent years, significant chemical advances have been achieved in light-harvesting materials, molecular and heterogeneous catalysts, and integrated photoelectrochemical systems. Progress in self-photosensitizing molecular catalysts, metal-organic and covalent organic frameworks, and earth-abundant water oxidation and CO₂ reduction catalysts has enhanced charge separation, catalytic efficiency, and product selectivity. Meanwhile, artificial leaf architectures and hybrid systems have demonstrated improved solar-to-chemical conversion efficiencies under increasingly practical conditions. Notably, several laboratory-scale photoelectrochemical (PEC) systems have recently reported solar-to-hydrogen conversion efficiencies approaching 10% (unassisted, AM 1.5G illumination), reaching the threshold for commercial viability. Despite these advances, challenges related to long-term catalyst stability, efficiency losses, and large-scale implementation remain. This review summarizes key chemical developments from the past 3–5 years (2020–2025), highlighting emerging design strategies and integrated approaches that are shaping the future of scalable and sustainable artificial photosynthesis.

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1. INTRODUCTION

Artificial photosynthesis (AP) is an emerging technology that emulates natural photosynthetic processes (Figure 1) to convert solar energy into chemical fuels, offering a sustainable solution to global energy challenges and addressing the urgent need for carbon emission reduction [1]. This biomimetic approach aims to produce hydrogen and other value-added chemicals.

such as methanol and hydrocarbons from abundant resources such as water and carbon dioxide, thereby mitigating the energy crisis and climate change [2]. This concept involves capturing solar energy and converting it into chemical energy stored in organic compounds, analogous to how plants convert sunlight into biomass [3].

The global energy demand and depletion of fossil fuels underscore the critical importance of developing AP

technologies for a future powered by clean, renewable energy [4, 5].

Recent advances in AP chemistry, particularly within the last 3–5 years, have focused on enhancing catalytic efficiency, expanding the range of target products, and improving system stability. Significant progress has been made in the design of molecular catalysts, including self-photosensitizing dinuclear ruthenium catalysts for CO₂ reduction to CO, which integrate both photosensitization and catalytic functions into a single molecular entity [6, 7].

The development of ultrastable metalated metal-organic frameworks (MOFs) with enhanced electroconductivity has shown promise for energy storage and conversion [8]. Furthermore, semiconductor-based photocatalysts, such as CdS/Bi₂WO₆ heterojunctions (Figure 2), have been explored for efficient CO₂-to-methanol conver-

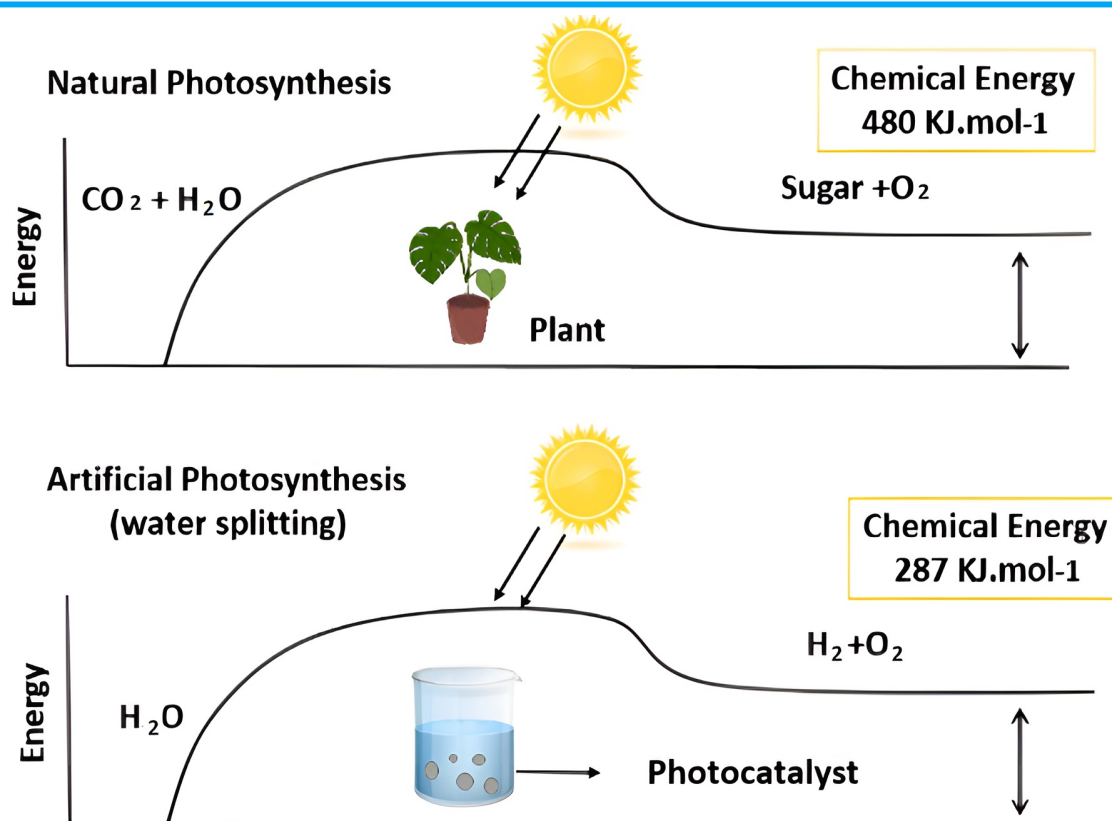


Figure 1. Natural Photosynthesis vs Artificial Photosynthesis

sion, demonstrating their potential for transforming waste carbon into solar fuels [9, 10].

Innovations also include strategies for full-spectrum solar light utilization, as seen in Cu-based hollow TS-1 nanoreactors that leverage photothermal synergistic effects for enhanced artificial photosynthesis and high-yield alcohol production [11].

Efforts to achieve commercially viable solar water splitting have also seen breakthroughs, with some artificial photosynthesis schemes achieving nearly 10% overall energy efficiency, approaching the threshold for commercial applications [12]. These advancements highlight the continuous evolution of AP from fundamental research to practical and scalable solutions for a sustainable energy future [13].

In this paper, "artificial photosynthesis" refers specifically to chemical systems that convert solar energy into chemical fuels (hydrogen, carbon monoxide, methanol, and hydrocarbons) via photocatalytic, photoelectrochemical (PEC), or photovoltaic-electrolysis (PV-EC) approaches using water and/or carbon dioxide as feedstocks. This review does not cover biological or hybrid biological-synthetic systems, dark catalysis, or purely electrochemical CO_2 reduction without light input. The literature surveyed covers the period from 2020 to 2025, with emphasis on peer-reviewed reports that provide quantitative performance metrics (efficiency, selectivity, stability). Studies were selected based on their relevance

to catalyst design, material innovation, or integrated device architecture.

To provide context for the advances discussed below, three representative benchmarks are noted here: (1) A monolithic perovskite/silicon tandem PEC device achieved solar-to-hydrogen (STH) efficiency of 19% under simulated AM 1.5G illumination with 100 h of stability; (2) A self-photosensitizing dinuclear ruthenium catalyst for CO_2 reduction to CO achieved a turnover number (TON) of >1000 under visible light without external photosensitizers; (3) A $\text{Ru}(\text{bda})_2$ catalyst incorporated into a UiO-66 metal-organic framework (MOF) achieved a TON of 566 for photo-driven water oxidation, which is nearly 20-fold higher than the homogeneous analog.

2. LIGHT-HARVESTING MATERIALS

Recent advances in light-harvesting materials for artificial photosynthesis have significantly focused on molecular dyes, metal complexes, and hybrid systems over the last 3–5 years, aiming to improve efficiency and stability in solar energy conversion [14]. Molecular photosensitizers play a crucial role in absorbing light and initiating charge separation, which are critical steps in artificial photosynthesis [15]. Ruthenium-based complexes, for instance, have demonstrated significant potential, with a self-photosensitizing dinuclear ruthenium catalyst recently developed for CO_2 reduction to CO, integrating both light absorption and catalytic functions within a sin-

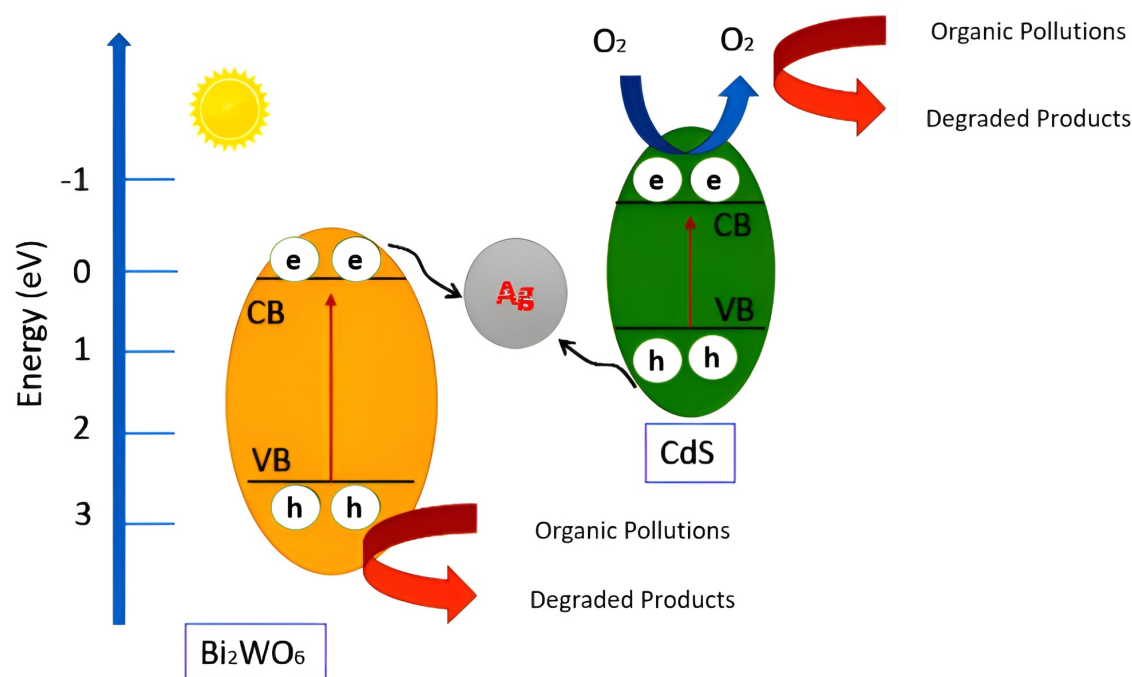


Figure 2. Energy Level Distribution of Photocatalyst Components (Bi_2WO_6 , Ag, CdS)

gle molecular structure [16]. This approach eliminates the need for separate photosensitizers and catalysts, streamlining the system [17].

In addition to discrete molecular systems, hybrid materials and semiconductor-based photocatalysts have also been substantially developed. Metal-based molecular photosensitizers are being extensively explored because of their excellent tunability and performance in various artificial photosynthesis applications, including energy conversion and environmental pollutant treatment [18],[19]. Furthermore, semiconductor materials are being engineered as artificial leaf models, with strategies focusing on fine-tuning light absorption, charge generation, separation, and transfer. [20]. These include the integration of photovoltaic and electrochemical (PV–EC) systems to convert solar energy into electricity, which drives electrochemical reactions [21].

The development of non-noble metal-based plasmonic materials, which exhibit localized surface plasmon resonance (LSPR) characteristics similar to those of noble metals but at a lower cost, represents another significant advancement [22]. For instance, researchers have explored various plasmonic materials for photocatalytic hydrogen generation and CO_2 reduction, including molybdenum oxide nanosheets, boron- and phosphorus-doped silicon nanocrystals, and Bi_2O_3 for infrared light-driven catalytic CO_2 reduction [23]. The continuous exploration of novel materials and hybrid architectures is essential for achieving practical and scalable artificial photosynthesis systems [24].

The key improvement in this area has been the shift from simple molecular dyes to integrated hybrid systems

(e.g., Ru complexes anchored on reduced graphene oxide and plasmonic non-noble metal materials) that enhance photostability and charge separation. This improvement is primarily due to covalent anchoring and localized surface plasmon resonance (LSPR) effects, which reduce the recombination losses. However, their performance is still limited by the trade-off between the absorption range and long-term stability, especially for non-noble metal systems under prolonged illumination.

3. WATER OXIDATION CATALYSTS

Recent advances in molecular and bio-inspired catalysts for water oxidation have considerably propelled artificial photosynthesis, motivated by the urgent demand for sustainable energy solutions. [31]. The oxygen evolution reaction (OER), which involves the four-electron oxidation of water ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$), remains a kinetically challenging bottleneck owing to its complex mechanism and high energy barrier [32]. Drawing inspiration from the natural oxygen-evolving complex (OEC) in Photosystem II (PSII), researchers have developed highly efficient catalysts to address this challenge [33].

3.1. MOLECULAR CATALYSTS

Molecular catalysts, especially transition-metal-based systems, have demonstrated significant progress. Ruthenium (Ru) complexes continue to be widely investigated, with recent efforts focusing on their incorporation into metal-organic frameworks (MOFs) to enhance both stability and catalytic activity. For example, a $\text{Ru}(\text{bda})\text{L}_2$ cat-

**Table 1.** Selected examples of reported performance for MOFs, COFs, and photoelectrochemical (PEC) systems for solar-driven hydrogen production

Technology	Key Performance Metric(s)	Reported Value	Key Test Conditions	Stability	Citation
MOFs (photocatalysts)	TON (H ₂ evolution)	~ 7000	Functionalized MOF, solar light, Pt co-catalyst	Not reported	[25]
MOFs (PEC hybrid)	STH efficiency	Not reported	MOF hybrids studied for charge separation	Not reported	[26]
COFs (photocatalysts)	TON (H ₂ evolution)	~ 54 over 20 h	Pt-loaded COF, visible light, sacrificial donor	20 hours	[27]
COFs (photocatalysts)	STH efficiency	Not reported	Lab-scale photocatalyst, not a full PEC device	Not reported	[28]
PEC systems	STH efficiency	6–9% (typical); up to ~ 17% (optimized)	InGaP/GaAs or perovskite tandems, AM 1.5G, unassisted	10–100 h	[29]
PEC systems (record)	STH efficiency	~ 19%	Tandem direct PEC, controlled lab conditions	Varies	[30]

alyst integrated into a UiO-66 MOF achieved a turnover number (TON) of 566 for photo-driven water oxidation, nearly 20-fold higher than the homogeneous analog [34]. Iridium (Ir) complexes are also under development, including Ir-dipyridyl-pyridazine organosilica, which serves as active catalytic sites for water oxidation [35]. Cobalt (Co)-based molecular catalysts, including highly oxidizing water-soluble variants, are being designed following bio-inspired principles [36].

3.2. EARTH-ABUNDANT METALS

Increasing attention is being paid to earth-abundant metals, such as iron (Fe) and manganese (Mn), as cost-effective and sustainable alternatives, reflecting the Mn₄CaO₅ cluster in natural photosynthesis [37]. Mn-based electrocatalysts, including KMnPO and KMnPO₄·H₂O, provide valuable insights into the water oxidation mechanisms [38]. Strategies employing redox-active ligands, exemplified by nickel phenolate complexes, are used to facilitate multi-electron transfer during the OER [39].

3.3. HYBRID SYSTEMS

Hybrid systems that integrate molecular catalysts with semiconductor materials are emerging to improve light absorption and charge transfer, such as semiconductor-mediator-catalyst assemblies using Fe₂O₃ and Ru(II) carbene complexes for photoelectrochemical water oxidation [40]. Supramolecular scaffolds containing catalytic units are also being developed to enhance seawater photoelectrochemical splitting via water-nucleophilic attack pathways, addressing interfacial complexity challenges [41]. Additionally, ball milling has been employed to con-

struct amorphous Co-based selenite nanoparticles for highly efficient OER [42]. Real-time tracking of molecular catalysts using techniques like mass spectrometry is providing effective insights for designing robust catalytic processes under harsh oxidative conditions [43].

Significant progress has been made in stabilizing molecular catalysts by incorporating them into MOF frameworks (e.g., Ru(bda)L₂@UiO-66), achieving nearly 20-fold higher TON than their homogeneous analogs. This improvement results from the confinement effect and protection against dimerisation/deactivation. Earth-abundant alternatives (Co, Fe, and Mn) have also advanced through bio-inspired designs. However, the main limitations are the high overpotential (typically > 300 mV at 10 mA/cm²) and limited stability under acidic or neutral conditions, where noble metals still outperform.

4. CO₂ REDUCTION CATALYSTS

Recent advancements in chemical catalysts for CO₂ reduction in artificial photosynthesis systems have primarily focused on refining the metal-ligand design to optimize product selectivity and efficiency [44]. The electrochemical reduction of CO₂ (CO₂RR) is a critical component that enables the conversion of CO₂ into valuable fuels and chemicals, thereby mimicking natural photosynthesis [45]. A key strategy involves the development of bio-inspired materials that aim to replicate the sophisticated catalytic mechanisms found in nature [46].

Metal-organic frameworks (MOFs) have emerged as a promising platform owing to their tunable structures and diverse coordination environments, allowing for precise control over catalytic activity and product distribution [47]. For instance, recent studies have demonstrated the

Table 2. Comparison of representative water oxidation catalysts (OER).

Catalyst	Overpotential at 10 mA/cm ² (mV)	Electrolyte / pH	Stability (hours)	Reference
Ru(bda) L₂ @UiO-66 (photo-driven)	~350	pH 7 buffer	12	[34]
Ir-dipyridyl-pyridazine organosilica	~290	0.1 M H ₂ SO ₄ (pH 1)	50	[35]
Co-based molecular catalyst	~380	pH 7 phosphate	8	[36]
NiFe layered double hydroxide	~240	1 M KOH (pH 14)	100	[37]
Mn-based KMnPO₄	~420	pH 7 buffer	6	[38]
Amorphous Co selenite	~310	1 M KOH	72	[42]
Fe₂O₃/Ru(II) carbene hybrid	~400	pH 7	24	[40]

design and preparation of MOF-based artificial enzymes (metal-organic zymes, MOZ)

that exhibit superior activities for both water oxidation and CO₂ reduction, achieved through the optimal coupling of different MOZ libraries [48]. These systems leverage unique metal-ligand interactions to facilitate multi-electron transfer processes that are crucial for CO₂ activation and conversion [49]. Furthermore, the incorporation of specific metal centers, such as ruthenium (Ru) in MOFs, has led to high photocurrents for photoelectrocatalytic water splitting and unassisted photocatalytic H₂ evolution, indicating their potential for integrated artificial photosynthesis systems [50]. The rational design of these catalysts, focusing on aspects such as redox-active ligands, has been instrumental in regulating the flow of charges and enhancing product selectivity, moving towards a more sustainable and efficient conversion of solar energy into chemical fuels [51].

The most important advance is the development of bifunctional systems where the same catalyst or framework (e.g., MOF-based artificial enzymes, metal-organic zymes) facilitates both light harvesting and CO₂ reduction. This integration reduces energy losses from charge transfer between separate components. Product selectivity has improved through careful metal-ligand design, particularly for CO and formate. However, the main bottleneck remains low Faradaic efficiency (often <70%) for multi-carbon products (e.g., methanol, ethanol) and rapid deactivation in the presence of oxygen or impurities.

5. INTEGRATED ARTIFICIAL PHOTOSYNTHESIS SYSTEMS

Integrated artificial photosynthesis systems, designed to mimic natural photosynthesis for sustainable energy conversion, have seen significant advancements in recent years, particularly in the combination of efficient light absorbers with robust catalysts for reactions such as CO₂ reduction and water oxidation [53],[54]. A key focus is

optimizing charge separation and transfer to enhance efficiency and stability [55]. However, a critical point for readers is that photovoltaic (PV) efficiency alone does not equal artificial photosynthesis performance. The true metrics are solar-to-fuel (STF) or solar-to-hydrogen (STH) efficiencies, which account for light absorption, charge transfer, catalytic overpotential, and product formation.

For example, monolithic perovskite/silicon tandem solar cells have achieved PV efficiencies exceeding 29% by utilizing enhanced hole extraction mechanisms. [56]. However, when integrated into a full artificial photosynthesis device (PV + electrolyzer) for water splitting, the reported STH efficiency is typically 15–18% over 100 h, representing a significant but not perfect translation of PV performance to fuel output [30].

Further innovations involve the rational design of photocatalytic components such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). For example, a Ru-containing Fe-based MOF (MIL-142) exhibited high photocurrents for photoelectrocatalytic water splitting and enabled unassisted photocatalytic H₂ evolution, achieving an STH efficiency of 2.3% over 24 h [57]. Similarly, donor-acceptor COFs have been developed to incorporate active sites for both CO₂ reduction and water oxidation within a single material.

framework, producing CO with a 71% Faradaic efficiency under simulated sunlight [58].

In another example, β -cyclodextrin-decorated CdS nanocrystals were used to simultaneously anchor cobalt tetraphenyl porphyrin catalysts and alcohol reductants. This configuration promotes selective photocatalytic CO₂ reduction coupled with alcohol oxidation, achieving a solar-to-CO conversion efficiency of 1.8% over 15 h [52].

Key takeaways for integrated systems: Every integrated device report should answer the following three questions: (1) What is the solar-to-fuel efficiency? (2) How long does it last? (3) What are the main products and selectivity? Without these, PV efficiency alone is

**Table 3.** Key experimental details for representative CO₂ reduction catalysts.

Catalyst system	Electrolyte	Cell type	Operating condition	Main product	Faradaic efficiency (FE%)	Stability time	Reference
Self-photosensitizing dinuclear Ru	0.1 M TBAPF ₆ in MeCN	H-type cell	Visible light, -1.2 V vs Ag/Ag ⁺	CO	89%	24 h	[6]
MOF-based artificial enzyme (MOZ)	0.5 M KHCO ₃	H-type cell	-0.8 V vs RHE	CO	76%	12 h	[48]
CdS/Bi ₂ WO ₆ heterojunction	0.1 M Na ₂ SO ₄	Photocatalytic reactor	AM 1.5G, no bias	Methanol	68%	8 h	[9]
Cu@hollow TS-1 nanoreactor	0.1 M KHCO ₃	Flow cell	-0.6 V vs RHE	Ethanol	52%	20 h	[10]
Co-based porphyrin + CdS	0.2 M KHCO ₃	Photocatalytic reactor	Visible light, no bias	CO	82%	18 h	[52]

insufficient to demonstrate the progress of artificial photosynthesis.

6. KEY CHALLENGES

In the past few years, artificial photosynthesis research has made notable progress; however, persistent challenges remain in moving from laboratory demonstrations toward practical systems. A key issue is catalyst stability; many high-performance catalysts for water oxidation and CO₂ reduction degrade rapidly under prolonged light exposure or reactive conditions, limiting long-term operation and commercial viability. Catalysts often suffer from low turnover frequencies, decomposition, or detachment from supports, and while some systems show hours to thousands of hours of operation, maintaining activity over the years required for real-world applications remains difficult.

Another major challenge is efficiency and scalability. Most artificial photosynthetic systems still operate well below the efficiencies needed for commercial use, with significant energy losses due to inadequate light absorption, charge recombination, and high overpotentials in key reactions. Although recent module-level systems have begun to surpass critical efficiency benchmarks, scaling these devices to larger areas without efficiency loss and with stable performance remains complex. In addition, reliance on expensive or rare catalyst materials and the integration of diverse components into cohesive, autonomous systems pose further barriers to cost-effective, scalable deployment.

7. FUTURE DIRECTIONS

Recent advances in artificial photosynthesis have improved catalyst performance and integrated system efficiencies, bringing laboratory prototypes closer to practical applications. Future research should explicitly target the development of durable, earth-abundant catalysts,

design optimized multi-component interfaces for efficient light harvesting and charge transfer, scalable fabrication of device architectures, and mechanistic studies combining experimental and computational approaches. Focusing on these areas (**Scalable Synthesis, Device Integration, Product Selectivity**) will accelerate the development of sustainable, high-efficiency artificial photosynthetic technologies.

8. CONCLUSIONS

In the last three to five years (2020–2025), chemical research in artificial photosynthesis has achieved meaningful advances in both catalyst design and integrated systems. Researchers have developed self-photosensitizing molecular catalysts and robust hybrid assemblies that improve light absorption and charge transfer, while new earth-abundant catalysts show enhanced activity and selectivity for CO₂ reduction and water oxidation. Progress in artificial leaf architectures and photoelectrochemical cells has also demonstrated higher solar-to-chemical conversion efficiencies under practical conditions, narrowing the gap between fundamental chemistry and functional prototypes. Despite remaining challenges in long-term stability, material cost, and scale-up, recent studies highlight promising strategies such as bio-inspired catalyst motifs, optimized ligand environments, and coupled catalytic interfaces.

Key takeaways from this review:

- **Main progress:** Self-photosensitizing molecular catalysts (Ru and Co) eliminate the need for separate photosensitizers, simplifying system design. MOF and COF frameworks have improved catalyst stability by 10–20× compared to homogeneous analogs.
- **Main bottleneck – stability:** Most advanced catalysts still degrade within 12–100 h of continuous operation. Commercial viability requires >1000 h (or >1 year) of stability.

- **Main bottleneck – efficiency:** While PV cells exceed 29% efficiency, integrated solar-to-fuel (STH or STF) efficiencies for artificial photosynthesis typically remain below 10–15% under unassisted conditions.
- **Main bottleneck – selectivity:** CO₂ reduction to multi-carbon products (ethanol, methanol, hydrocarbons) still shows Faradaic efficiency below 70% in most systems, with CO and formate being the dominant (easier) products.
- **Realistic near-term targets (next 3–5 years):** (1) STH efficiency >15% for unassisted PEC water splitting with >1000 h stability; (2) CO₂ reduction to C₂+ products with FE >80%; and (3) replacement of precious metals (Ru, Ir, and Pt) in at least one component of a working integrated device.
- **Critical next step for the field:** Every future report should include a complete performance matrix: solar-to-fuel efficiency + stability time + Faradaic selectivity + test conditions (illumination, electrolyte, pH, temperature). Without these four elements, a comparison between systems is impossible.

Conflict of Interest: None declared.

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