ADVANCEMENTS IN ARTIFICIAL PHOTOSYNTHESIS: A COMPREHENSIVE EXPLORATION OF PROCESSES, CATALYSTS, AND STRATEGIES FOR SUSTAINABLE ENERGY PRODUCTION AND CO_2 REDUCTION

1. Introduction

The global challenges stemming from the continuous rise in carbon dioxide (CO_2) emissions are largely attributed to the reliance on finite fossil fuel resources. With 80% of energy consumption being fuel-based, there is a pressing need to address resource depletion and climate change acceleration [1, 2]. While conventional alternatives like solar and wind power contribute to cleaner energy, their limitation lies in providing converted energy primarily in the form of electricity. This poses challenges in terms of storage and transportation and thus prompting the search for other chemical energy carriers.

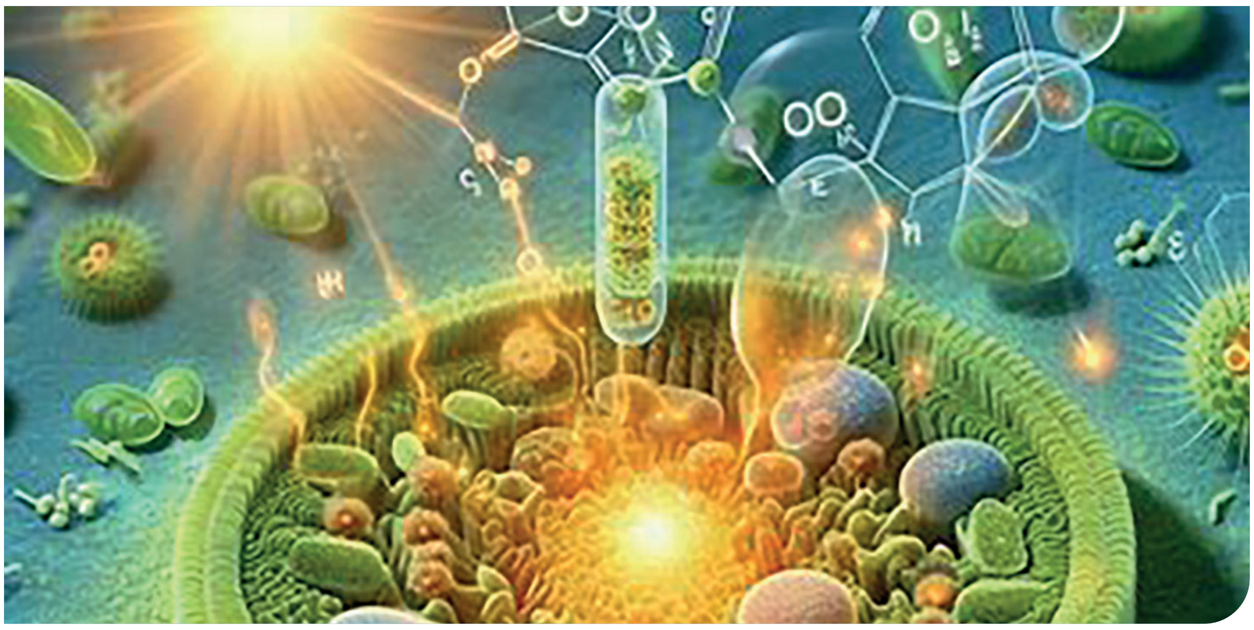
Inspiration may be drawn from fossil resources that store sunlight in high-energy chemicals, despite the current time-consuming and non-recyclable processes. This prompts consideration for alternative energy carriers that mimic the characteristics of fossil fuels. In this context, artificial photosynthesis emerges as a promising solution. The process of artificial photosynthesis leverages sunlight to convert water and CO_2 into energy-rich compounds, offering a perpetual and renewable energy source. This, in turn, contributes significantly to reducing CO_2 emissions, helping to combat the intensified climate damage.

The revolutionary potential of artificial photosynthesis is acknowledged, but challenges remain. The complex processes involved demand the use of advanced materials and technologies, raising concerns about overall sustainability. These concerns include resource-intensive production requiring rare metals, environmental impact during material use, and energy-intensive manufacturing processes. Moreover, artificial photosynthesis is still in its early stages of development, requiring further research and refinement before becoming a practical energy solution.

In the present time, there has been notable research in the field of artificial photosynthesis, exploring innovative approaches such as Z-scheme heterojunctions and stable heterometallic Fe2M cluster-based metal-organic frameworks (MOFs). These endeavors aim to achieve artificial photosynthetic overall reaction by simultaneously coupling CO_2 reduction and water (redox) oxidation. In the broader context, artificial photosynthesis emerges as a promising solution to address the current energy and climate crises. This comprehensive review navigates through the fundamental processes and recent advancements in artificial photosynthesis, shedding light on ongoing efforts to make it a viable and sustainable solution for evolving energy needs. The focus narrows to optimizing structural designs, enhancing charge transfer efficiency, and addressing challenges like CO_2 inertness and slow reaction kinetics. As researchers delve into designing well-defined crystalline systems and exploring novel nanocomposite strategies, the pathway to a more efficient and environmentally friendly artificial photosynthetic future becomes increasingly promising.

2. Fundamental Processes in Artificial Photosynthesis

In nature, plants employ photosystem II (PSII) in chloroplasts to convert sunlight into chemical energy. This process, as outlined in Figure 1, generates electron–hole pairs, powering redox reactions. The oxidative holes activate the oxygen-evolving center (OEC), leading to the oxidation of water and the production of O_2. The electrons then travel through photosystem I (PSI), resulting in the generation of energy-rich bio-reducing agents like NADPH or ATP [1]. These agents play a vital role in the Calvin cycle, where CO_2 is transformed into carbohydrates, representing nature's cyclical and sustainable carbon-based fuel system.



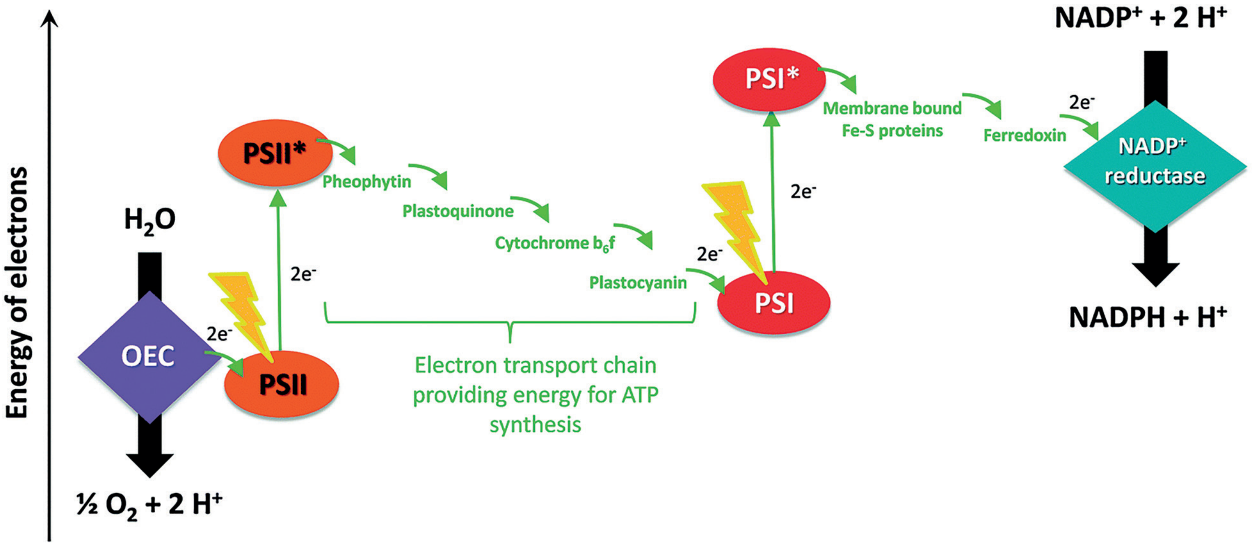


Figure 1. Schematic representation of photosynthesis with light absorbing units PSI and PSII, electron transport chain, oxygen evolving center (OEC) and NADP+ reductase [2].

The concept of storing solar energy in chemical bonds serves as the basis for constructing an artificial photosynthetic system. This system mimics natural photosynthesis by oxidizing water to produce O_2, and the resulting electrons are utilized to reduce CO_2 to chemical compounds with higher energetic content. These chemicals, such as methane, methanol, or carbon monoxide (CO), exhibit fuel-like properties, allowing them to be stored, transported, and burned to release energy.

The artificial photosynthesis system closely mimics the natural process by which plants, algae, and bacteria produce food and energy. This biomimicry centers on replicating PS II found in natural photosynthesis, where water is split into oxygen (O_2) and H+. The system involves three fundamental processes: light harvesting, charge separation, and redox catalysis [3]. Light harvesting involves the use of photosynthesizers to absorb light energy broadly, initiating photochemical reactions. Charge separation relies on semiconductors to separate charges generated during light absorption, providing components for subsequent redox reactions. Redox catalysis involves electron transport molecules, such as redox mediators, crucial for transporting electrons from photosensitizers or semiconductors to catalysts responsible for water oxidation and carbon dioxide reduction. The visual representation in Figure 2 illustrates these steps, providing a clear depiction of the respective reactions involved.

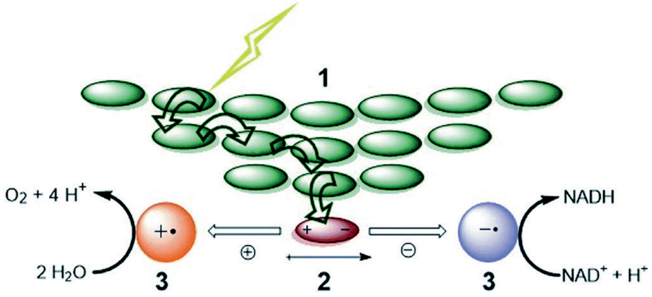


Figure 2. Key steps in photosynthesis. (1) Gathering light, (2) Separating charges, and (3) Catalyzing redox reactions. Energy transfer between chromophores (green arrows) leads to charge separation, with subsequent movement to catalysts for uphill chemical reactions [3].

Ongoing research is dedicated to enhancing each component's performance and exploring new materials for overall efficiency improvement in artificial photosynthesis. Advances include improved catalysts, various semiconductors, and promising photocatalysts. Strategies like tuning interfacial energetics and introducing site-specific single copper atoms are employed, and innovative approaches such as triphasic interfacial photocatalytic systems aim to boost CO_2 conversion rates. The ultimate goal is to benefit eco-friendly solar fuel production and climate change mitigation through the refinement of artificial photosynthesis technologies.

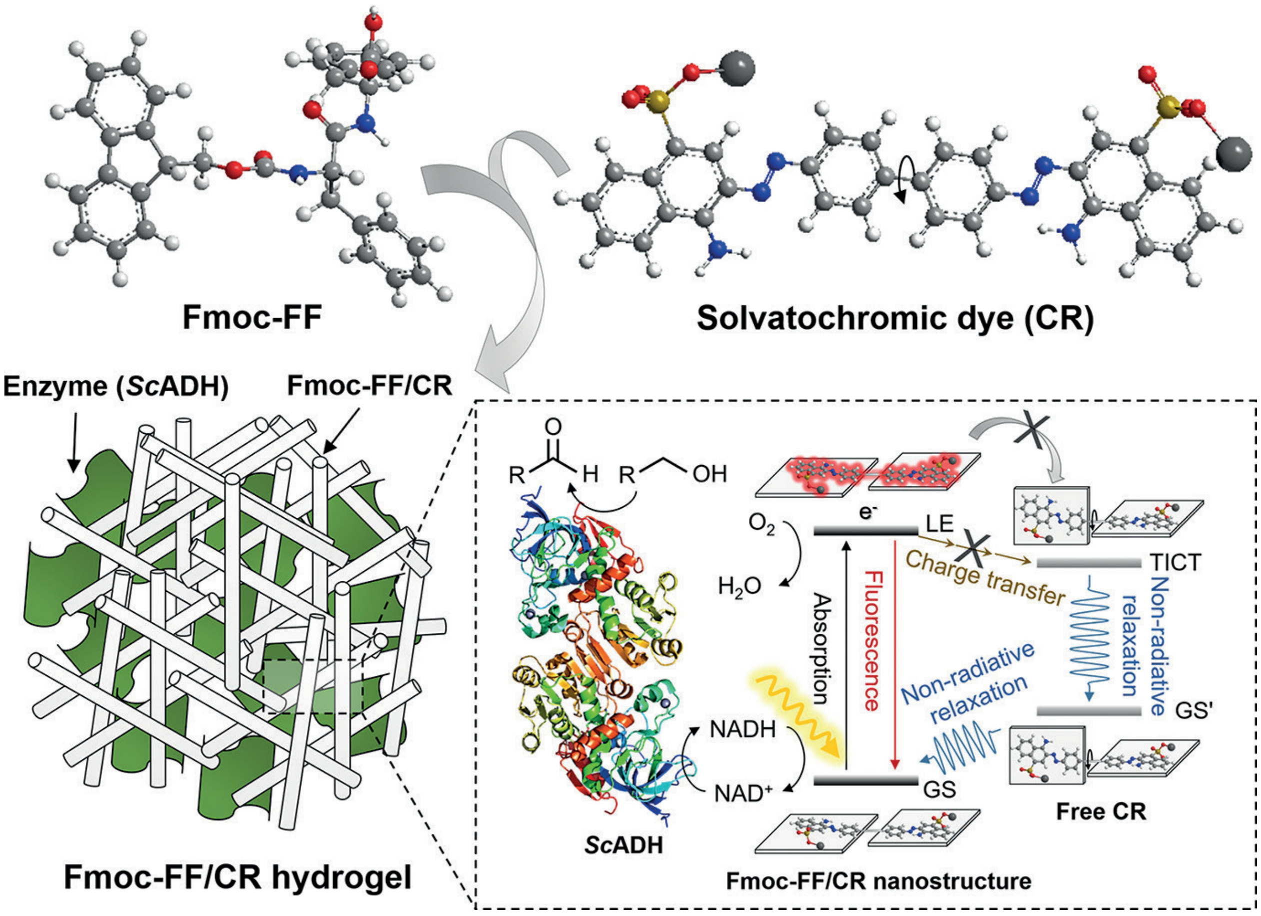


Figure 3. Illustration of the suppression of free rotation of solvatochromic CR dyes in amyloid-derived hydrogel for light-driven biocatalytic oxidation [7].

Table 1. Comparative analysis of the present work with a few similar literature reports [8].

s. no.	nanomaterials	photocatalyst amount	light source with reaction time	final product with selectivity	quantum yield (%)	recycles
1.	MnNFs−SnO_2@Pt (present report)	0.5 mg/mL	visible light (5 h)	HCOOH (94%)	3.21	10
2.	Fe-*p*-TMA and Phen2[68]	0.33 mg/mL	visible light (47 h)	CH_4 (85%)	0.47	NR
3.	InPC-sensitized TiO_2[69]	10.1 mg/mL	visible light (24 h)	HCOOH	2.1	NR
4.	MPA&MUA QDs[70]	1 mg/mL	visible light (32 h)	HCOOH	23.2	NR
5.	electrocatalyst-linked nitrogen-doped Ta_2O_5[71]	1.25 mg/mL	visible light (16 h)	HCOOH	1.9	NR
6.	alumina-supported alpha-iron(III) oxyhydroxide[72]	1 mg/mL	visible light (3 h)	HCOOH (80−90%)	4.3	5
7.	Cu@Cu_2O[73]	0.5 mg/mL	visible light (3 h)	HCOOH (NR)	0.12	5
8.	In/TiO_2[74]	50 mg (gaseous phase reaction)	visible light (10 h)	CO (94.39%)	0.10	NR
9.	Pt-TiO_2[37]	0.7 mg (gaseous phase reaction)	visible light (8 h)	CH_4 (NR)	2.41	NR
10.	rGO_x@TpPa-1[75]	2 mg/mL	visible light (3 h)	CO (89%)	0.5	6
11.	ZnO-Cu_2O[76]	0.95 mg/mL	visible light (3 h)	CH_4 (99%)	1.5	NR

[a] NR = not reported.

3. Research on Artificial Photosynthesis

3.1 Light harvesting

Light harvesting involves capturing sunlight through specialized molecules such as organic dyes or metal complexes. These molecules enable the absorption of a broad spectrum of light energy, energizing them and initiating photochemical reactions. This process marks the initial step in the conversion of solar energy into practical forms within the artificial photosynthesis framework.

Recent advancements in light harvesting are driven by innovative strategies, including exploring new organic dyes and pigments, designing conjugated polymers, and employing nanostructured materials such as quantum dots and nanowires [4]. These efforts aim to enhance light absorption properties, broaden the absorbed wavelength range, and optimize sunlight utilization, contributing to more effective light harvesting.

Efforts to boost photosynthetic efficiency focus on accelerating light-dependent reactions and optimizing biocatalytic processes. For instance, Jiang et al. proposed an interfacial control strategy to improve CO_2 conversion by enhancing synergy between semiconductors and active centers. This involves constructing self-assembled organic semiconductors with controlled surface architectures, utilizing 1,6-bis(phenylethynyl)pyrene (BPEPy) building blocks as light-harvesting semiconductors (LHS) [5]. The study achieves enhanced synergy between LHS and molecular active centers (MAC) by optimizing the biphase interface between solid catalytic materials and liquid-phase reaction solutions. Similarly, Wang and colleagues employ conjugated polymers (CPs) as "artificial antennas" on photosynthetic organisms, addressing the limitations of natural pigments, enhancing photosynthetic efficiency, and broadening the photosynthetically active radiation (PAR) range [6]. Unlike traditional semiconductors, CPs exhibit both electronic and ionic conductivity, acting as "electron bridges" and accelerating electron transfer at the material-organism interface.

In addition, innovative materials like hybrid hydrogel and manganese (Mn)-based nanocomposites showcase potential in advancing light-driven biocatalytic oxidation and sustainable CO_2 conversion. Park and coworkers explored a novel approach to light-driven NAD+ regeneration for enzymatic alcohol oxidation within a self-assembled peptide nanostructure [7]. Using Fmoc-diphenylalanine as a building block, the researchers created β-sheet-enriched amyloid-like nanostructures, forming a hydrogel that served as a scaffold as shown in Figure 3. Incorporating the solvatochromic dye Congo red (CR) into this structure via π–π interactions resulted in a hydrogel with enhanced solvatochromic properties. The Fmoc-FF/CR hydrogel efficiently regenerated NAD+ under visible light, demonstrating a fivefold higher regeneration rate for NAD+ coupled with O_2 reduction—showcasing superior performance compared to free CR dyes. The enhanced regeneration rate positions the hydrogel as a potential catalyst for artificial photosynthetic systems, where continuous and efficient coenzyme regeneration is essential for sustained energy conversion.

In another study, Kumar et al. elevated the efficiency of converting CO_2 through photocatalysis. They used manganese nanospheres (MnNSs) and nanoflowers (MnNFs) as catalysts, coating them with layers of tin dioxide (SnO2) and platinum (Pt) nanodots. The resulting nanocomposites demonstrated highly efficient CO_2 conversion when exposed to visible near-infrared sunlight. One specific composite, MnNFs–SnO_2@Pt, exhibited superior performance with a quantum yield of 3.21%, a chemical yield of 5.45%, and an impressive 94% selectivity for producing formic acid (HCOOH) under visible light conditions [8]. The research suggests that these nanocomposites could be promising catalysts for artificial photosynthesis, contributing to sustainable CO_2 conversion. The study also highlighted advantages such as higher quantum yield, reduced catalyst amount, enhanced selectivity, and improved recyclability compared to previous works, as summarized in Table 1, providing valuable insights for advancing artificial photosynthesis technologies.

3.2 Charge separation

Charge separation is a foundational process integral to various technologies, including solar cells and artificial photosynthesis. Within the context of artificial photosynthesis, charge separation is essential for converting solar energy into chemical energy. In processes such as the water-splitting reaction, specialized molecules like dyes or metal complexes absorb light, generating electrons and holes. These separated charges are then harnessed to drive chemical reactions that transform water into O_2 and hydrogen (H_2), effectively storing solar energy in chemical bonds. The Mn-based nanocomposites serve as a practical example of charge separation in the context of CO_2 photoreduction. When MnNSs and MnNFs are coated with SnO_2 and Pt nanodots and exposed to light, charge separation occurs, enabling the conversion of CO_2 into formic acid.

To improve the efficiency of electron transfer, carbon-based materials such as graphene, graphene oxide (GO), and carbon nanotubes (CNT) are employed due to their high conductivity. These materials act as conductors in heterogeneous photoreactions, aiding in efficient charge separation and transfer. Additionally, ensuring efficient spatial separation of photogenerated electron-hole pairs is important to prevent rapid recombination. Su et al. created a metal-halide perovskite (MHP)-based nanoscale Janus Z-scheme heterojunction of $CsPbBr_3$/TiOx. The Caesium Lead Tribromide ($CsPbBr_3$) nanocrystals were formed in situ from the transformation of Cs_4PbBr_6 nanocrystals at the hexane/water interface, and a titanium matrix (TiOx) was deposited on one side of $CsPbBr_3$ through in-situ hydrolysis of titanium butoxide (TBO) [9]. This resulted in the formation of a nanoscale Janus heterojunction with swift interfacial charge transfer. The $CsPbBr_3$/TiOx heterojunction exhibited significantly enhanced photocatalytic activity for CO_2 reduction compared to traditional $CsPbBr_3$:TiOx heterojunctions as seen on Table 2. The electron consumption rate for CO_2 reduction coupled with water oxidation was remarkably high under 1 sun irradiation, without the need for organic sacrificial agents. The study proposes a Z-scheme mechanism for the photocatalytic process, highlighting the effective spatial separation of photoinduced electron–hole pairs and the preserved strong redox capacities in $CsPbBr_3$/TiOx as key factors for the enhanced performance.

In a different application, Li et al. used a photocatalytic process to synthesize urea from nitrogen (N_2), CO_2, and H_2O under mild conditions. Traditional urea production relies heavily on ammonia and involves energy-intensive processes. The researchers propose a green synthesis method using a TiO_2 photocatalyst immobilized with reversible single-atom copper (Cu SA-TiO_2) to accelerate electron-transfer dynamics with the photoactivation cycle shown in Figure 4. The Cu SA-TiO_2 catalyst demonstrated rapid extraction of photogenerated electrons, over 30 times faster than reference photocatalysts (Table 2) [10]. This efficient electron transfer ensures a continuous supply for the co-photoactivation of N_2 and CO_2, leading to significant rates of urea production.

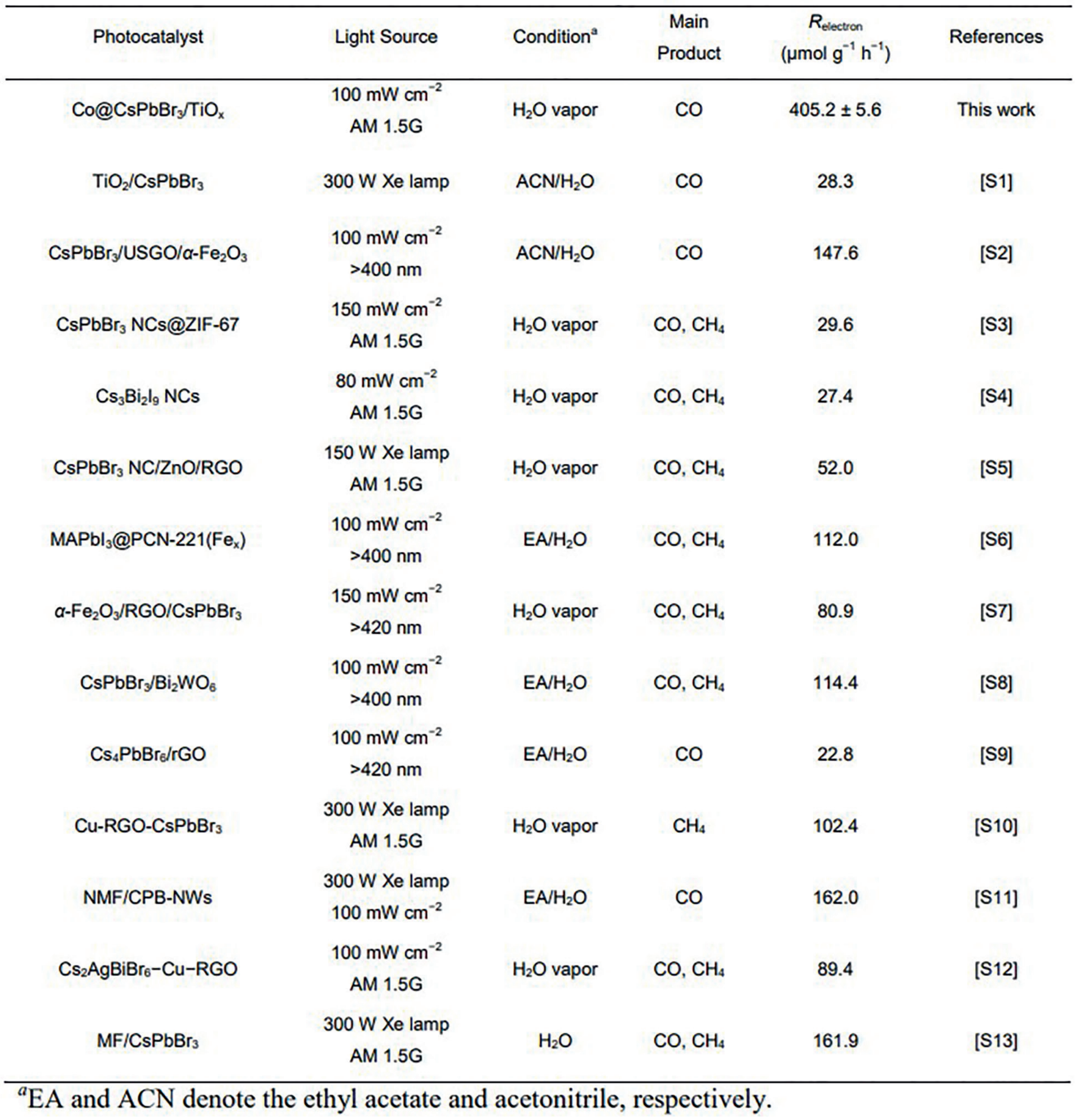
3.3 Redox catalysis

Redox catalysis refers to the use of catalysts to facilitate electron transfer during the conversion of solar energy into chemical energy. These catalysts mediate redox reactions, which are fundamental steps in the synthesis of energy-rich molecules. For example, in the process of water splitting, a redox catalyst can accelerate the separation of water molecules into O_2 and H_2. This involves the reduction of water to produce H_2 gas ($2H_2O \rightarrow 2H_2 + O_2$). The hydrogen generated can then be utilized as a clean and storable energy source. Another application of redox catalysis is seen in the reduction of O_2 to form hydrocarbons or other carbon-based fuels. Using redox catalysts, this reduction process contributes to capturing and converting carbon emissions. The overarching objective is to replicate and optimize these redox processes within a controlled environment, allowing for the efficient capture and storage of solar energy in the form of chemical bonds.

3.3.1. CO_2 Reduction Reaction (CRR)

The CO_2 reduction reaction (CRR) aims to convert CO_2 into

Table 2. Summary of the halide perovskite based photocatalysts for CO_2 reduction with water as electron source under similar light irradiation [10].



Photocatalyst	Light Source	Condition^a	Main Product	$R_{electron}$ (μmol g^{-1} h^{-1})	References
Co@$CsPbBr_3$/TiO_x	100 mW cm^{-2} AM 1.5G	H_2O vapor	CO	405.2 ± 5.6	This work
TiO_2/$CsPbBr_3$	300 W Xe lamp	ACN/H_2O	CO	28.3	[S1]
$CsPbBr_3$/USGO/α-Fe_2O_3	100 mW cm^{-2} >400 nm	ACN/H_2O	CO	147.6	[S2]
$CsPbBr_3$ NCs@ZIF-67	150 mW cm^{-2} AM 1.5G	H_2O vapor	CO, CH_4	29.6	[S3]
$Cs_3Bi_2I_9$ NCs	80 mW cm^{-2} AM 1.5G	H_2O vapor	CO, CH_4	27.4	[S4]
$CsPbBr_3$ NC/ZnO/RGO	150 W Xe lamp AM 1.5G	H_2O vapor	CO, CH_4	52.0	[S5]
$MAPbI_3$@PCN-221(Fe_x)	100 mW cm^{-2} >400 nm	EA/H_2O	CO, CH_4	112.0	[S6]
α-Fe_2O_3/RGO/$CsPbBr_3$	150 mW cm^{-2} >420 nm	H_2O vapor	CO, CH_4	80.9	[S7]
$CsPbBr_3$/Bi_2WO_6	100 mW cm^{-2} >400 nm	EA/H_2O	CO, CH_4	114.4	[S8]
Cs_4PbBr_6/rGO	100 mW cm^{-2} >420 nm	EA/H_2O	CO	22.8	[S9]
Cu-RGO-$CsPbBr_3$	300 W Xe lamp AM 1.5G	H_2O vapor	CH_4	102.4	[S10]
NMF/CPB-NWs	300 W Xe lamp 100 mW cm^{-2}	EA/H_2O	CO	162.0	[S11]
$Cs_2AgBiBr_6$–Cu–RGO	100 mW cm^{-2} AM 1.5G	H_2O vapor	CO, CH_4	89.4	[S12]
MF/$CsPbBr_3$	300 W Xe lamp AM 1.5G	H_2O	CO, CH_4	161.9	[S13]

^{a}EA and ACN denote the ethyl acetate and acetonitrile, respectively.

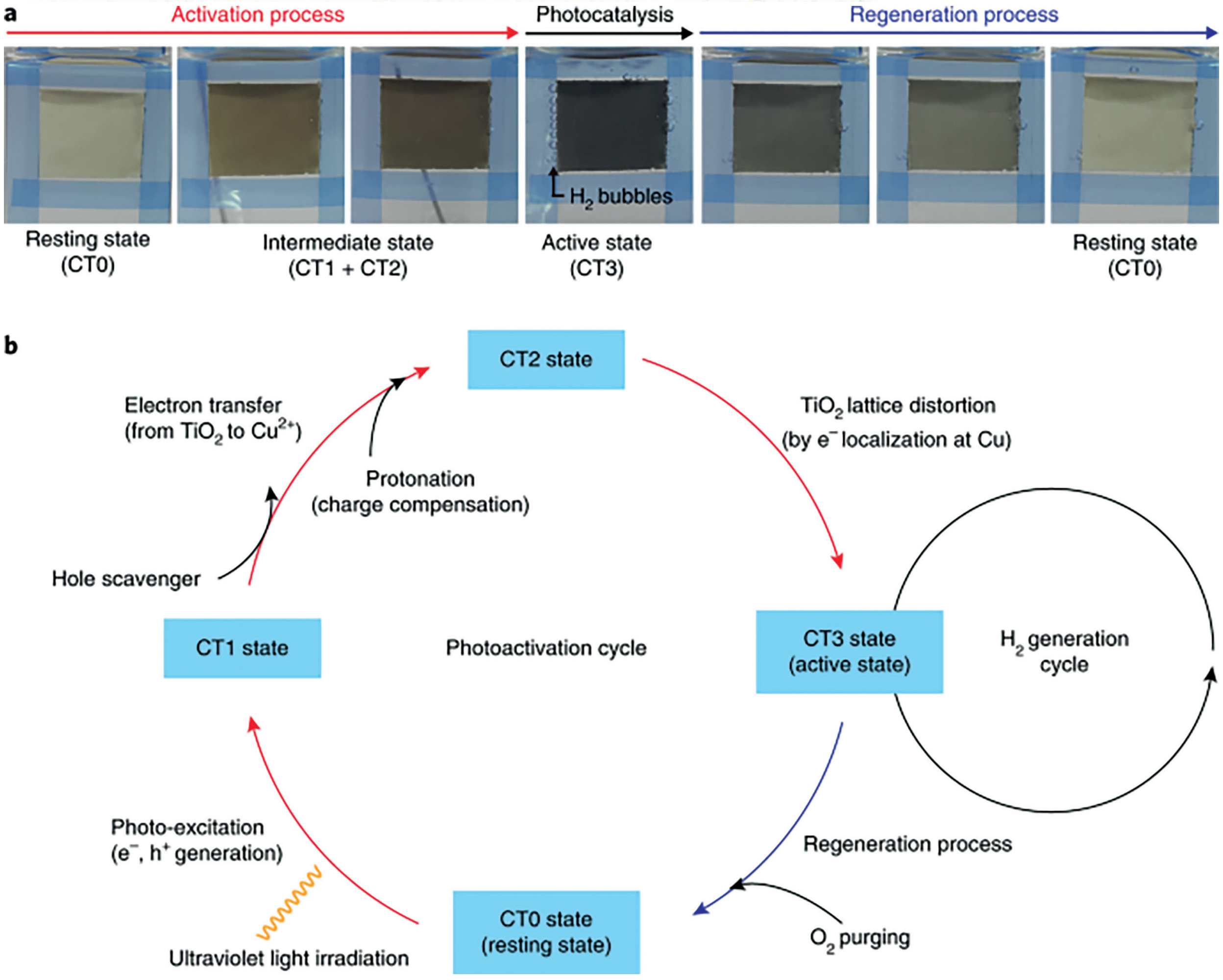


Figure 4. (a) Pictures showing different stages of the photoactivation cycle of the Cu/TiO_2 film. (b) Diagram illustrating the photoactivation cycle of Cu/TiO_2 [9].

valuable and environmentally friendly products. In this reaction, CO_2 serves as a feedstock for the synthesis of various compounds, typically using renewable energy sources. The objective is to mitigate the impact of CO_2 emissions on the environment by transforming this greenhouse gas into useful chemicals or fuels. During CO_2 reduction, electrons from an external source, often driven by solar energy, are introduced to CO_2 molecules, leading to the production of carbon-based compounds.

Efforts to optimize the performance of photocatalysts in this context involve manipulating the energetics at sites where redox oxidation reactions occur. One proposed strategy is the use of a binary cocatalyst, employing two distinct materials or components to enhance overall efficiency. This concept is inspired by successful systems like photoelectrochemical water splitting, where different cocatalysts are used to drive specific reactions [11]. However, when dealing with particulate photocatalysts (composed of small particles), implementing this binary cocatalyst strategy becomes challenging. Achieving effective and controlled placement of distinct cocatalysts on these particles is difficult due to their complex and detailed structure, potentially impacting the overall efficiency of the artificial photosynthesis system.

On the other hand, an ideal CO_2 reduction photocatalyst should have a low-energy pathway and high selectivity. The energy barrier represents the minimum energy required for a chemical reaction to occur. In the case of CO_2 reduction, a lower energy barrier means that the reaction can proceed more readily and at a faster rate. This is essential for achieving a higher production rate of CO, as demonstrated by the optimized Ni-SA-x/ZrO_2 photocatalyst. Xiong et al. found that a photocatalyst consisting of isolated nickel (Ni) single atoms on defect-rich zirconia (Ni-SA-x/ZrO_2) exhibited excellent activity and a strong preference for producing CO under xenon (Xe) lamp irradiation, all without the need for sacrificial agents. When optimized, this catalyst achieved a remarkable CO production rate, being 6 and 40 times higher than defective ZrO_2 and perfect ZrO_2, respectively [12]. Moreover, it demonstrated a selectivity of 92.5%, outperforming various other nickel-based systems. The strategic placement of dispersed nickel sites in the catalyst played a key role in reducing the energy barrier for converting CO_2 to CO and suppressing H_2 desorption in the water splitting reaction.

Another example further illustrates the significance of specific catalyst systems. The polyoxometalate (POM), a Keggin-type polyoxometalate, can potentially act as an electron and proton reservoir, facilitating the reduction of CO_2. Benseghir and colleagues created a composite material by combining a POM called PW12O403– and a catalytic complex (CpRh(bpydc)Cl_2) within a metal-organic framework (MOF) called UiO-67. They ensured the structural integrity of each component through various techniques like spectroscopy, NMR, X-ray diffraction, and advanced methods like Pair Distribution Function (PDF) analysis with the spatial arrangements shown in Figure 5. This composite, referred to as (PW12,CpRh)@UiO-67, demonstrated improved stability and performance in the photocatalytic reduction of CO_2 to formate and H_2 compared to catalysts without the POM as shown in Figure 6 [13].

3.3.2. CRR and WOR combination

The effective coupling of the photocatalytic CO_2 reduction reaction (CRR) and water oxidation reaction (WOR) is important for achieving artificial photosynthesis, utilizing water as a hole scavenger and providing a green means to recycle atmospheric CO_2 [14]. Both CRR and WOR involve multielectron and multiproton transfer processes where photocatalysts supply multiple electrons, and water serves as an abundant source of protons [15].

A challenge in metal cluster-based compounds lies in simultaneously achieving CRR and WOR due to the difficulty in realizing independently and synergistically reductive and oxidative active sites in one compound. Li et al. addressed this challenge by designing and synthesizing crystalline reduction–oxidation (RO) cluster-based catalysts, specifically connecting reductive {M3L8(H2O)2} (M = Zn, Co, and Ni) clusters and oxidative {PMo9V7O44} clusters through a single oxygen atom bridge. This design enables artificial photosynthesis, allowing these clusters to photocatalyze CO_2-to-CO and H_2O-to-O_2 reactions simultaneously [16]. The specific catalysts developed, named RO-1, RO-2, and RO-3, consist of linear trinuclear reduction clusters and phosphovanadomolydate oxidation clusters. These clusters exhibit efficient light absorption and suitable band structures for reducing CO_2-to-CO and oxidizing H2O-to-O2. Among them, RO-1 demonstrated the highest CO yield of 138 μmol/g with nearly 100% selectivity in a gas–solid system, showcasing the success of the artificial photosynthetic overall reaction (Figure 7). Density functional theory (DFT) calculations revealed that efficient electron transfer between the reduction and oxidation clusters, along with their strong redox capabilities, contributed to the superior performance of RO-1.

Another advancement involves the design and synthesis of nanocomposites with tailored structures for efficient photocatalytic conversion of CO_2 and H2O into useful chemical products, resembling fundamental processes in artificial

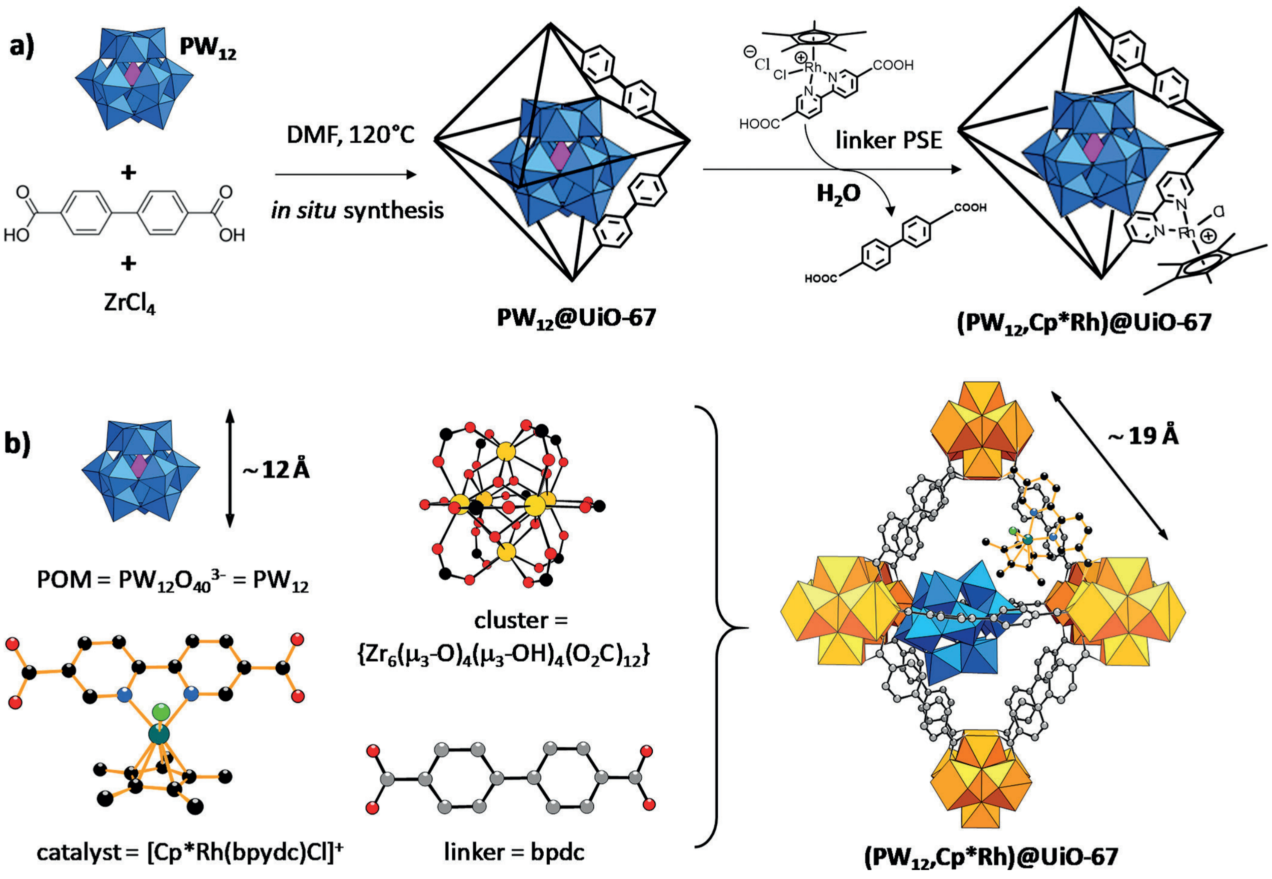


Figure 5. (a) Schematic representation of the two-step in situ synthesis and linker's postsynthetic exchange (PSE) procedure to obtain the composite material (PW12,Cp*Rh)@UiO-67. (b) Components of (PW12,Cp*Rh)@UiO-67: The illustration showcases the key elements, including the PW12 polyoxometalate, the Zr-based UiO-67 inorganic subunit, the [Cp*Rh(bpydc)Cl]+ molecular catalyst, and the bpdc linkers. Different colors distinguish WO6 (blue polyhedra), ZrO8 (orange polyhedra), PO4 (pink polyhedron), Zr (orange spheres), O (red spheres), C (gray or black spheres), N (blue spheres), Rh (dark green spheres), and Cl (green spheres). The spatial arrangement is determined through density function theory (DFT) calculations [13].

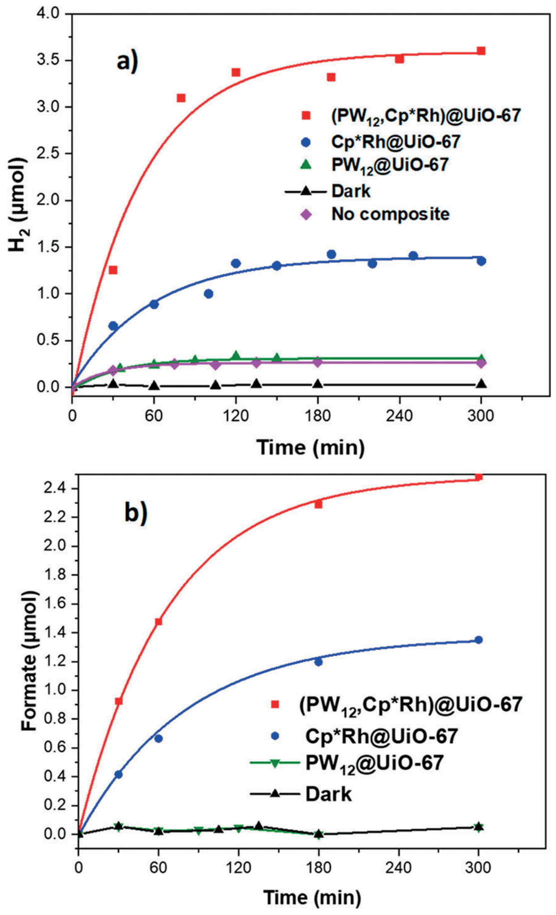


Figure 6. Kinetics of (a) H_2 and (b) HCOO− production during CO_2 photoreduction reaction by (PW12,Cp*Rh)@UiO-67 compared to Cp*Rh@UiO-67. Reactions conditions: 0.17 μmol of catalyst, 0.8 mL of CH_3CN/TEOA 5:1, 1 mM $Ru(bpy)_3Cl_2$, 280 W, λ > 415 nm [13].

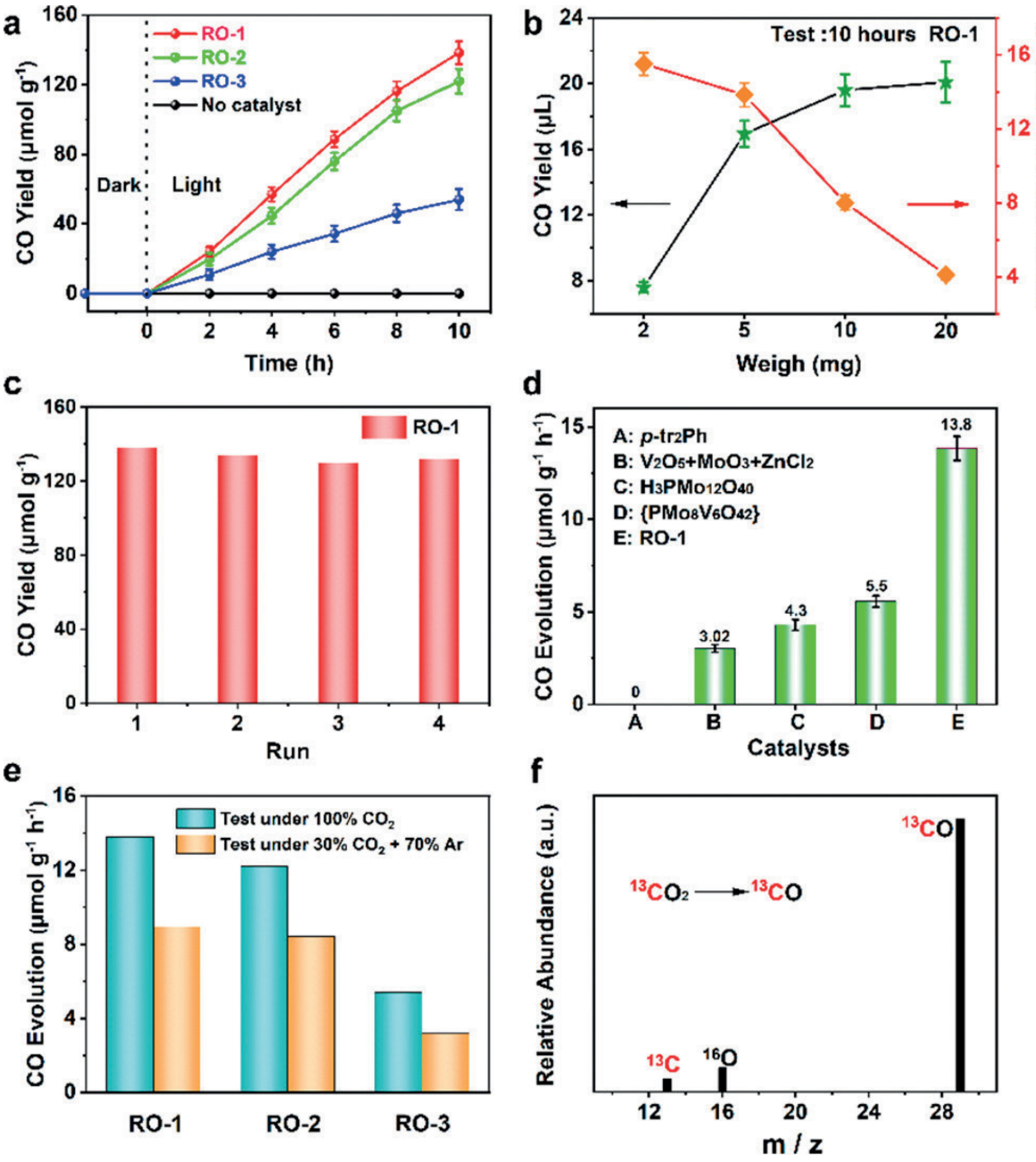


Figure 7. Study of CO_2 reduction through photosynthesis using various catalysts. (a) CO production over time for RO-1, 2, and 3. (b) Correlation between CO yield and generation rate for different qualities of RO-1. (c) CO yield for RO-1 in four consecutive runs. (d) CO yield in comparative tests. (e) CO generation by RO-1, 2, and 3 in 100% CO_2 and 30% CO_2 (+70% Ar) atmospheres. (f) Mass spectrum of generated 13CO from 13CO_2 catalyzed by RO-1 [16].

photosynthesis. Zhang and coworkers introduced a MOF-sacrificed in situ acid-etching (MSISAE) strategy to achieve controlled synthesis of various covalent organic frameworks (COFs)-based nanocomposites with distinct architectures. The strategy involves the sacrificial use of a core MOF (NH2-MIL-125) that undergoes acid etching to produce nano-sized TiO_2 while tuning the reaction parameters. The resulting nanocomposites include uniform core-shell MOFs@COFs, yolk-shell MOFs/TiO_2@COFs, and hollow-sphere TiO_2@COFs. The unique yolk-shell structure with three components (NH_2-MIL-125/TiO_2@COF-366-Ni-OH-HAc) demonstrated exceptional photocatalytic CO_2-to-CO conversion efficiency in the gas-solid mode [17]. The MSISAE strategy allows for the precise design and control of multicomponent hybrid composites based on COFs, showcasing diverse architectures, and enhanced catalytic properties. The developed yolk-shell structure (MTCN-H (ys)) exhibits coexistence of Z-scheme and II-type heterojunctions, providing multiple active sites, efficient carrier transfer, and increased light utilization. This specific nanocomposite outperforms pure COFs, MOFs, TiO_2, and other nanocomposites in terms of photocatalytic CO_2 reduction. The study offers insights into designing porous crystalline materials for multifunctional catalytic reactions, particularly in the context of artificial photosynthesis.

3.4 Photosynthetic overall reaction

The effective combination of CO_2 reduction and H_2O oxidation half-reactions, constituting the overall artificial photosynthetic reaction, is challenging due to the inherent chemical inertness of CO_2 and slow reaction kinetics. Some nanostructured photocatalysts, such as Z-scheme heterojunctions like Cu_2O/WO_3 and α-Fe_2O_3/Cu_2O, have achieved the overall reaction. However, the influence of defects, impure phases, and complicated structural components in these catalysts hinders a clear understanding of specific catalytic sites.

To address these challenges, Dong and colleagues developed a novel approach to artificial photosynthesis using stable heterometallic Fe_2M cluster-based MOFs, denoted as NNU-31-M (M=Co, Ni, Zn). These MOFs, denoted as NNU-31-M (M=Co, Ni, Zn), are constructed by combining stable Fe_2M clusters with a photosensitive tricarboxytriphenylamine (TCA) ligand [18]. The key innovation lies in the ability of these MOFs to act as photocatalysts, simultaneously facilitating the essential CO_2 reduction and H_2O oxidation reactions under visible light. When exposed to light, the MOFs generate separated electrons and holes, with the low-valent metal M accepting electrons for CO_2 reduction, and the high-valent Fe using holes to oxidize H_2O. These MOFs achieve the overall conversion of CO_2 and H_2O into formic acid (HCOOH) and O_2 without

Table 3. Comparative experiments under different conditions for the artificial photosynthetic overall reaction of NNU-31-Zn [18].

Photocatalyst	Solvent	Atmosphere	Light Source	Yield HCOOH (μmol g^{-1} h^{-1})	Yield O$_2$ (μmol g^{-1} h^{-1})
NNU-31-Zn	Water	CO$_2$	420-800	26.3	12.6
NNU-31-Zn	Water	CO$_2$	dark	n.d.	n.d.
NNU-31-Zn	Water	Ar	420-800	n.d.	n.d.
no catalyst	Water	CO$_2$	420-800	n.d.	n.d.
TCA	Water	CO$_2$	420-800	trace	n.d.

Note: All measured using the same instruments, optical set-up except reaction conditions listed in the table. n.d. = Not detectable.

the need for additional sacrificial agents or photosensitizers. Among the MOFs tested, NNU-31-Zn demonstrated outstanding performance, exhibiting the highest formic acid yield rate (26.3 μmol g^{-1} h^{-1}) and remarkable selectivity (ca. 100 %) as shown in Table 3. The advantages of these MOFs include improved visible light absorption, structural stability, effective utilization of photogenerated electrons and holes, increased CO$_2$ adsorption due to porosity, and well-defined structures, providing insights into photocatalytic reaction mechanisms. This research represents a significant advancement, marking the first instance of an MOF system serving as a photocatalyst to accomplish the artificial photosynthetic overall reaction.

4. Conclusion

In summary, the exploration of artificial photosynthesis to convert CO$_2$ into valuable products has witnessed notable progress. Researchers are employing various strategies to enhance the efficiency of overall reactions, specifically in achieving both CO$_2$ reduction and H$_2$O oxidation simultaneously. Although challenges like the chemical inertness of CO$_2$ and slow reaction kinetics persist, recent studies showcase promising approaches.

These collective findings contribute to a better understanding of factors influencing the efficiency of artificial photosynthesis, including structural integrity, active sites, and effective charge transfer. While challenges persist, these studies pave the way for the development of more efficient and sustainable artificial photosynthetic systems. These diverse strategies, ranging from innovative catalyst designs to complex interface control, mark significant progress in the field and provide valuable insights for future research and practical applications in the realm of artificial photosynthesis.

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