Biofuel Research Journal 42 (2024) 2082-2098

Biofuel Research Journal

Journal homepage: www.biofueljournal.com

Review Paper

The role of semi-artificial photosynthetic systems in energy and environmental solutions: a critical review

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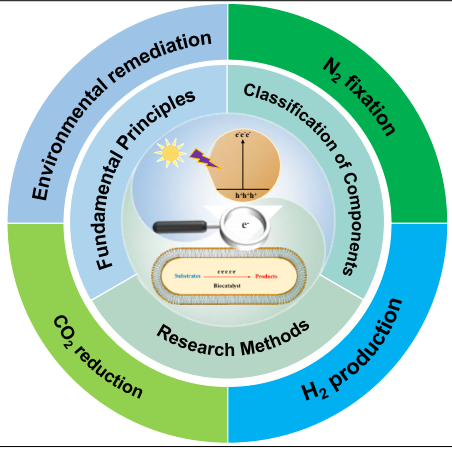
HIGHLIGHTS

- Semi-artificial photosynthetic systems (SAPS) enhance photosynthesis efficiency by synthetic. microorganism integration.
- Combining natural selectivity, SAPS offers superior light harvesting capability.
- SAPS can be used for environmental remediation and renewable energy generation.
- Synthetic materials play a crucial role in photon capture and transfer in SAPS.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 April 2024
Received in revised form 7 May 2024
Accepted 12 May 2024
Published 1 June 2024

Keywords:
Semi-artificial photosynthetic systems
Microorganisms
Photocatalysts
Electron transfer
Energy conversion
Environmental remediation

ABSTRACT

Creatively integrating synthetic materials (semiconductors and electrodes) and microorganisms, the semi-artificial photosynthetic system (SAPS) couples the advantages of natural photosystems (high catalytic reaction selectivity) and artificial photosystems (excellent light-harvesting performance). This combination effectively overcomes the shortcomings of poor selectivity in artificial photosystems, bringing new opportunities for developing photosynthetic systems. It also provides a promising strategy for addressing the current energy crisis and environmental pollution. The design and selection of synthetic materials play a crucial role in this system, aiming to achieve efficient photon capture and electron transfer. This review begins by exploring the fundamental principles of SAPS, emphasizing the integration of materials and microorganisms and the factors that influence their interactions. It provides a critical analysis of the diverse compositional arrangements and systematically elucidates the foundational research methodologies employed in the investigation of SAPS. Grounded in their distinctive redox characteristics, it comprehensively surveys their recent applications in environmental remediation and sustainable energy production over the past years. Finally, reflections on future research are proposed, beginning with the challenges that limit the application of SAPS. Building on previous studies, the present review identifies the factors that limit SAPS and suggests potential avenues for future research. Additionally, this review delves into the environmental and economic policies and practical implications. In conclusion, by critically assessing the existing research landscape, delineating challenges, and charting future research directions, the present review aims to provide valuable insights for researchers and practitioners, guiding efforts toward advancing SAPS for enhanced environmental sustainability and economic feasibility.

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Please cite this article as: Zhao S., Liu Q., Li Y., Feng L., Fu S., Mazarji M., Pan J. The role of semi-artificial photosynthetic systems in energy and environmental solutions: a critical review. Biofuel Research Journal 42 (2024) 2082-2098. DOI: 10.18331/BRJ2024.11.2.3.

Contents

Abbreviations

APS	Artificial photosynthetic systems
AuNPs	Gold nanoparticles
FDH	Formate dehydrogenase
NPS	Natural photosynthetic systems
SAPS	Semi-artificial photosynthetic systems
TA	Transient absorption
TRIR	Time-resolved infrared spectroscopy

1. Introduction

With the acceleration of industrialization and urbanization, coupled with the rapid growth of the global population, energy shortages and environmental pollution have become significant factors limiting the progress of human society (Alkhadra et al., 2022; Asgari et al., 2022). To better protect the environment and alleviate the energy crisis, the search for and development of sustainable, renewable, and clean energy has garnered widespread attention from researchers (Turner, 2022; Ou et al., 2023). In this pursuit, solar energy emerges as one of the most critical renewable and clean energy sources, offering advantages such as abundance, accessibility, and ease of conversion into thermal, electricity, and biomass energy, with tremendous potential to replace traditional energy sources (Wang et al., 2023b; Flores et al., 2024).

As a typical example, natural photosynthetic systems (NPS) based on green plants and algae, among other photosynthetic organisms, provide a blueprint for efficient solar energy utilization. These systems involve the assimilation of CO_2 and H_2O to produce organic matter and release O_2, utilizing the absorption of solar energy by the chloroplasts of photosynthetic organisms (Chen et al., 2023a; Guirguis et al., 2023). As shown in **Figure 1a**, the NPS can typically be divided into two stages based on the requirement of light: light reactions and dark reactions. Additionally, based on the chronological order, it can be further categorized into three processes: light capture, energy transfer, and energy conversion (Zhang and Wang, 2023). In this process, the primary conversion occurs from light energy to chemical energy.

Processes within NPS are independent yet mutually coordinated, occurring at different times and locations both temporally and spatially (Zhang and Wang, 2023). However, photosynthetic organisms primarily rely on natural photosynthetic systems for growth rather than synthesizing metabolites. As a result, secondary processing is necessary to produce valuable chemicals. Moreover, natural photosynthetic systems face several energy conversion bottlenecks that restrict their efficiency. Studies have shown that crops in temperate and tropical regions typically achieve a solar energy conversion efficiency of no more than 1%, while plants and algae exhibit a conversion efficiency of only around 3.2% (Blankenship et al., 2011; Hann et al., 2022). The NPS can only absorb visible light, and their light-capturing performance is relatively poor (Guirguis et al., 2023; Li et al., 2024a). Additionally, these systems reach light saturation at around 20% of standard solar radiation intensity, and higher solar radiation intensity can cause photodamage to photosynthetic organisms, reducing the efficiency of solar energy conversion to biomass (Xiao et al., 2022). Therefore, to overcome the disadvantages of low catalytic efficiency and a narrow range of solar light utilization in NPS, researchers have proposed artificial photosynthetic systems (APS).

The basic principle of APS involves photocatalysts generating photoexcited electrons (e^-) and holes (h^+) under light excitation. Subsequently, these photoexcited e^- and h^+ migrate to the surface of the photocatalyst, driving multi-electron catalytic reactions and facilitating processes like CO_2 reduction (Jiang et al., 2020), H_2 production (Zhou et al., 2023), and nitrogen fixation (Xiong et al., 2023). Additionally, depending on their compositional structures, the APS can be classified into three types: photocatalysis, photoelectrochemistry, and photovoltaic electrochemistry (as illustrated in **Fig. 1b-d**) (Zhang and Wang, 2023; Campbell et al., 2024). Compared to NPS, the APS offers the following advantages, including significantly improved light-capturing performance, with a photoelectric conversion efficiency exceeding 20% (Zhang et al., 2021; Wang et al., 2023c), and a simple structure conducive to modular production and improvement (Yoshino et al., 2022; Zhao et al., 2023a).

However, the APS often relies on high-purity semiconductor materials, which entail complex preparation processes, high costs, and susceptibility to electrolyte decomposition, lacking the self-repair ability observed in biocatalysts in NPS. Furthermore, while APS show promise in producing high-value-added multi-carbon compounds (CO_2→C2+), they often yield mixtures, resulting in drawbacks such as low efficiency and poor selectivity (Gwon et al., 2023; Wang et al., 2023d). Therefore, the feasibility of large-scale commercializing artificial photosynthetic systems is currently limited.

Recognizing the limitations of both NPS and APS, researchers have pioneered the development of semi-artificial photosynthetic systems (SAPS). These systems combine the high catalytic reaction selectivity of NPS with the excellent light-harvesting performance of APS (Xiao et al., 2022; Yang et al., 2023b). This approach achieves a synergistic combination of the strengths of both systems, aiming to address the shortcomings of poor selectivity in APS, and has thus attracted considerable attention. This review delves into the essential elements of SAPS, including photosensitizers, electron donors, and biocatalysts. Finally, the challenges currently faced by material-microorganism SAPS are summarized and discussed. **Table 1** delineates the various aspects covered in this review regarding material-microorganism SAPS, juxtaposed with previously published reviews spanning 2019–2024. The results underscore a significant

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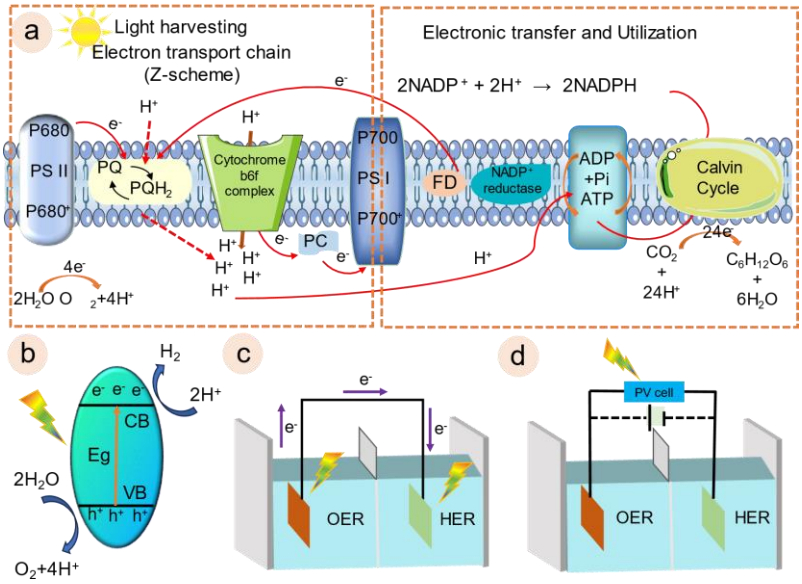

Fig. 1. The principles of NPS **(a)** and APS, including photocatalysis **(b)**, photoelectrochemistry **(c)**, and photovoltaic electrochemistry **(d)** (PS I: Photosystem I; PS II: Photosystem II; PQ: plastoquinone; PC: plastocyanin; FD: ferredoxin; E_g: band gap energy; CB: conduction band; VB: valence band; OER: oxygen evolution reaction; HER: hydrogen evolution reaction).

Table 1.
Comparison of this review with previously published reviews on material- microorganism SAPS (2019–2024).

Material-microorganism Constituted SAPS				Applications of Material-microorganism Constituted SAPS				Reference
Fundamental Principle	Composition Classification	Influencing Factors	Research Methodology	Environmental Remediation	CO_2 reduction	N_2 fixation	H_2 production	
✓	✓	×	×	×	×	×	×	Brown and King, (2020)
✓	✓	×	×	×	✓	×	×	Fang et al. (2020b)
✓	✓	×	✓	×	✓	×	✓	Sahoo et al. (2020)
×	✓	✓	✓	×	✓	×	×	Cestellos-Blanco et al. (2020)
✓	✓	×	✓	✓	✓	✓	✓	Ye et al. (2021)
×	✓	×	✓	×	×	×	×	Cestellos-Blanco et al. (2021)
×	✓	×	✓	×	✓	×	×	Weliwatte and Minteer (2021)
✓	✓	×	✓	×	✓	✓	✓	Xiao et al. (2022)
✓	✓	×	×	×	✓	✓	✓	Shi et al. (2022)
✓	×	×	✓	×	✓	✓	✓	Shen et al. (2023)
✓	✓	✓	✓	×	×	×	×	Yang et al. (2023b)
✓	✓	×	×	×	✓	×	×	Wu et al. (2023b)
✓	✓	✓	×	×	✓	×	✓	Okoro et al. (2023)
✓	✓	✓	✓	✓	✓	✓	✓	**This Review**

✓: Included.
×: Not included

enhancement in the depth and breadth of coverage within this review pertaining to material-microorganism SAPS.

2. Basic overview of semi-artificial photosynthetic systems

The SAPS are innovative technologies that combine non-biological photosensitive materials with biological components to mimic the photosynthetic process in plants. Through artificially designed photosensitive catalysts, light energy is absorbed to enhance the synthetic metabolism of biological catalysts, thereby producing valuable chemicals and fuels. The primary focus of research on SAPS is to achieve efficient conversion of solar energy and product synthesis, reducing dependence on traditional fossil fuels and opening up new possibilities for renewable energy research.

2.1. The fundamental principles and notable advantages of semi-artificial photosynthetic systems

The basic processes of SAPS, akin to NPS and APS, can be divided into three stages: light harvesting, electron transfer, and energy conversion. As shown in **Figure 2**, in SAPS, when photosensitive materials such as semiconductor photocatalysts absorb photons with energy (hν) greater than or equal to their bandgap energy (E_g) under light irradiation, the photosensitizer is excited, leading to the generation of photo-induced e^- and

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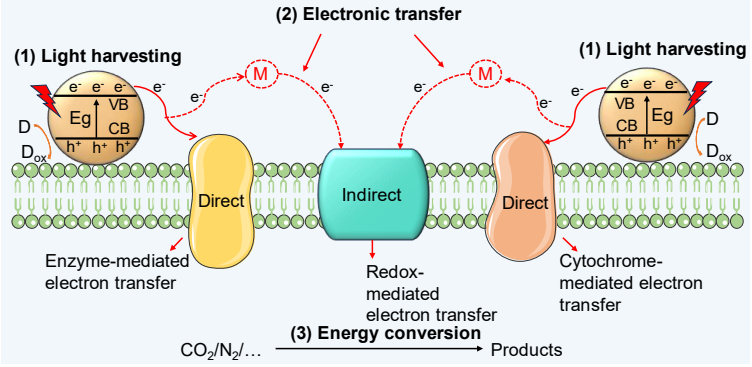

Fig. 2. Schematic diagram illustrating the mechanism of semi-artificial photosynthesis. D: electron donor. M: Redox medium.

h^+ (Cui et al., 2022; Pan et al., 2023). Subsequently, the photo-induced e^- can be transferred to the active sites of biocatalysts (such as whole-cell microorganisms) through both direct transfer pathways (electron transfer mediated by cytochromes or enzymes) and indirect transfer pathways (electron transfer mediated by redox mediators or hydrogen/formate-mediated electron transfer) (Sakimoto et al., 2016; Xiao et al., 2022).

The photo-generated electrons are then transported into the biocatalyst cells, where they participate in the regeneration of bioactive cofactors. This process ultimately provides a continuous energy supply for the synthetic metabolism of the biocatalyst (Gao et al., 2023; Wu et al., 2022a). During this process, artificially synthesized photosensitive materials are responsible for the excitation and transfer of photo-induced e^- and the protection and immobilization of biocatalysts. The biocatalysts, in turn, utilize the photo-induced e^- generated by synthetic materials to accelerate the inherent and complex chemical reactions, converting solar energy into fuels and value-added chemicals (Shi et al., 2022; Okoro et al., 2023).

Compared to NPS, the SAPS offers the advantage of utilizing the solar spectrum more extensively and overcoming certain metabolic limitations. This capability enables SAPS to improve the efficiency of biocatalysts by avoiding competing metabolic steps. Unlike APS, the SAPS can selectively convert solar energy into high-value fuels and value-added chemicals, thereby minimizing the production of unwanted by-products and maximizing solar energy utilization (Chen et al., 2023b; Liu et al., 2023b). The advantages and disadvantages of the three photosynthetic systems, NPS, APS, and SAPS, are summarized in **Table 2**. It is important to note that these outcomes require contributions from synthetic biology and materials science.

2.2. The influencing factors of semi-artificial photosynthetic systems

The performance of SAPS is limited by a variety of factors that collectively impact the energy conversion efficiency and operational stability of the system. Therefore, a comprehensive analysis and discussion of these factors are essential. Overall, these factors mainly include:

(1) The properties of photosensitizers

As depicted in **Figure 3**, one of the most critical factors influencing SAPS is the nature of the photosensitizer. Photosensitizers play a crucial role in SAPS, significantly impacting their functionality. The properties of photosensitizers, such as morphology and E_g, are critical determinants of the overall performance of the SAPS. Studies have shown that photosensitizers generate free radical ions and reactive oxygen species, which can impede bacterial cell activity, potentially causing damage to cell structure and disrupting normal metabolic functions. While concerns exist regarding the biotoxicity of nanomaterials, the potential interactions between nanomaterials and bacterial cells present promising opportunities (Xiong et al., 2022; Okoro et al., 2023).

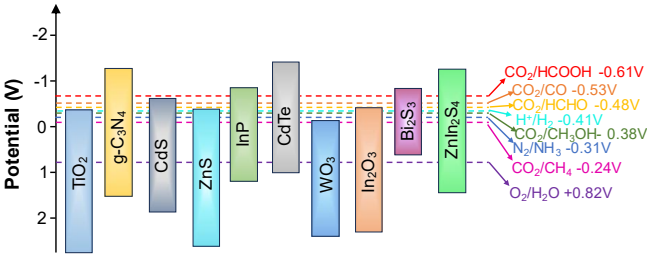

Fig. 3. The band structure of common semiconductors in semi-artificial photosynthesis systems.

Furthermore, existing reports suggest that the ratio of surface area of nanomaterials to bacteria can determine the potential level of bacterial toxicity. Therefore, by rationally designing the shape of nanomaterials, it is possible to reduce the biotoxicity associated with nanomaterials effectively.

Table 2.
The advantages and disadvantages of various photosynthetic systems (Chen et al., 2023b; Liu et al., 2023b).

Type of Photosynthetic System	Advantages	Disadvantages
NPS	High catalytic reaction selectivity, cost-effectiveness, excellent stability	Inefficiency, high system complexity
APS	Excellent light-harvesting performance, superior solar conversion efficiency with a straightforward design, tunability, characterization, straightforward structure and facile modular production	Low product selectivity, high cost, absence of inherent self-healing capability
SAPS	Enhanced light capture performance and increased selectivity, ability to synthesize more sophisticated compounds, self-repair capability	Emphasized the discrepancies in biocompatibility and sensitivity to environmental conditions

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Mutalik et al. (2022) and Okoro et al. (2023) demonstrated that, among various morphologies of CuS (microspheres and nanoplates), spherical CuS nanoparticles exhibited minor microbial toxicity. The type of photosensitizer plays a crucial role in determining the biocompatibility of SAPS. Metal semiconductors are known to have higher levels of biotoxicity, a topic that will be explored further in *Section 3.1*.

The E_g of photosensitizers plays a crucial role in the performance of SAPS as it determines the range of light energy absorption in the system, affecting both the photovoltaic conversion and product synthesis efficiency (Weliwatte and Minteer, 2021; Yang, 2021). The band structures of common semiconductors in SAPS are illustrated in **Figure 4**. Guo et al. (2018) combined highly efficient light-harvesting InP nanoparticles with genetically modified *Saccharomyces cerevisiae*. In this semi-artificial photosynthetic system, InP nanoparticles have a smaller bandgap than CdS nanoparticles, leading to better absorption of solar radiation. This improved absorption enhances the cytoplasmic regeneration of bioactive cofactors. However, this is not always the case. Zhang et al. (2024) developed SAPS by combining twinned $Cd_{0.8}Zn_{0.2}S$ nanoparticles with ordered homojunction and the acetogenic bacterium *Sporomusa ovata*. Despite the higher bandgap energy of $Cd_{0.8}Zn_{0.2}S$ nanoparticles compared to traditional CdS nanoparticles, the presence of twinned homojunction facilitates effective spatial separation of photogenerated electrons and holes. This results in a sevenfold increase in the quantum yield of acetate production when compared to the initial CdS/*Sporomusa ovata* SAPS. Therefore, it is crucial to consider the multifaceted properties of the photosensitizers when making selection decisions.

(2) Selection of Biological Catalysts

As illustrated in **Figure 3**, in addition to material selection and design, the inherent characteristics of microorganisms also play a crucial role in the performance and efficiency of SAPS and can be considered as a determining factor. The emerging field of synthetic biology offers an effective approach to engineering organisms. Wang et al. (2022d) genetically engineered *Escherichia coli* biofilm-forming protein CsgA, which forms starch-like protein curli fibers, by fusing it with semiconductor material-mineralizing short peptides, enabling *in-situ* mineralization of the biofilm. The addition of mineralizing ions to the biofilm culture medium allowed simultaneous mineralization of semiconductor materials during biofilm expression and secretion, resulting in the generation of CdS nanoparticles. Subsequently, exogenous addition of isoleucine dehydrogenase or intracellular expression of formate dehydrogenase was employed to develop SAPS for photocatalytic reduction of trimethylpyruvic acid and photocatalytic reduction of carbon dioxide , respectively. This work utilized synthetic biology approaches in conjunction with nanotechnology to achieve targeted modification of organisms, offering new avenues for bioremediation (Wang et al., 2022d). The genetic manipulation features of *Escherichia coli* can be exploited to engineer a range of biocatalytic pathways. However, the combination of inorganic photocatalytic nanomaterials with bacteria can potentially exert cytotoxic effects, thereby impeding catalytic reaction efficiency.

Wang et al. (2024) developed *Escherichia coli* strains through genetic engineering to overexpress hydrogen peroxide enzymes and electrostatically adsorb nanosensitizers, aiming to enhance and target sonodynamic therapy. These engineered bacteria can colonize and penetrate deeply into tumors, allowing for sustained expression of hydrogen peroxide enzymes to alleviate tumor hypoxia. Additionally, they aid in the accumulation and extended distribution of sensitizers at tumor sites, ultimately leading to effective sonodynamic therapy. Furthermore, the utilization of diverse biocatalysts enables selective product synthesis (such as acetic acid, H_2, methane, and methanol) (Liu et al., 2021; Lin et al., 2023). Thus, biocatalysts play a crucial role in SAPS.

(3) The structural design of semi-artificial photosynthetic systems

The structural design of SAPS is essential for efficient electron transfer and directly affects system stability and light utilization efficiency (as shown in **Fig. 3**). By enabling precise control of photosensitizer distribution, the design maximizes light utilization efficiency (Wang et al., 2022d). In previous studies, bio-inorganic interfaces involving microorganisms and photosensitizers were typically established on cell membrane surfaces. However, Wang et al. (2022d) employed synthetic biology techniques to impart in situ mineralization capabilities to the biofilm. Through *in situ* mineralization of CdS nanoparticles on the biofilm surface, a biofilm with photocatalyst mineralization was successfully achieved. By combining purified isoleucine dehydrogenase or intracellularly expressed formate dehydrogenase, a variety of photocatalytic reaction systems ranging from single enzymes to whole cells could be realized (Wang et al., 2022d).

However, the insulating nature of the phospholipid bilayer of the cell membrane poses a challenge for photogenerated electrons from photosensitizers to interact with intracellular biological electron carriers effectively. To overcome this obstacle, Zhu et al. (2023) developed a method for utilizing photosynthesis to biomineralize gold nanoparticles (AuNPs). In this process, photosynthesis facilitates the reduction of Au^{3+} to Au^0, leading to the preferential accumulation of the formed AuNPs around the thylakoid membrane structures within *Chlorella* cells. The study revealed that photogenerated electrons from AuNPs could efficiently transfer to hydrogenases (Zhu et al., 2023).

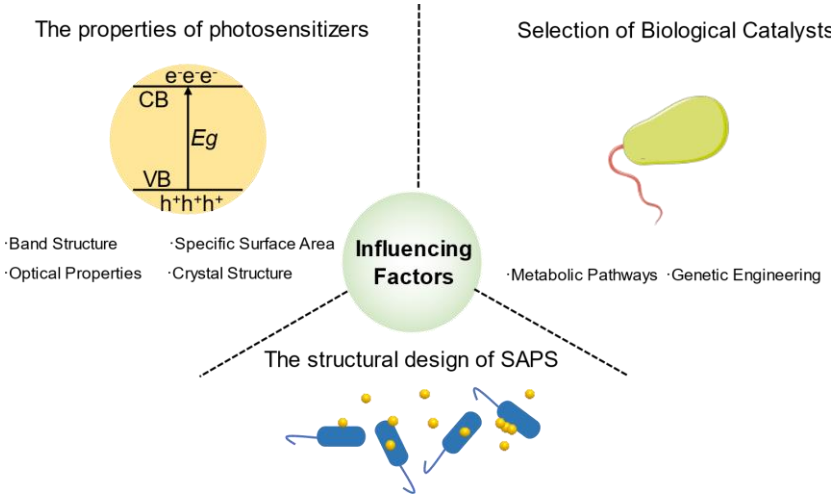

Fig. 4. Factors influencing semi-artificial photosynthetic systems.

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Compared to traditional SAPS, where photosensitizers are located on the cell membrane surface, this significantly reduces the distance for photogenerated electrons to travel, resulting in efficient electron transfer and light utilization. Under monochromatic light illumination, the hydrogen production capacity of *Chlorella* cells is significantly increased (Zhu et al., 2023). Moreover, photosensitizers absorb light energy to produce photogenerated electrons, but the energy the cell utilizes is bioenergy (adenosine triphosphate (ATP) and (NADP)H) (Gao et al., 2023; Zhao et al., 2023b). Therefore, the efficient conversion of photoexcited electrons into biologically usable energy for bacteria is currently an urgent issue to be addressed. Lin et al. (2023) found that the spacious periplasmic space in Gram-negative bacteria offers additional opportunities for biomineralization. In light of this, they demonstrated a non-genetic approach by mineralizing metastable semiconductors to create nanostructured skeletons and establish semiconductor-based periplasmic interfaces, providing a hybrid biological platform for solar-driven biocatalysis. This approach effectively facilitates the compatibility between photosensitizers and microorganisms and serves as a source of electrons for microbial metabolism (Lin et al., 2023).

Furthermore, selecting electron donors and redox mediators plays a crucial role in determining the stability of SAPS. Factors such as the stability and renderability of these components need to be carefully considered. It is important to note that conventional chemical-based electron donors and redox mediators may have issues related to toxicity and environmental impact, which could hinder their long-term sustainability and safety in real-world scenarios (Ye et al., 2022a; Zhang et al., 2023a). Zeng et al. (2023b) developed SAPS by combining cobalt-based photosensitizers with nitrogen-fixing bacteria. This innovative system allows the bacteria to convert nitrogen gas into organic nitrogen, creating a localized anaerobic environment. The organic nitrogen serves as an electron donor, enabling the biohybrid system to fix CO_2. By using nitrogen gas as an electron donor, the system avoids the toxicity of traditional chemical reagents and promotes efficient CO_2 reduction within the nitrogen-fixing bacteria (Zeng et al., 2023a). Cui et al. (2022) developed a tightly coupled SAPS that integrates the metabolic capacity of *Escherichia coli* with the light-harvesting ability of intracellular self-assembled $CdSe_xS_{1-x}$ nanoparticles to enhance hydrogen production. This system eliminates the need for redox mediators for transmembrane electron transfer and additional hole scavengers (Cui et al., 2022). Other external environmental factors, such as variations in the difference in illumination, pH, and temperature, will also impact the overall efficiency of semi-artificial photosynthetic systems (Gamache et al., 2023; Li et al., 2024b). However, these factors are not the primary focus of this review.

3. The composition and classification of semi-artificial photosynthetic systems

The SAPS, which integrates synthetic materials with microorganisms, offers significant advantages. Firstly, they have substantial environmental adaptability, allowing them to thrive under various conditions, such as changes in temperature, pH, and solution salinity. This adaptability expands the potential applications of the SAPS (Yang et al., 2023a; Zhang et al., 2023b). Secondly, microbial cells are multifunctional, containing enzymes and harbor other metabolic pathways and functionalities. This capacity enables them to catalyze a broader range of substrates and synthesize compounds with adjustable complexity (Paoli et al., 2022; Sun et al., 2022). Lastly, microorganisms exhibit excellent self-repair and replication capabilities (Gilbert et al., 2021; McBee et al., 2022). Given these advantages, material-microorganism hybrid systems can be classified into two primary types depending on the synthetic materials employed: semiconductor-microorganism hybrid and electrode-microorganism hybrid systems.

3.1. Semiconductor-microorganism hybrid systems

Semiconductor-microorganism hybrid systems are a unique catalytic system that combines semiconductors with microorganisms to achieve specific chemical production or applications. In these systems, semiconductor photocatalysts absorb light energy, causing e^- to move from the valence band to the conduction band. These excited electrons are then transferred to the interior of microbial cells through cytochromes on the cell surface and extracellular proteins. This process accelerates microbial cell metabolism and energy conversion (Liu et al., 2023a; Lv et al., 2024). Meanwhile, excess h^+ is oxidized by the electron donor to maintain the continuous operation of the systems (common electron donors are illustrated in **Figure 5** (Lee et al., 2018)).

One of the primary scientific challenges in SAPS is the efficient conversion of light energy and the synthesis of products. Current research is predominantly centered on the advancement of nanoscale semiconductor materials that exhibit high biocompatibility and broad spectral response, aiming to enhance electron transfer efficiency at the interfaces between biological and abiotic components (Matsuo et al., 2023; Yu et al., 2023). Sakimoto et al. (2016) capitalized on the abundance of hydroxyl and ether groups in the outer membrane of biocatalysts to synthesize CdS nanoparticles on the outer membrane surface of the acetogenic bacterium *Moorella thermoacetica*. This groundbreaking work achieved direct contact between a photosensitizer and a biocatalyst. When illuminated, photoexcited electrons from CdS, with the assistance of cytochromes and membrane-associated proteins, travel through the cell membrane via the Wood-Ljungdahl pathway, facilitating the conversion of CO_2 to CH_3COOH. The quantum efficiency of light energy conversion to CH_3COOH under low-intensity simulated sunlight reaches 2.4%, comparable to the average observed values over a year for plants and algae (Sakimoto et al., 2016).

To further enhance the responsiveness of the photosensitizer to light and improve light energy conversion efficiency, Lv et al. (2024) introduced defect structures into TiO_2, resulting in increased visible light absorption by TiO_{2-x} nanoparticles. Experimental findings show that the *Escherichia coli*-TiO_{2-x} biohybrid system exhibits significantly higher hydrogen production than the *Escherichia coli*-TiO_2 and pure *Escherichia coli* systems. In three h, the *Escherichia coli*-TiO_{2-x} biohybrid system generated 1.25 mmol of hydrogen, 3.31 times more than the pure *Escherichia coli* system (Lv et al., 2024). To enhance the selectivity of synthesized metabolites in SAPS, Ye et al. (2022b) incorporated NiCu alloy at the interface of *Methanosarcina barkeri* and CdS nanoparticles (**Fig. 6a**). The self-assembled *Methanosarcina barkeri*-NiCu@CdS hybrid system demonstrated methane selectivity close to 100%. The high selectivity is attributed to the vacancy

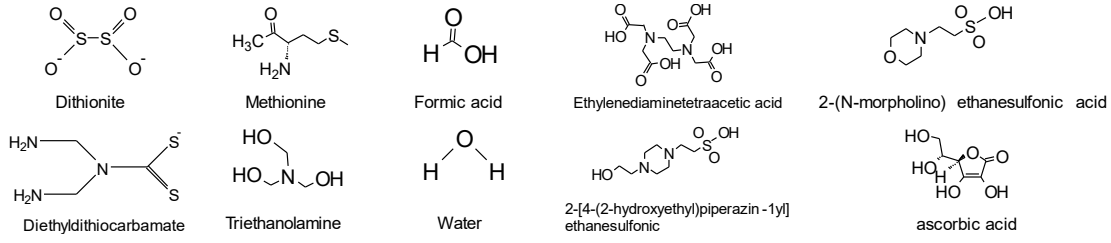

Fig. 5. Electron donors commonly used in semiconductor-microorganism hybrid systems. Adapted with permission from Lee et al. (2018). Copyright @2018 Wiley.

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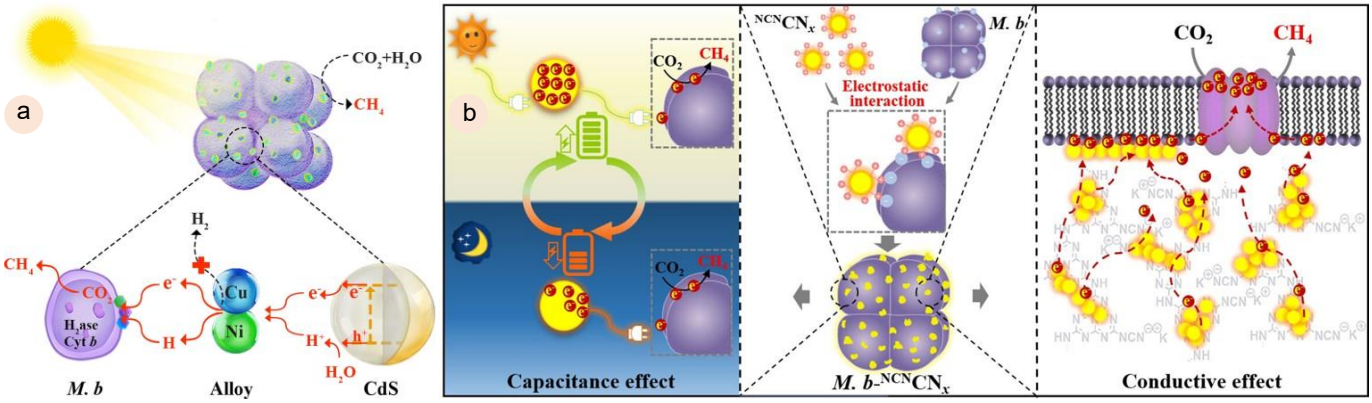

Fig. 6. (a) The schematic diagram illustrating the use of NiCu alloy-assisted semiconductor material- microorganism photosynthesis for methane production. Adapted with permission from Ye et al. (2022b). Copyright 2022 Nature; **(b)** The mechanism diagram illustrating methane production by *Methanosarcina barkeri*-NCNCNx. Adapted with permission from Hu et al. (2022b). Copyright @2022 Wiley.

sites in the Ni-Cu-Cu alloy, which provide hydrogen atoms and photoexcited electrons for *Methanosarcina barkeri*, facilitating methane production through extracellular and intracellular hydrogen cycles. This mechanism effectively suppresses the generation of H_2 byproducts, ultimately enhancing the selectivity of CH_4 as the synthesized metabolite (Ye et al., 2022b).

In addition, the currently developed metal semiconductors include TiO_2 (Bo et al., 2023), InP (Koh et al., 2022), ZnO (Matsuo et al., 2023), CdTe (Gao et al., 2023), and ZnS (Luo et al., 2021). The energy band structures of common metal-based semiconductors and their corresponding reduction potentials are illustrated in **Figure 4** and **Table 3**. Their basic construction principles and composition methods are similar.

Table 3.
Reduction potentials and equations for CO_2, N_2, and H_2 evolution reactions (Fang et al., 2023).

Product	Reduction Reaction	Redox Potential (V)
HCOOH	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.61
CO	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.53
HCHO	$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.48
H_2	$2H^+ + 2e^- \rightarrow H_2$	-0.41
CH_3OH	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38
NH_3	$N_2 + 3H_2 \rightarrow 2NH_3$	-0.31
CH_4	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24

The susceptibility of metal photosensitizers to photocorrosion over time can lead to the degradation of cellular structures in biological entities, disrupting the overall system balance. Thus, the research and advancement of non-metallic photosensitizers are essential (Zhou et al., 2022; Y. Yang et al., 2023; Yu et al., 2022). As shown in **Figure 6b**, Hu et al. (2022b) employed electrostatic self-assembly to create *Methanosarcina barkeri*-$^{NCN}CN_x$ biohybrids by combining cyanamide-functionalized non-metallic, polymeric nitrogen carbon ($^{NCN}CN_x$) with *Methanosarcina barkeri*. This method could improve the quantum yield of CO_2 reduction to CH_4 when exposed to light, achieving quantum yields of 50.3% and a product selectivity of 92.3%. The capacitive and conductive properties of $^{NCN}CN_x$ played a crucial role in storing and redistributing photo-generated electrons at the bio-inorganic solid interface, effectively addressing the challenge of mismatched electron generation and utilization rates. As a result, this approach successfully reduced energy loss and minimized the production of by-products (Hu et al., 2022b).

Of note, in the *Methanosarcina barkeri*-$^{NCN}CN_x$ SAPS, sacrificial reagents play a crucial role as electron donors for microbial photoelectrochemical methane production, ensuring the reactions proceed efficiently and continuously. Given the high cost of traditional chemical sacrificial reagents, there is a significant need to explore new, affordable, and easily accessible alternatives in SAPS. Ye et al. (2022a) developed SAPS using *Methanosarcina barkeri*-carbon dot-functionalized polymer carbon nitride, showcasing the potential of microplastics as sacrificial reagents for microbial photoelectrochemical methane production. This innovative approach efficiently converted thermally pretreated biodegradable microplastics, like polylactic acid, into CH_4 with almost 100% selectivity, facilitated by CO_2 (Ye et al., 2022a).

Currently developed inorganic non-metallic semiconductor catalysts also include black phosphorus (Hu et al., 2022a), carbon dots (Liu et al., 2023d and e), Rose Bengal (dye) (Park et al., 2015), poly(fluorene-co-phenylene) (Gai et al., 2020), marine colloids (Kang et al., 2022) and soluble organic compounds (Huang et al., 2022b). In contrast to traditional semiconductor sensitizers, researchers observed that after microalgae died, the photosynthetic pigments in their cells remained active, while the intracellular ferredoxin-nicotinamide adenine dinucleotide phosphate reductase became inactive. As a result, the deceased microalgae could generate photoelectrons under light, transferred outside the cells to act as sensitizers for electroactive microorganisms. This process collectively drove various anaerobic microbial reduction reactions. This study reveals a photoelectric symbiotic relationship between dead microalgae and electroactive bacteria (Chen et al., 2023b).

Despite the advantages of semiconductor-microorganism hybrid systems, some urgent issues still need to be addressed. Firstly, the long-term stability and reliability of the system require more attention. While existing studies have shown good stability in long-term experiments, it is essential to consider factors such as microbial activity decay, decomposition of conductive materials, and the physicochemical properties of microbial culture media to ensure prolonged stability and reliability (Okoro et al., 2023). Additionally, certain conductive materials may have metal toxicity or susceptibility to photocorrosion, which can potentially harm microorganisms (Huang et al., 2024; Xiang et al., 2024). Secondly, there is a need to improve electron transfer efficiency. Enhancing electron transfer efficiency is a critical challenge in ensuring the high efficiency of electron transfer between microbial metabolism and materials. Some other typical semiconductor-microorganism SAPS are shown in **Table 4**, as outlined.

3.2. Electrode-microorganism hybrid systems

Reconstructing photosynthetic organisms with electrodes enables sustainable semi-artificial bioelectricity generation and fuel production. These systems aim to utilize the metabolic activity of microorganisms and

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Table 4.
Summary of typical material-microorganism SAPS.

Biocatalyst	Synthetic Material	Electron Donor	Electronic Transfer Method	Substrates/ Products	Conversion Efficiency	Reference
Bacillus thuringiensis	CdS	As^{3+} and Sb^{3+}	Extracellular	Cr^{6+} to Cr^{3+}; Se^{4+} to selenium nanoparticles	After 24h, 92.25% of Cr^{6+} was reduced.	Zuo et al. (2021)
Sporomusa ovata	Silicon nanowires	-	Extracellular	CO_2/acetate	A 3.6% solar-to-acetate efficiency realized over 1 week	Su et al. (2020)
Moorella thermoacetica	CdS	Cysteine	Extracellular	CO_2/acetate	2. 44% (with simulated sunlight)	Sakimoto et al (2016)
Sporomusa ovata	InP quantum dots	Cysteine	Intracellular	CO_2/acetate	The production efficiency of acetate was 0.6mmol L^{-1} h^{-1}	Wen et al. (2022)
Methanosarcina barkeri	Carbon dot-functionalized polymeric carbon nitrides	microplastics	Extracellular	CO_2/CH_4	The CH_4 yield was 6.97 mmol g^{-1} at 0.8 mW cm^{-2} light intensity for 24 days, with a selectivity of nearly 100%	Ye et al. (2022a)
Methanosarcina barkeri	NiCu@CdS	H_2	Extracellular	CO_2/CH_4	The selectivity reaches 100%, with a quantum efficiency of 12.41%	Ye et al. (2022b)
Clostridium tyrobutyricum	UiO-66	-	Extracellular	Glucose/butyrate	The yield of butyrate was 11.71 vs 9.36 g L^{-1}.	Zhao et al. (2023b)
Methanosarcina barkeri	CdS	CO	Extracellular	CO/CH_4	The CH_4 yield is 2.89mmol g^{-1} catalyst	Wang et al. (2022a)
Cupriavidus necator	CdS	Cysteine	Extracellular	CO_2/PHB	28mg PHB from CO_2 over 48h.	Xu et al. (2021)
Methanosarcina barkeri	$^{NCN}CN_x$	-	Extracellular	CO_2/CH_4	A quantum yield of 50.3% and a selectivity of 92.3% for CH_4	Hu et al. (2022b)
Paenibacillus azotofixans	Cobalt porphyrin	-	Extracellular	N_2/organic nitrogen compounds, CO_2/HCOOH	The HCOOH yield is 1.41×10^{-14} mol h^{-1} $cell^{-1}$	Zeng et al. (2023a)
Thiobacillus denitrificans	Anthraquinon-e-2-sulfonate	Sodium lactate	Extracellular	NO_3^-/N_2O	The conversion efficiency of N_2O was 96.2%	Chen et al. (2022a)
Azotobacter Chroococcum	PFP	Amino acids	Extracellular	N_2/NH_3	The total photosynthetic efficiency reached 0.83 %.	Zeng et al. (2023b)
Saccharomyces cerevisiae	CdS	Cysteine	Intracellular	H_2O/H_2	The H_2 production rate is 1063.51μmol g^{-1}_{cds} h^{-1}	Liu et al. (2023c)
Escherichia coli	TiO_{2-x}	-	Extracellular	Glucose/H_2	The H_2 yield within 3h was 1.25 mmol.	Lv et al. (2024)

the conductive properties of electrodes for electron transfer, energy production, and various other applications (Fang et al., 2020a; Su et al., 2020). The critical aspect of such systems is to harness the biological metabolic functions of microorganisms in order to facilitate electron transfer with external electrodes, thereby generating electric current or enabling the production and transformation of specific chemicals (Kim et al., 2022; Li et al., 2022). Electrode-microorganism systems exhibit good tunability and operability, typically involving selecting suitable electrode materials during construction.

In their study, as shown in **Figure 7a**, Fang et al. (2020a) utilized polystyrene microspheres and indium tin oxide nanoparticles to create an inverse opal structure (IO-ITO). This electrode was combined with the electroactive bacteria *Geobacter sulfurreducens* to utilize electrons produced during bacterial metabolism for chemical synthesis (reduction of fumarate) and modification of nanomaterials (reduction of graphene oxide). The IO-ITO electrodes had average diameters of 10 μm and 50 nm, demonstrating strong hydrophilicity and a porous structure that facilitated bacterial adhesion and growth. *Geobacter sulfurreducens*, which bear a

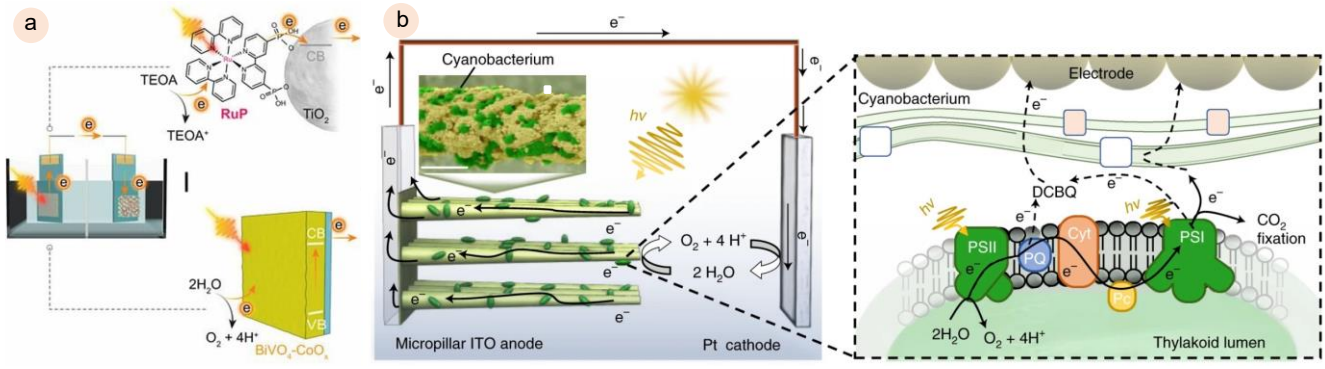

Fig. 7. Schematic diagram of the SAPS composed of IO-ITO and *Geobacter sulfurreducens* **(a)**. Adapted with permission from Fang et al. (2020a). Copyright @2020 PNAS; Illustration of the Bio-photoelectrochemical cell (left) and schematic of the cyanobacteria-anode interface (right) **(b)**. Adapted with permission from Chen et al. (2022b). Copyright @2022 Springer Nature.

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negative charge adhered to and penetrated the IO-ITO electrode when the electrode was positively charged. Bacteria on the electrode surface could thrive by utilizing acetate as a carbon source while simultaneously transferring excess electrons produced in this process directly to the electrode through membrane-bound cytochrome C proteins, thereby reducing energy consumption (Fang et al., 2020a).

Chen et al. (2022b) utilized indium tin oxide nanoparticles in an aerosol jet printing method to create hierarchical electrode structures. They printed microcolumn array electrodes with varying heights and submicron surface features to study energy/electron transfer processes at the bioelectrode interface. The microbranch-containing microcolumn array electrodes connected to cyanobacteria showed significant biocatalyst loading, light utilization efficiency, and high electron flux output, as seen in **Figure 7b**. The most advanced porous structure exhibited nearly double the photocurrent at the same height (Chen et al., 2022b). However, not all microorganisms are closely associated with photoelectrodes. In another study, Liu et al. (2016) developed a Co-P cathode that exhibited resistance to reactive oxygen species and a self-healing CoPi anode catalytic system. The combined effect of these electrodes resulted in the maintenance of foreign cobalt ions at a low concentration, facilitating efficient H_2 production through water decomposition. This capability, in turn, supported *Raistonia eutropha* effectively reduced CO_2 to complex organic molecules (Liu et al., 2016).

While electrode-microorganism-based SAPS present advantages in biocompatibility, sustainability, and applicability over semiconductor-microorganism systems, the need for external electrodes introduces extra energy consumption, leading to higher operational costs (Zhou et al., 2019; Neu et al., 2022). Furthermore, the development and optimization of electrode materials necessitate additional research.

4. Methodological frameworks for semi-artificial photosynthetic systems research

Research methods to investigate the charge transfer mechanisms in SAPS hold significant theoretical and practical importance. Studying these systems encompasses various disciplines, such as biology, physics, and chemistry, and relies heavily on advanced characterization techniques. The techniques typically encompass spectroscopy, proteomics, and transcriptomics, as illustrated in **Figure 8**. Currently, the mechanism of the system can be explored into two parts based on the migration process of photo-induced charges in SAPS (Cestellos-Blanco et al., 2021).

The first entails investigating the excitation transitions and transfer processes of photo-induced e^- through spectroscopy and electrochemistry. This process involves analyzing the absorption of light, electronic level transitions, and the transfer of excited-state e^- from conductive materials to biocatalysts, either directly or indirectly. The main objective is to understand the electron transitions, transfer paths of excited-state e^-, and the efficiency of the transfer process in order to enhance electron transfer efficiency and minimize energy losses. In this section, the characterization techniques employed include time-resolved infrared spectroscopy, transient absorption spectroscopy, fluorescence spectroscopy, microarray scanning, electrochemical imaging, and various electrochemical techniques.

For instance, in their study, Kornienko et al. (2016) investigated the relationship between CO_2 and hydrogenase activity in CdS-*Moorella thermoacetica* using transient absorption (TA) spectroscopy and time-resolved infrared spectroscopy (TRIR) at different time scales (Kornienko et al., 2016). Analyzing TA to understand the lifetime of charge carriers, it was observed that the decay lifetime of electron transfer dynamics is decreased with increased hydrogenase activity. The decay rate was the slowest for the single CdS, faster for the hybrid system without H_2 incubation, and the fastest for the hybrid system with H_2 incubation. These findings suggest the establishment of an electron transfer pathway for CdS-hydrogenase. However, the inhibition of hydrogenase did not result in significantly different lifetimes, indicating the presence of at least two electron uptake mechanisms.

TRIR spectra were utilized to explain the decrease in photosynthetic rates on short-time scales. The absence of vibrational modes characteristic of the catalytic cycle of hydrogenase confirms the dominance of alternative electron transfer mechanisms at shorter time scales, particularly in cases where hydrogenase expression has not increased. Therefore, photoexcited CdS-generated electrons can transfer either through a molecular hydrogen intermediate or charge transfer in cell proteins (Cestellos-Blanco et al., 2021). To gain a deeper understanding of the excitation and transfer processes of photoexcited e^-, Ye et al. (2019) employed scanning electrochemical microscopy (SECM) to monitor the variations in photocurrent within the CdS-*Methanosarcina barkeri* bio-nano hybrid system during light-dark cycling processes. In the absence of irradiation, the observed photocurrent in the bio-nano hybrid system was negligible, implying that it has insulating characteristics (Ye et al., 2019).

However, when irradiated, the photocurrent of the hybrid system was significantly increased, surpassing the photocurrent of *Methanosarcina barkeri* and CdS under light exposure. This result indicates that the hybrid system exhibits higher conductivity under irradiation conditions. This enhanced conductivity can be attributed to membrane-bound electron acceptors in *Methanosarcina barkeri*, which facilitates electron transfer and suppresses the recombination of photoelectrons with photogenerated h^+ (Ye et al., 2019). Nawrocki et al. (2023) employed a combination of TRIR and electrochemical identification techniques to investigate the loss processes in a reaction center-based bio-photoelectrode. The experimental findings suggest that the efficiency of the bio-photoelectrode is negatively affected by high-intensity illumination. This issue led to a reduction in efficiency due to the deactivation of both the reaction and charge separation centers, creating a bottleneck in electron transfer (Nawrocki et al., 2023).

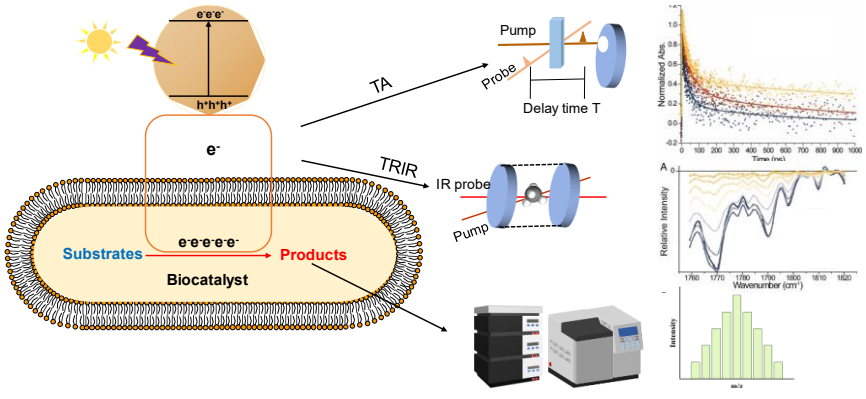

Fig. 8. Research methodologies of semi-artificial photosynthetic systems. Some of the images were adapted with permission from Kornienko et al. (2016). Copyright @2016 PNAS.

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The second part of this section focuses on utilizing proteomics and genomics to investigate the process of utilizing photoexcited e^- by biocatalysts. Various physiological processes within cells exhibit unique gene expressions. By examining genetic material at the molecular level, researchers can differentiate the reaction pathways of SAPS. This analysis is followed by a more detailed exploration of specific cellular metabolic pathways using proteomics and metabolomics techniques. During this process, the excited-state e^- from the catalytic center was reduced, releasing energy used to synthesize organic compounds or other biological metabolic activities. Researchers are particularly interested in understanding how e^- are converted into biochemical energy and the efficiency of this energy conversion (Huang et al., 2022a; Ye et al., 2022a).

This step is crucial in SAPS and serves its ultimate purpose. By studying proteomics and metabolomics, researchers can better understand how specific gene enhancements can activate certain metabolic pathways. Ye et al. (2022b) conducted a study using transcriptomics to investigate the physiological changes of Methanosarcina barkeri in the *Methanosarcina barkeri*-NiCu@CdS biogenic nanohybrid under different irradiation conditions (Ye et al., 2022b).

The analysis revealed a significant upregulation in the transcription levels of energy-converting ferredoxin-dependent hydrogenase, F420-reducing hydrogenase, and membrane-bound methanophenazine-dependent hydrogenase. These findings contribute to understanding *Methanosarcina barkeri* extracellular and intracellular hydrogen cycling. Interestingly, the expression of *Methanosarcina barkeri* unique Methenyltetrahydromethanopterin cyclohydrolase gene was significantly upregulated, which plays a crucial role in CO_2 reduction to CH_4. On the other hand, the expression of membrane-bound F420 dehydrogenase did not show significant changes, indicating that hydrogen atoms are the preferred and primary intermediates for CH_4 production in the biogenic nanohybrid (Ye et al., 2022b). Furthermore, Jin et al. (2021) conducted transcriptomic analysis between *Clostridium autoethanogenum* and CdS nanoparticles, differentiating the direct electron transfer mechanism from the H_2-mediated indirect electron transfer mechanism (Jin et al., 2021). Zhang et al. (2020) used high-sensitivity mass spectrometry techniques to analyze proteomics and metabolomics, elucidating the charge transfer mechanism in photosensitive bacteria (Zhang et al., 2020). The framework for studying the mechanism of SAPS is formed by the mutual influence and interdependence of the two systems mentioned above. A thorough understanding of the working principles of these systems is crucial for rational design and optimization. This understanding can be achieved through comprehensive theoretical and experimental foundations.

5. Applications of semi-artificial photosynthetic systems research

The SAPS, representing an emerging and cutting-edge research direction, has demonstrated significant potential and promising prospects despite its relatively short development history. These versatile systems find applications in diverse fields, including clean energy production, environmental remediation, and innovative biomedical applications. In the energy sector, SAPS introduce new ideas and technological approaches to tackle energy shortages and mitigate carbon emissions.

In the realm of environmental remediation, SAPS exhibit the ability to degrade organic pollutants efficiently and reduce heavy metals, contributing to environmental purification efforts. Moreover, in the biomedical field, the promising potential exists for synthesizing complex drug precursors using SAPS technology. The applications of SAPS can be categorized into four main types: environmental remediation, which harnesses their oxidative capabilities, and clean energy production, which encompasses carbon fixation, nitrogen fixation, and hydrogen production based on their reductive capabilities.

5.1. Environmental remediation

The environmental remediation efforts of SAPS mainly concentrate on two aspects: the degradation of organic pollutants and the treatment of heavy metal ions in wastewater. In addressing organic pollutants, Huang et al. (2019) pioneered the development of a surface-sulfurized *Geobacter sulfurreducens*-CdS biogenic nanohybrid for the photo-driven biological reduction of the typical azo dye methyl orange, achieving a remarkable Turnover Frequency of 1.441 h^{-1} (Huang et al., 2019). Similarly, Wang et al. (2022b) innovatively deposited nano-CdS on the surface of *Clostridium thermocellum* cells, constructing a novel *Clostridium thermocellum*-CdS biotic hybrid. Under thermophilic conditions, the decolorization rate of triphenylmethane dyes is significantly enhanced (Wang et al., 2022b).

In the treatment of heavy metal ions in wastewater, Zuo et al. (2021) introduced a novel *Bacillus thuringiensis*-CdS SAPS and proposed a new methodology. The CdS photocatalyst generated photo-induced e^- upon exposure to light, facilitating the microbial reduction of highly toxic ions (Cr^{6+} and Se^{4+}) in the wastewater. Additionally, low-valence toxic metal ions (As^{3+} and Sb^{3+}) served as electron donors in the SAPS. This approach ensured the proper functioning of the hybrid system and enabled the oxidation and detoxification of these metals (Zuo et al., 2021). As depicted in **Figure 9a**, Fu et al. (2023) achieved highly active and stable biomineralization of electroplating wastewater (Cr^{6+}) by sulfidizing the surface of *Shewanella oneidensis* to generate FeS under weak alkaline conditions (Fu et al., 2023).

While SAPS have demonstrated considerable efficacy in addressing environmental challenges through their reductive capabilities, their potential applications based on oxidizing properties have not received widespread attention. Future research endeavors on SAPS could aim to broaden their scope of applications, including the detoxification of degraded pollutants through processes such as the oxidation of nitrite to nitrate, arsenite to arsenate, and others. Additionally, exploring novel applications for SAPS, such as the selective oxidation of organics into high-value chemicals, presents an exciting avenue for further investigation and innovation in the field. By expanding the horizons of SAPS applications, researchers can unlock new opportunities for environmental remediation and sustainable chemical synthesis, contributing to the advancement of green technologies and addressing pressing environmental challenges.

5.2. CO_2 reduction

Currently, the primary challenge lies in overcoming the energy barriers for CO_2 reduction and achieving the coupling of C-C bonds in APS. However, specialized carbon-fixing bacteria have emerged as valuable assets in effectively utilizing CO_2 under mild reaction conditions, offering high selectivity and diversity. Integrating synthetic materials has significantly improved the energy conversion efficiency of biocatalysts (Edwardes Moore et al., 2021; Liu et al., 2023a). As a result, SAPS have made notable strides in converting CO_2 into a wide range of organic compounds. In a pioneering study on the synthesis of C1 carbon products, Ye et al. (2019) conducted groundbreaking research demonstrating that a methanogenic bacterium, *Methanosarcina barkeri*-semiconductor bioheterotroph, could efficiently reduce CO_2 to CH_4. The bacterium produced CH_4 at a rate of 0.19 μmol h^{-1}, demonstrating a quantum efficiency of 0.34% (Ye et al., 2019). To enhance the production rate and quantum yield of CH_4, Ye et al. (2022a) conducted a study integrating NiCu alloy into the interface of *Methanosarcina barkeri* and CdS nanoparticles. This integration resulted in the creation of the *Methanosarcina barkeri*-NiCu@CdS hybridized system, which exhibited a remarkable selectivity of CH_4 close to 100% and a high quantum yield of 12.41% (Ye et al., 2022a).

In addition to CH_4, another prominent C1 product is HCOOH. Lam et al. (2023) employed formate dehydrogenase (FDH) immobilized on the surface of TiO_2 to create the FDH/TiO_2 biogenic nanohybrid. The study observed that HCOOH generated within 24h reached 1.16 $mmol_{HCOOH}\ g_{TiO2}^{-1}$. To further enhance the fluidity and photocatalytic capability of FDH/TiO_2 in the liquid phase, the FDH/TiO_2 hybrid was immobilized on hollow glass microspheres. This process involved the hydrolysis of cellulose using cellulase, which was coupled with the reaction of FDH/TiO_2. Using CO_2 and cellulose as substrates, the study found that 0.36 mmol of HCOOH was produced per square meter of irradiated area after 24h (Lam et al., 2023).

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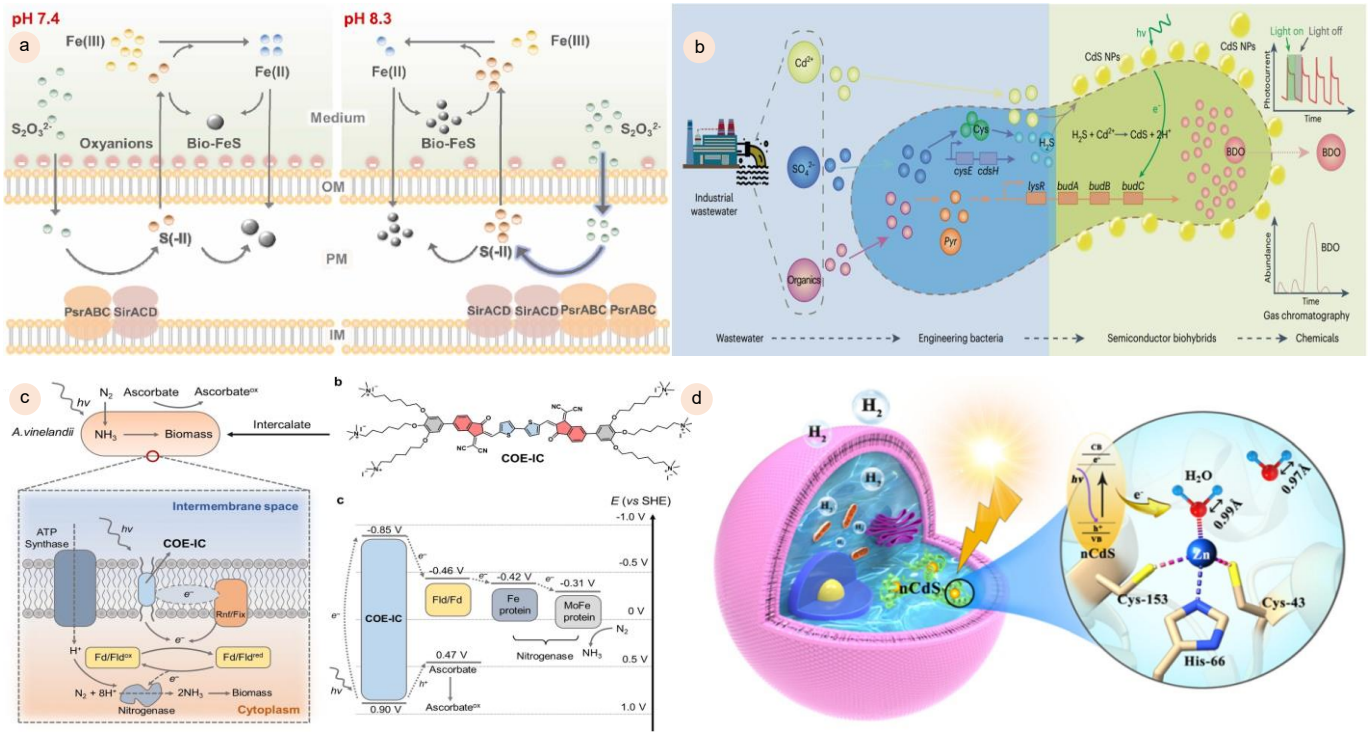

Fig. 9. (a) The synthesis of FeS under different pH conditions and its mineralization of Cr^{6+}. Adapted with permission from Fu et al. (2023). Copyright @2023 Elsevier; **(b)** Semiconductor material-bacteria hybrid photodriven biomanufacturing based on wastewater. Adapted with permission from Pi et al. (2023). Copyright @2023 Nature; **(c)** Mechanism diagram of COE-IC/*Azotobacter vinelandii* hybrid reducing N_2 to NH_3. Adapted with permission from Chen et al. (2023a) Copyright @2023 Wiley; **(d)** Diagram of the mechanism of hydrogen production by nCdS nanoparticles-*Saccharomyces cerevisiae*. Adapted with permission from Liu et al. (2023b). Copyright @2022 Royal Society of Chemistry.

In the synthesis of C2 carbon products, the essential product is CH_3COOH (Wang et al., 2022c). As illustrated in **Figure 9b**, Pi et al. (2023) reported a novel SAPS where the non-photosynthetic acetate-producing bacterium *Sporomusa ovata* was grown on a photocatalyst. This photocatalyst consisted of layered La and Rh co-doped strontium titanate ($SrTiO_3$: La, Rh) and molybdenum-doped bismuth vanadate ($BiVO_4$: Mo). This innovative hybrid system exhibited the adequate utilization of sunlight, CO_2, and H_2O to produce acetate (CH_3COO^-) and O_2. The observed conversion efficiency of solar-to-acetate was 0.7% under ambient conditions (25℃ and 1 kPa). The photocatalyst played a crucial role in oxidizing H_2O to O_2 and providing electrons and H_2 to *Sporomusa ovata*, enabling the selective synthesis of CH_3COO^- from CO_2 (Pi et al., 2023).

In synthesizing various carbon products, a notable example in recent years involves the large-scale production of heterocycles and light energy-driven 2,3-butanediol from actual industrial wastewater by Pi et al. (2023). This approach was reported to achieve light energy-driven conversion of pollutants to high-value chemicals and establish a photovoltaic biomanufacturing route. The conversion of organic pollutants to 2,3-butanediol occurred in a 5-L photoreactor with yields reaching up to 13 g L^{-1}. The established hybrid photodriven biofabrication route was found to be more cost-effective in terms of greenhouse gas emissions and product production costs compared to conventional petroleum-based and sugar-based biofermentation chemicals through life cycle analysis. This approach opens new possibilities for cleaner production, reduced carbon emissions, enhanced resource utilization, and the advancement of a circular economy. In addition, various other types of carbon products have emerged in recent years, such as oxalic acid (Guo et al., 2018), 2-oxobutyrate (Yu et al., 2022), and polyhydroxybutyrate (Wang et al., 2023a), among others. Overall, future research should focus on modifying photosensitive molecules and carbon sequestration pathways in microbial cells. This modification can be done with synthetic biology and metabolic engineering to produce light-driven, high-value carbon chemical production.

5.3. N_2 fixation

Nitrogen fixation refers to the process in SAPS where specialized nitrogen-fixing bacteria or large enzymes are driven to convert N_2 into NH_3 or other nitrogen compounds. In this context, Chen et al. (2023a) employed a conjugated oligoelectrolyte with insertable bacterial cell membranes in co-culture with the bacterium *Azotobacter vinelandii* to create bio-nanohybrids named COE-IC/*Azotobacter vinelandii* (as shown in **Fig. 9c**). This innovative system successfully achieved 20.6 nmol.mL^{-1} increased in photosynthetic nitrogen fixation and a 2.4-fold increase in ammonia production compared to the control group. Moreover, COE-IC contains an electron acceptor-donor-acceptor-type conjugated center, enabling efficient visible light absorption and exhibiting a high molar extinction coefficient (Chen et al., 2023a).

Zeng et al. (2023b) conducted a study where they combined the conductive polymer PFP with the non-photosynthetic nitrogen-fixing bacterium *Azotobacter chroococcum*. This combination resulted in a significant enhancement of nitrogenase activity within the bacteria. PFP, known for its good conductivity, facilitated electron transfer to the bacteria, thereby promoting their nitrogen metabolism. The enhancement of nitrogenase activity was demonstrated through various tests, showing increased H_2, NH_4^+-N, and L-amino acid production by 260%, 37%, 44%, and 47%, respectively (Zeng et al., 2023b).

Nitrogen-fixing bacteria have been found to produce more than just nitrogen compounds. For instance, in a study conducted by Zeng et al. (2023a), a molecular compound called Cobalt(II) 5,10,15,20-tetra(4′-N, N, N-trimethylanilinium) porphyrin (Co-TTAP) was incorporated into *Paenibacillus azotofixans* bacteria. This incorporation resulted in the

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creation of a light-driven microbial hybrid system. In this system, the bacteria can convert N_2 into reductive organic nitrogen compounds, which serve as electron donors for CO_2 photochemical reduction. Additionally, the bacteria create a local anaerobic environment, facilitating the photochemical reduction of CO_2 to HCOOH by Co-TTAP. This innovative approach enables the simultaneous coupling of CO_2 photocatalytic reduction and N_2 fixation (Zeng et al., 2023a).

5.4. H_2 production

Hydrogen proves to be an efficient and environmentally friendly renewable clean energy source, with enormous potential to replace fossil fuels to meet the growing energy demands of modern society (Lu et al., 2023; Wu et al., 2023). As depicted in **Figure 9d**, Liu et al. (2023b) developed SAPS by synthesizing cadmium sulfide nanocrystals within *Saccharomyces cerevisiae* yeast cells. Although the yeast cells themselves do not possess photosynthetic characteristics and hydrogen production capabilities, the combination of cadmium sulfide nanocrystals and the yeast-secreted alcohol dehydrogenase resulted in the production of H_2 with a high yield of up to 1063.51 μmol g^{-1}_{nCdS} h^{-1} (Liu et al., 2023b).

Polymer dots (Pdots) are biocompatible photocatalysts that remain stable at pH=7 and have a modifiable surface morphology. In a study by Pavliuk et al. (2022). The adsorption of hydrogenase on Pdots formed a stable biohybrid assembly, allowing sustained H_2 production for several days. Cui et al. (2022) utilized an industrial *Escherichia coli* strain as a host to self-assemble $CdSe_xS_{1-x}$ as an intracellular semiconductor. This approach eliminated the need for externally added artificial nanoparticles. The resulting SAPS facilitated fermentative H_2 production without requiring redox mediators for transmembrane electron transfer or additional electron donors. Under intermittent light conditions, the H_2 production rate was 2.9 times higher than pure bacteria, with an apparent quantum yield of 27.6%. This substantial H_2 production increase can be attributed to the efficient utilization of photo-induced electrons, which enhanced the hydrogen-producing NADH generation and the formate utilization. Additionally, the hybrid system maintained a self-sustained lower level of reactive oxygen species (Cui et al., 2022).

While SAPS show promise in environmental remediation and clean energy production, there is a need for further technological innovation to enhance energy conversion efficiency, system stability, material biocompatibility, and cost-effectiveness.

6. Challenges and future research directions

The SAPS offer valuable insights and methods for producing clean energy and environmental remediation. One of the main challenges in these systems is achieving efficient electron transfer between synthetic materials and biological catalysts while maintaining the activity and stability of the biological catalysts. However, as a relatively new field, current research is still in its early stages and faces various challenges. These include ensuring the stability and sustainability of the system, improving the efficiency of solar-to-chemical energy conversion, enhancing the compatibility of interfaces between synthetic materials and biological catalysts, and addressing the engineering and practical aspects of SAPS (Shi et al., 2022). To tackle these challenges, researchers have proposed several modification strategies. These include surface modification of synthetic materials or biological catalysts, designing nanostructures, selecting synthetic materials with good biocompatibility, genetic engineering, and improving and optimizing the bio-non-bio interfaces, as mentioned earlier (Yang et al., 2023b).

The SAPS are at the forefront of life sciences, materials science, and physics research. These systems are constantly being improved and refined through ongoing technological advancements and interdisciplinary collaborations. They provide innovative solutions to global challenges, like energy crises and environmental protection. As a result, this research direction holds excellent potential for development and carries significant research value. Therefore, building upon previous research, future studies should focus on the following aspects:

(1) To achieve a broader range of chemical reactions and products, exploring various combinations of synthetic materials and biocatalysts is recommended. Currently, commonly used synthetic materials include semiconductor photocatalysts like CdS, InP, and TiO_2. Additionally, enzymes and bacteria related to processes like carbon fixation, nitrogen fixation, and H_2 production are commonly used as biocatalysts. However, many of these catalysts remain unmodified and unaltered. Therefore, synthetic materials can be modified through doping, defect engineering, and the construction of heterojunction interfaces. New types of synthetic materials, such as quantum dots, metal-organic frameworks, covalent organic frameworks, Mxenes-based two-dimensional materials, single atoms, and multi-atomic alloys, can also be applied. By utilizing synthetic biology and genetic engineering methods, biocatalysts can be redesigned to enhance their catalytic efficiency, specificity, and adaptation to the environment of SAPS. With the development of SAPS, it is gradually transitioning from a proof-of-concept stage to practical application. Therefore, future research should be aimed at assessing the stability and recyclability of SAPS.

(2) To thoroughly investigate the electron transfer mechanisms between synthetic materials and biocatalysts, and the factors influencing the processes of electron excitation, transition, and utilization. These factors encompass the energy band structure of synthetic materials, the interface properties of the bio-non-bio interface, the selection of electron donors, and the electron transfer chain. The understanding of electron transfer and utilization mechanisms in SAPS is limited. This issue necessitates the development of more advanced characterization and monitoring methods to observe and evaluate the operational status and performance indicators of these systems in real time. Such advancements are crucial for developing higher-performance SAPS.

(3) To explore new applications of SAPS in fields such as energy production and storage, environmental restoration and protection, pharmaceuticals, agricultural fertilizers, and food production, further expanding their socioeconomic impact. Additionally, it is crucial to consider practical production factors, such as the cost of synthetic materials, system repeatability, technical simplicity, and the efficiency of converting solar energy to synthetic chemicals. To expedite the industrial and commercial applications of SAPS, it is recommended that technological innovations be focused on and thorough cost-benefit analyses conducted.

7. Policy and practical implications

As an emerging technological field, the SAPS aims to integrate the respective advantages of NPS and APS techniques to convert from simple small-molecule substances such as CO_2, N_2, and H_2O to high-value macromolecular products (Shen et al., 2023). This transformation can yield high-value products such as food, medicine, and fuels, providing a novel avenue for efficiently utilizing solar energy. However, with the rapid development of this field, policymakers, researchers, and the public should all pay attention to its policy implications and practical impacts.

(1) Environmental impact

From an environmental perspective, applying SAPS promises to positively impact global environmental issues. Firstly, this technology can efficiently harness solar energy to convert greenhouse gases such as CO_2 into high-value products, thereby aiding in reducing greenhouse gas emissions and mitigating global climate change. Secondly, applying SAPS can also reduce reliance on fossil fuels, lowering energy consumption and environmental pollution. This reduction is crucial for protecting the ecological environment and achieving the dual carbon goals of peak CO_2 emissions and carbon neutrality.

However, not all environmental impacts of SAPS are positive. The widespread adoption and application of new technologies may also introduce new environmental challenges. For instance, the production

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process of SAPS may generate novel waste and pollutants (such as synthetic materials and biological residues), adversely affecting the ecological environment. Moreover, the extensive application of new technologies may lead to alterations in ecosystems and a reduction in biodiversity. Therefore, policymakers and researchers must closely monitor the potential environmental risks associated with advancing SAPS and implement corresponding measures to prevent and address these risks. Alongside technological advancements, establishing comprehensive ecological monitoring systems and formulating scientifically grounded environmental protection policies are essential to ensure that the application of SAPS maximizes their environmental benefits while minimizing their potential negative impacts (Yang et al., 2023b).

(2) Economic impact

From an economic perspective, SAPS offers significant development opportunities across multiple industries. Firstly, its high solar energy conversion capability enables the environmentally friendly and cost-effective production of high-value products, such as food, medicine, and fuels. This technology reduces production costs, enhances efficiency, and drives the transformation and upgrading of related industries. Secondly, the research and application of SAPS will also give rise to new industry chains and employment opportunities, further promoting economic prosperity and development (Ye et al., 2021).

However, it is worth noting that the research and application of SAPS also face several economic challenges. For example, the widespread adoption and application of new technologies require significant financial investment, which may be burdensome for some developing countries and regions. Additionally, the proliferation of new technologies may lead to declining traditional industries and exacerbating unemployment issues. Therefore, policymakers need to consider the impact of these economic factors while promoting the development of SAPS and take appropriate policy measures to mitigate potential risks and challenges. These measures include formulating supportive fiscal policies, establishing research and innovation funds to promote technology research and application, providing technology transfer and training support, and facilitating industrial restructuring and job transition. This step ensures that the development of SAPS not only promotes economic growth but also achieves the goals of sustainable development.

In summary, the research and application of SAPS have significant implications for both the economy and the environment. Policymakers need to thoroughly consider these impacts when formulating relevant policies and take appropriate measures to balance economic and environmental interests, thus promoting the healthy development of SAPS. Additionally, researchers should continue to delve into this technology to enhance its efficiency and stability, reduce costs and risks, and make more significant contributions to the sustainable development of human society.

8. Conclusions

This review comprehensively examines various aspects of material-microorganism SAPS. Firstly, starting from the basic principles of SAPS, it elaborates on the advantages and disadvantages of material-microorganism SAPS and systematically analyzes their influencing factors. Subsequently, based on different synthetic materials, material-microorganism SAPS are categorized into semiconductor-microorganism hybrid systems and electrode-microorganism hybrid systems, with in-depth discussions on each system's development and pros and cons. The review systematically discusses the research methods and application scope of material-microorganism SAPS and analyzes the challenges they currently face and potential future directions. Finally, the importance of environmental and economic policies for the development of SAPS is emphasized, calling for joint efforts from policymakers and researchers to promote their sustainable development and widespread application, thus contributing to the construction of a sustainable society.

Acknowledgments

This review was supported by the National Natural Science Foundation of China (No. 22278435), the Strategic Cooperation Technology Projects of CNPC and CUPB (No. ZLZX2020-04), and Carbon Neutrality Research Institute Fund (No.20220202, No.20230102).

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Please cite this article as: Zhao S., Liu Q., Li Y., Feng L., Fu S., Mazarji M., Pan J. The role of semi-artificial photosynthetic systems in energy and environmental solutions: a critical review. Biofuel Research Journal 42 (2024) 2082-2098. DOI: 10.18331/BRJ2024.11.2.3.

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Please cite this article as: Zhao S., Liu Q., Li Y., Feng L., Fu S., Mazarji M., Pan J. The role of semi-artificial photosynthetic systems in energy and environmental solutions: a critical review. Biofuel Research Journal 42 (2024) 2082-2098. DOI: 10.18331/BRJ2024.11.2.3.

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Please cite this article as: Zhao S., Liu Q., Li Y., Feng L., Fu S., Mazarji M., Pan J. The role of semi-artificial photosynthetic systems in energy and environmental solutions: a critical review. Biofuel Research Journal 42 (2024) 2082-2098. DOI: 10.18331/BRJ2024.11.2.3.