Abiotic–Biological Hybrid Systems for CO₂ Conversion to Value-Added Chemicals and Fuels

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Abstract

Abiotic–biological hybrid systems that combine the advantages of abiotic catalysis and biotransformation for the conversion of carbon dioxide (CO₂) to value-added chemicals and fuels have emerged as an appealing way to address the global energy and environmental crisis caused by increased CO₂ emission. We illustrate the recent progress in this field. Here, we first review the natural CO₂ fixation pathways for an in-depth understanding of the biological CO₂ transformation strategy and why a sustainable feed of reducing power is important. Second, we review the recent progress in the construction of abiotic–biological hybrid systems for CO₂ transformation from two aspects: (i) microbial electrosynthesis systems that utilize electricity to support whole-cell biological CO₂ conversion to products of interest and (ii) photosynthetic semiconductor biohybrid systems that integrate semiconductor nanomaterials with CO₂-fixing microorganisms to harness solar energy for biological CO₂ transformation. Lastly, we discuss potential approaches for further improvement of abiotic–biological hybrid systems.

Keywords CO₂ conversion · Abiotic–biological hybrid systems · Microbial electrosynthesis systems · Photosynthetic semiconductor biohybrid systems

Introduction

In recent years, excessive greenhouse gas emission resulting from fierce fossil fuel combustion has caused a global environmental crisis [1, 2]. Data from the Climate Resilience Handbook (2018) suggested that disasters, such as rising sea levels, mountain fires, heat waves, and drought caused by global warming, have brought about \$31 billion losses to the world [3]. Among the greenhouse gases belched out to the atmosphere, carbon dioxide (CO₂) accounts for 68% of the total emissions, making it the main cause of climate warming [4]. CO₂ levels in the atmosphere increase by 33.4 Gt per year, and the concentration is currently about 400

parts per million (ppm) [5, 6]. If this situation continues to worsen, annual CO₂ emissions will reach up to 66.8 Gt by 2050 and the concentration of CO₂ in the atmosphere will be 500 ppm [7]. Such concentrations will cause the rise of the average global temperature by 2 °C compared with that in 1900, resulting in the disintegration of the West Antarctic Ice Sheet and rise in sea level by 4–6 m [8]. Therefore, reducing the concentration of CO₂ in the atmosphere has become a matter of global concern.

Scientists have employed various methods to capture and store CO₂ from the atmosphere, such as physical adsorption, chemical absorption, and geological isolation of CO₂ [9–12]. However, the “carbon capture and storage” strategy has many drawbacks, including difficulty in finding sufficient underground storage space, leakage risk, long-term liability issues, and public acceptance [13]. From this perspective, CO₂ capture and conversion to value-added chemicals and fuels has emerged as an appealing way to address the global energy and environmental crisis caused by increasing CO₂ emission [14]. To date, several approaches have been developed to convert CO₂ to other carbon compounds; these methods include photocatalysis [15, 16], electrocatalysis [17, 18], chemical reforming [19–21], and biological method [22].

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Abiotic catalytic materials with high catalytic efficiency of CO₂ reduction and product specificity were intensively studied and developed in the last decades [23–25]. Abiotic catalysts for CO₂ reduction have remarkable energy conversion efficiency and short reaction period. However, abiotic catalysts cannot easily achieve long carbon chain-forming reactions due to energetic penalties associated with the re-activation of desorbed reactants [26]. In particular, the biological transformation of CO₂ has a unique advantage in the conversion of CO₂ to long carbon chain products. In biosynthetic pathways, CO₂ is first reduced and transformed to acyl-CoA via CO₂ fixation pathways. Subsequently, acyl-CoA, as an activated form of carbon compound, functions as a building block to produce long carbon chain compounds through various synthetic pathways. Various long carbon chain products such as isoprene, limonene, and farnesene have been synthesized from CO₂ via biological methods [27]. Moreover, these enzymes in biosynthetic pathways have specific conformations that drive CO₂ reduction intermediates toward specific multi-carbon products. The biological transformation of CO₂ has received tremendous attention due to its mild reaction condition, product selectivity, and low substrate activation barriers [1].

Biological CO₂ fixation is mainly achieved by CO₂ fixation pathways, which consist of dozens of enzymes that all function in concert to continually and selectively transform CO₂ to organic carbon compounds [28]. Over thousands of years of evolution, these enzymes feature specific conformation that can stabilize CO₂ reduction intermediates, thereby significantly reducing the energetic barrier for activation of CO₂ and enabling steric hindrances that guide reactions toward specific products. For the reduction of CO₂, a certain amount of reducing equivalents is required by biological systems [29]. In natural carbon-fixing organisms, the reducing equivalents are derived from natural photosystems or reducing substances such as hydrogen, CO, and Fe(II) minerals. However, the inherent low efficiency and vulnerability of photosystems and inconvenient availability and unsustainability of the reducing substances make natural carbon-fixing organisms unlikely to be a long-term solution for the transformation of CO₂. At the same time, abiotic photocatalysts and electrocatalysts demonstrate promising capability of energizing microbial growth and biological synthesis of specific products by providing reducing power [30, 31]. Reducing power is provided by intracellular electron carriers, such as NAD(P)H and FMN_{red}, which usually play the role of cofactors of many reductive enzymes to facilitate enzymatic reduction reactions and transfer electrons to the oxidized state of substrates. Upon the occurrence of reduction reactions, these molecules are oxidized to their corresponding oxidized forms, i.e., NAD(P)⁺ and FMN_{ox}. These abiotic materials have excellent stability, catalytic efficiency, and scale-up feasibility, and they can be engineered

to adapt to any specific environment. Such materials have benefitted from decades of intense research and technological development. For these reasons, coupling photochemical/electrochemical materials with CO₂-fixing organisms offers an appealing solution for the sustainable transformation of CO₂ to value-added chemicals and fuels.

In this review, we lay out the recent progress in abiotic–biological hybrid systems for CO₂ reduction on two fronts: (i) microbial electrosynthesis systems (MESs) that utilize electricity to support whole-cell biological CO₂ conversion to products of interests and (ii) photosynthetic semiconductor biohybrid systems (PSBSs) that integrate semiconductor nanomaterials with CO₂-fixing microorganisms to harness solar energy for biological CO₂ transformation. The details of abiotic–biological hybrid systems are summarized in Table 1. Before diving fully into abiotic–biological hybrid systems, we first introduce the natural CO₂ fixation pathways for an in-depth understanding of the biological CO₂ transformation strategy and why sustainable provision of reducing power is important. Lastly, we illustrate potential approaches for further improvement of abiotic–biological hybrid systems.

Natural CO₂ Fixation Pathways

Natural CO₂ fixation dominated by plants and autotrophic microorganisms is the basis of life activities and biological processes on earth. To date, six forms of natural CO₂ fixation pathways have been discovered [32]. Thorough investigations revealed specific functional enzymes and genes that play critical roles in each pathway. These pathways include the reductive pentose pathway (Calvin–Benson–Bassham [CBB] pathway), reductive tricarboxylic acid cycle, reductive acetyl-CoA pathway (Wood–Ljungdahl pathway), 3-hydroxypropionate pathway, 3-hydroxypropionate/4-hydroxybutyrate cycle, and dicarboxylate/4-hydroxybutyrate cycle (Fig. 1).

The reductive pentose pathway, found in plants and reported in 1954, is the first CO₂ fixation pathway discovered in nature [33]. Since then, this pathway has been confirmed to exist in a variety of prokaryotic and eukaryotic organisms, and sufficient research on it has been conducted [34–36]. The CBB pathway includes three stages, namely carboxylation, reduction and regeneration, which involve 13 important enzymes. Ribulose-1,5-bisphosphate carboxylase oxygenase (RubisCO) is the core enzyme in this pathway to catalyze CO₂ fixation [37–39]. This pathway requires two NAD(P)H molecules for the fixation of one CO₂ molecule.

Reductive TCA cycle was found in *Chlorobium limicola* [40] in 1966. This pathway starts from citric acid, which cleaves into acetyl-CoA and oxaloacetate [41]. Acetyl-CoA is further converted to oxaloacetate and eventually returns

Table 1 A summary of abiotic–biological hybrid system for CO₂ reduction

Source of reducing power	Microorganism	Material	Electron transport mode	Product	Yield	References
Electricity	<i>Sporomusa ovata</i>	Unpolished graphite electrode	Direct contact	Acetate	0.15 mmol/ day	[54]
	<i>Ralstonia eutropha</i>	In cathode and Pt anode	Formate-mediated	Isobutanol	169.2 mg/(L day)	[58]
				3 MB	114 mg/(L day)	
	<i>Ralstonia eutropha</i>	Co-P alloy cathode and CoPi anode	H ₂ -mediated	PHB	117 mg/(L day)	[59]
Light				Isopropanol	97.3 mg/(L day)	[61]
	<i>Ralstonia eutropha</i>	Pt anode and Carbon cloth anode	Neutral red-mediated	PHB	97 mg/(L day)	
	<i>Sporomusa ovata</i>	Silicon nanowire array	Direct contact	Acetate	750 mg/(L day)	[63]
	<i>Ralstonia eutropha</i>	Core–shell quantum dots	Direct contact	PHB	100 mg/(g DW day)	[69]
				2,3-Butanediol	10 mg/(g DW day)	
				Isopropanol	2 mg/(g DW day)	
				Ethylene	1 mg/(g DW day)	
	<i>Ralstonia eutropha</i>	g-C ₃ N ₄ -catalase	H ₂ -mediated	PHB	20.51 mg/(L day)	[71]
	<i>Moorella thermoacetica</i>	CdS	Direct contact	Acetate	0.3 mmol/ day	[64]
	<i>Moorella thermoacetica</i>	Gold nanoclusters	Direct contact	Acetate	0.86 mmol/(g day)	[67]
	<i>Moorella thermoacetica</i>	π -Conjugated organic semiconductor	Direct contact	Acetate	0.23 mmol/day	[68]

to the beginning of the cycle in the form of citric acid. Pyruvate: ferredoxin oxidoreductase is the core enzyme [42]. This pathway requires two NAD(P)H molecules for the fixation of one CO₂ molecule.

The reductive acetyl-CoA pathway mainly exists in autotrophic acetogenic and methanogenic bacteria with two branches carried out simultaneously [43–45]. In brief, two CO₂ molecules are catalyzed into one formate molecule and one CO molecule, respectively, and then flow to the methyl and carboxyl branches. After further catalysis, acetyl-CoA is formed. In this process, carbon monoxide dehydrogenase, which reduces CO₂ to CO, and acetyl-CoA synthase, which produces acetyl-CoA, are the core enzymes [46]. This pathway requires two NAD(P)H molecules for the fixation of one CO₂ molecule.

The 3-hydroxypropionate pathway was originally discovered in *Chloroflexus aurantiacus* [47, 48]. The pathway begins with acetyl-CoA undergoing multiple catalytic conversions to propionyl-CoA. In the second stage, propionyl-CoA is converted to methylmalonyl-CoA. The third stage is the conversion of methylmalonyl-CoA to succinic acid. In the last stage, succinic acid is converted into acetyl-CoA and glyoxylic acid, which is further converted into propionyl-CoA to complete the entire cycle. Malonyl-CoA reductase is considered the most critical enzyme in the pathway [49]. This pathway requires 1.67 NAD(P)H molecules for the fixation of one CO₂ molecule.

The 3-hydroxypropionate/4-hydroxybutyrate cycle was first found in cell extracts of *Metallosphaera sedula* [50].

The whole pathway can be briefly divided into two phases. In the first phase, one acetyl-CoA and two bicarbonate molecules are converted into one succinyl-CoA. In the second phase, one succinic acid is converted into two acetyl-CoA molecules. The pathway begins with ATP-dependent acetyl-CoA carboxylase carboxylating acetyl-CoA to malonyl-CoA, which is also a core enzyme in the entire pathway [51]. This pathway requires two NAD(P)H molecules for the fixation of one CO₂ molecule.

The dicarboxylate/4-hydroxybutyrate cycle has been acknowledged as the sixth CO₂ fixation pathway in recent years [52]. Similar to the 3-hydroxypropionate/4-hydroxybutyrate cycle pathway, it also has two stages, but the only difference between these two cycles is the method of generating succinyl-CoA [53]. In the first stage, acetyl-CoA and two inorganic substances are converted into succinyl-CoA; in the second stage, succinyl-CoA is regenerated into acetyl-CoA. Pyruvate synthase and pyruvate carboxylase involved in the first stage are the key enzymes of this pathway [51]. This pathway requires two NAD(P)H molecules for the fixation of one CO₂ molecule.

In summary, all of these CO₂ fixation pathways require not only a carbon substrate but also a certain amount of reducing equivalents (NADH, NADPH, and/or reduced ferredoxin). Abiotic photocatalysts and electrocatalysts with excellent stability and catalytic efficiency are the prominent materials to sustainably energize microbial growth and biological synthesis of specific products by providing reducing power from light and electricity.

Fig. 1 Six natural CO₂ fixation pathways. **a** Reductive pentose pathway [34], **b** 3-hydroxypropionate pathway [44], **c** Reductive acetyl-CoA pathway [40], **d** Reductive TCA cycle [36], **e** Dicarboxylate/4-hydroxybutyrate cycle [48], **f** 3-hydroxypropionate/4-hydroxybutyrate cycle [46]

Microbial Electrosynthesis Systems for CO₂ Conversion

Electricity is the key product of most green energy conversion technologies such as photovoltaic cells and wind and water turbines. The use of electricity to support biological CO₂ conversion relies on the discovery of electrotrophic bacteria that can take up reducing power from nanostructured electrodes. Nevin et al. [54] first found that *Sporomusa ovata*, a kind of acetogen, can obtain electrons directly from graphite cathode and reduce CO₂ to acetate without H₂ as reducing power. On the basis of their findings, they developed a microbial electrosynthesis system (MES) for the conversion of CO₂ into acetate. In this system, they designed an H-type double-chamber electrosynthesis device where bacteria are cultivated in the cathode chamber (Fig. 2a). When −0.4 V voltage is applied to the system, acetate and a small amount of 2-oxobutyrates are sustainably produced from CO₂. After reaction for 6 days, 1.0 mM acetate is synthesized by this system. The

calculated Faradic efficiency of this system demonstrated that the reducing power transferred into the cells mostly turns to organic acid products instead of biomass. Subsequently, they further discovered a series of acetogenic microorganisms that can directly take up electrons from electrodes [55], including *Sporomusa sphaeroides*, *Clostridium ljungdahlii*, and *Moorella thermoacetica*. The discovery expanded the range of microorganisms capable of directly taking up electrons from electrodes and provided multiple options for optimizing MESs. Faraghiparapari and Zengler [56] investigated the effect of operating temperature on the performance of MES using *M. thermoacetica*, *Moorella thermoautotrophica*, and *Thermoanaerobacter kivui* as the CO₂ reduction bacteria. Their work showed that increasing operating temperature can improve the product recovery of the MES, and the optimal operating temperature is close to the optimal temperature for microbial growth. For *M. thermoautotrophica*, acetate production was 11.6 mM/(m² days).

To expand MES to non-electrophilic microorganisms, strategies using electron shuttles for the transfer of reducing

Fig. 2 Schematic illustration of mediator-based MESs. **a** H-cell device for supplying cathode biofilms of *S. ovata* electrons derived from water [54]. **b** The integrated electromicrobial device for CO₂

reduction to higher alcohols [58]. **c** Water splitting–biosynthetic system with Co-P alloy cathode and CoPi anode [59]. **d** The FDH-assisted MES to reduce CO₂ for the synthesis of PHB [61]

power from electrodes into bacteria have been proposed to catalyze CO₂ reduction at low energy barriers [57]. Li et al. [58] employed formic acid as an electron shuttle and designed an integrated electromicrobial system to synthesize liquid fuel (Fig. 2b). In this system, In and Pt electrodes were used as the cathode and anode, respectively. Upon applying 4 V voltage between them, formic acid was produced from CO₂ and H₂O via electrocatalysis and transferred into the engineered *Ralstonia eutropha* strain for the biosynthesis of isobutanol and 3-methyl-1-butanol (3 MB). In *R. eutropha*, formic acid is first converted into NADH and CO₂ by formate dehydrogenase, and NADH and CO₂ are transferred to the Calvin–Benson–Bassham cycle for further conversion into isobutanol or 3 MB via a series of metabolic pathways. Therefore, in this work, formic acid was not only a good electron mediator but also a CO₂ carrier that facilitated the transfer of CO₂ into bacteria for the synthesis of desired products. Upon applying voltage to the system, inhibited microbial growth was also observed, which was caused by reactive oxygen and nitrogen generated at the Pt anode. To address this problem, they creatively used a porous ceramic cup to encase the anode, thereby isolating these toxic matters from microorganisms. Finally, this hybrid system accumulated about 846 mg/L isobutanol and 570 mg/L 3 MB after 120 h of reaction.

Liu et al. [59] developed a hybrid water splitting–biosynthetic system for the bioconversion of CO₂ to poly(3-hydroxybutyrate) (PHB) or liquid fusel alcohols. In this system, a cobalt-phosphorus (Co-P) alloy cathode and CoPi anode were used to catalyze the water-splitting reaction (Fig. 2c). With applied voltage of 2.0 V, H₂ was produced at the cathode and used as electron shuttles transferring into *R. eutropha* for CO₂ reduction and synthesis of desired products. Co-P alloy and CoPi electrodes with excellent biocompatibility and robustness have exhibited prominent advantages for the MES. The results of thermodynamic analysis demonstrated that reactive oxygen species (ROS) accumulation is very low at the electrodes. Moreover, the electrode pair possesses self-healing ability, maintaining a very low level of toxic Co²⁺ cations in electrolyte, which is beneficial for the growth of *R. eutropha* and CO₂ reduction. The whole system can accumulate 701 mg/L PHB or 584 mg/L isopropanol with high energy efficiency in 6 days and fix 180 g of CO₂ with one kilowatt-hour consumed.

The low solubility of H₂ is one of the limiting factors in H₂-based MESs, which may limit the flux of reducing power and affect the efficiency of CO₂ fixation. To address this issue, Rodrigues et al. [60] reported an MES using a biocompatible perfluorocarbon nanoemulsion to enhance the solubility of H₂. In their system, Co-P alloy and CoPi served as electrode pairs for the water-splitting reaction; acetogen *S. ovata* was responsible for CO₂ biotransformation. On the basis of the transfer kinetics analysis, the nanoemulsion can

encapsulate hydrogen molecules and adsorb to the surface of microorganisms, increasing mass transfer efficiency by three times. In this system, 6.4 g/L (107 mM) was produced in 4 days with near 100% faradaic efficiency.

Recently, a novel MES was developed by Song et al. [61], with neutral red as an electron carrier for the conversion of CO₂ to PHB. Given the low redox potential of neutral red, the system can operate at an applied voltage of 0.6 V, which reduces environmental stress on microorganisms and saves power significantly. The entire system was divided into a cathode chamber and an anode chamber, separated by a proton exchange membrane in the middle (Fig. 2d). A platinum mesh electrode was used as the anode and placed in PBS in the anode chamber. The carbon cloth electrode served as the cathode and was in the minimal inorganic medium of the cathode chamber together with the engineered *R. eutropha* strain. For the double-chamber design, protons would pass through the exchange membrane, but toxic substances produced by the electrolysis would be isolated at the anode. In the cathode compartment, part of the electrons carried by neutral red were directly transferred into the microbial cells for the supply of reducing power, and another portion was given to formate dehydrogenase for CO₂ reduction to formate, which also entered the cellular CBB pathway for the biosynthesis of PHB. Furthermore, the CO₂ fixation capacity of *R. eutropha* was improved by genetic engineering. Finally, 485 mg/L PHB was obtained after 120 h of reaction.

There are two modes of electron transfer between electrodes and microbes in microbial electrosynthesis. One is direct electron transfer between electrophilic microorganisms (e.g., *S. ovata*, *C. ljungdahlii*, and *M. thermoacetica*) and electrodes; the other is the indirect electron transfer to non-electrophilic microorganisms (e.g., *R. eutropha*) mediated by electron shuttles (e.g., formate, hydrogen, and NR). In-depth research should be conducted on electron shuttles to improve electron transfer efficiency, reduce applied voltage, decrease cytotoxicity, and explore highly efficient electronic carriers.

Photosynthetic Semiconductor Biohybrid Systems for CO₂ Conversion

Semiconductor-based light absorption devices have a relatively high efficiency in capturing and converting solar energy. Photosynthetic biohybrid systems are constructed upon coupling with biocatalysis, and they demonstrate excellent performance for the photoconversion of CO₂ into organic carbon compounds. The PSBS combines high-efficiency semiconductor light harvesters and whole-cell biocatalysts. Upon illumination, the excited semiconductor material generates electrons, which are directly or indirectly transferred to cells and supply intracellular reducing power

that reduces CO₂ to synthesize higher alcohols and biopolymers. The systems overcome the limitations of natural and artificial photosynthesis, as well as provide an opportunity to investigate their respective functionality [62].

Liu et al. [63] developed a photosynthetic biohybrid system that coupled a silicon nanowire array and anaerobic bacterium, *S. ovata*, to capture solar energy and reduce CO₂ to acetate. In this process, the photo-induced electrons can be directly used as the reducing equivalent by microorganisms for acetate production. Moreover, the produced acetate can be used as a substrate and further converted to various value-added chemicals by introducing another engineered bacterial strain. This system can stably run for more than 200 h with low overpotential under aerobic conditions, and it demonstrates a faradaic efficiency of up to 90%. The intermediate acetate was reported to reach 6 g/L and was converted to 198 mg/L n-butanol or 490 mg/L PHB.

Sakimoto et al. [64] went a further step and developed a tightly integrated photosynthetic biohybrid system via bioprecipitation of cadmium sulfide (CdS) nanoparticles on the surface of *M. thermoacetica*, thereby enabling the photosynthesis of acetate from CO₂. On illumination of this system, the CdS nanoparticles absorbed a photon, $h\nu$, and produced an electron–hole pair. The electron was transferred onto the bacterial cytomembrane, which was used by the bacteria to generate reducing equivalents. The generated reducing equivalents were subsequently passed on to the Wood–Ljungdahl pathway (WLP) for the production of acetic acid from CO₂ (Fig. 3a). Given that most reducing equivalents flow toward the product (around 90% of the electrons were directed to acetate), the quantum yield of this biohybrid is extremely high at $85\% \pm 12\%$. When cultured under low-intensity simulated sunlight (air mass 1.5 global spectrum, 2 W/m²) with a light–dark cycle to mimic day–night cycles, this biohybrid system can achieve a peak quantum yield of $2.44\% \pm 0.62\%$, which is higher by one order of magnitude compared to the year-long averages

determined for plants and algae (range = ~0.2% to 1.6%). This system enables non-photosynthetic microorganisms to possess photosynthetic capacity. Kornienko et al. [65] used transient absorption spectroscopy and time-resolved infrared spectroscopy to monitor the hybrid system and concluded that electron transfer between catalyst and microorganism exists in two different ways: the long-term pathway and the short-term pathway. For the long-term pathway, a highly efficient electron transfer to hydrogenase (H₂ase) occurs, and H₂ is produced as an intermediate that dominates at long time-scales (24 h). For the short-term pathway, a direct energy-transducing enzymatic pathway is responsible for acetic acid production at short time scales (3 h). Zhang et al. [66] further studied the global protein and metabolite changes of this system. Their work confirmed the metabolic processes in the biocatalytic part and proposed an energy conservation method for system optimization.

Further research on this *M. thermoacetica*–CdS hybrid system found that CdS nanoparticles attached on the cell membrane would peel off during the reaction, which would lead to artificial photosynthesis system failure. To solve this problem, Zhang et al. [67] developed a new photosynthetic biohybrid system (Fig. 3b), in which gold nanoclusters (AuNCs), an efficient light absorber, were translocated into *M. thermoacetica*, allowing for a much faster photogenerated electron transfer and improved biocompatibility than before. The intracellular AuNCs can directly transfer the reducing power into the WLP, shorten the mass transfer path, and reduce energy consumption. Moreover, AuNCs are an excellent ROS eliminator that avoid damage to microorganisms during photofermentation. After a week of photosynthesis, the accumulated acetic acid production was found to be 6.01 mmol/g, showing an increase of around 80% compared with the *M. thermoacetica*–CdS hybrid system.

To further improve the energy conversion efficiency of photosynthetic biohybrid systems, Gai et al. [68] coated two π -conjugated organic semiconductor materials,

Fig. 3 Schematic illustration of photosynthetic biohybrid systems. **a** *M. thermoacetica*–CdS hybrid artificial photosynthetic system [64]. **b** *M. thermoacetica*/AuNC hybrid artificial photosynthetic system [67].

c Schematic of hybrid photosynthesis with g-C₃N₄-catalase and *R. eutropha* producing PHB from CO₂ [71]

perylene diimide derivative (PDI) and poly(fluorene-co-phenylene) (PFP), onto the surface of *M. thermoacetica* to harness and convert light energy in this system. The PFP/PDI layer could form a p-n heterojunction, thereby affording high light capture ability, low hole/electron recombination efficiency, and excellent biocompatibility. The cationic side chains of the organic semiconductors can insert into cell membranes and ensure the direct transfer of light-excited electrons into *M. thermoacetica*. The solar-to-chemical efficiency of the organic semiconductor–bacteria biohybrid system was reported to be 1.6%. The accumulation of acetic acid was close to 0.7 mM in 3 days.

By directly anchoring photosensitizer onto a specific enzyme function in different strains of *Azotobacter vinelandii* and *Cupriavidus necator*, Ding et al. [69] developed novel photosynthetic biohybrid systems that enable the photosynthesis of different biofuels and chemicals using CO₂, water, and N₂ as substrates. In this work, they designed seven different core–shell quantum dots (QDs) with excitations ranging from ultraviolet to near-infrared energies. Upon translocation into bacteria and illumination by light, these QDs can use their zinc-rich shell facets for affinity attachment to MoFe nitrogenase in *A. vinelandii* or hydrogenases in *C. necator*, efficiently driving the production of biofuels (such as 2,3-butanediol, isopropanol, C₁₁–C₁₅ methyl ketones, and hydrogen) and chemicals (e.g., ethylene, formic acid, ammonia, and polyhydroxybutyrate). With optimal condition, this light-driven microbial nanofactory can obtain maximum achievable quantum efficiency of 16%–20%, which is much higher than that of natural photosynthesis.

Non-photosynthetic and non-electrophilic microorganisms can also participate in hybrid systems for photosynthesis. Xu et al. [70] found that adding g-C₃N₄ to fructose medium can increase the PHB accumulation of *R. eutropha* under illumination by light. Considering that *R. eutropha* is a non-electrophilic bacteria, photogenerated electrons cannot directly transmit into cells. An electron carrier might be present to assist the metabolism of microorganisms and PHB synthesis. The following year, Tremblay et al. [71] figured out how the reducing power transmits and develops the g-C₃N₄-catalase-*R. eutropha* photosynthetic biohybrid system. This system includes a photocatalytic part dominated by g-C₃N₄-catalase and biological carbon fixation part dominated by *R. eutropha*. Under illumination by light, g-C₃N₄ catalyst can generate H₂O₂, which is subsequently decomposed by catalase into hydrogen (Fig. 3c). The generated H₂, as an excellent reducing power carrier, transfers into bacteria and participates in CO₂ fixation in *R. eutropha*. The photocatalytic part demonstrates outstanding solar conversion efficiency, and H₂ production is 55.72 mmol/h. PHB production was reported to be 41.02 mg/L after 48 h with the initial microbe OD₆₀₀ of 0.05.

Different semiconductor photocatalysts can form various contact modes with microorganisms and directly or indirectly transfer photogenerated electrons to the biocatalyst upon photoexcitation. Thus, exploration of electron transport mechanisms and development of high-performance photocatalysts are highly required for the construction of photosynthetic semiconductor biological hybrid systems. Extensive attention should be paid to synthesize photocatalysts with excellent performance to improve the efficiency of light capture and conversion, stability, and biocompatibility.

Perspective

Conversion of CO₂ to value-added chemicals and fuels has recently acquired tremendous interests, because they can possibly alleviate the global energy and environmental crisis caused by increased CO₂ emission. Abiotic–biological hybrid systems combining the advantages of abiotic catalysis and biotransformation have emerged as a promising method to convert CO₂ into value-added chemicals and fuels. In these systems, abiotic photocatalysts and electrocatalysts sustainably provide reducing power from light and electricity to microbes, and these microorganisms obtain the reducing equivalents via direct or shuttle-mediated routes for CO₂ reduction and product accumulation. Various MESs and PSBSs with excellent catalytic performance have been developed, and they demonstrate prominent capability for the conversion of CO₂ into value-added chemicals and fuels. The similarities between MES and PSBS include the following: (i) the photo-semiconductor material attached on the surfaces of microorganisms can be regarded as many nanoscale batteries, which, similar to the anodes in microbial electrosynthesis, inject photogenerated electrons into cells; (ii) both the electrode and photo-semiconductor materials provide reducing power to the cells for CO₂ reduction and chemical biosynthesis. The difference between MES and PSBS is that PSBS is a hybrid system that integrates abiotic material and microbial cells, while MES is composed of a set of bio-electrochemical devices.

A number of critical issues should be addressed in abiotic–biological hybrid systems. The mechanism of electron transfer between abiotic and biological interfaces remains unclear, and matching electron flux and microbial turnover frequency precisely is rather difficult. Scale-up feasibility and long-term stability of hybrid systems need to be improved.

Two perspectives can be considered to design an efficient abiotic–biological hybrid system for CO₂ conversion. The first is to select a high-performance abiotic material with features of high energy conversion and transfer efficiency, good stability and robustness, biocompatibility, and low cytotoxicity. The other is to optimize the metabolic flow of

microorganisms and enhance the capacity of CO₂ reduction via synthetic biology approaches.

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