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Review

Biophotoelectrochemistry for renewable energy and environmental applications

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SUMMARY

Biophotoelectrochemistry (BPEC) is an interdisciplinary research field and combines bioelectrochemistry and photoelectrochemistry through the utilization of the catalytic abilities of biomachineries and light harvesters to accomplish the production of energy or chemicals driven by solar energy. The BPEC process may act as a new approach for sustainable green chemistry and waste minimization. This review provides the state-of-the-art introduction of BPEC basics and systems, with a focus on light harvesters and biocatalysts, configurations, photoelectron transfer mechanisms, and the potential applications in energy and environment. Several examples of BPEC applications are discussed including H_2 production, CO_2 reduction, chemical synthesis, pollution control, and biogeochemical cycle of elements. The challenges about BPEC systems are identified and potential solutions are proposed. The review aims to encourage further research of BPEC toward development of practical BPEC systems for energy and environmental applications.

INTRODUCTION

Biophotoelectrochemistry (BPEC) takes advantages of the catalytic abilities of biomachineries (e.g., enzymes and microorganisms) to realize the specific solar-to-power/chemical conversion with the aid of light harvesters. Compared with the traditional bioelectrochemistry that relies on the synergistic interaction between biocatalysts and electrodes (Schmid et al., 2001; de Carvalho, 2011) and the photoelectrochemistry that utilizes solar light as an electron pump to realize redox conversion (Nozik, 1978; Tryk et al., 2000), BPEC is an emerging and interdisciplinary research field at the convergence of bioelectrochemistry and photoelectrochemistry and focuses on the interactions among biocatalysts, light harvesters, and electrodes. In addition to "biophotoelectrochemistry" (Jeuken, 2017; Hartmann et al., 2018), other terms such as photo-assisted biosynthesis, biophotovoltaics, and photobiocatalysis have also been used in the literature (Gupta et al., 2021; Schmermund et al., 2019; McCormick et al., 2015). BEPC has experienced great development in the past decade and evolved from the natural photosynthesis (e.g., photosynthetic proteins and photoautotrophs) to the semiartificial photosynthesis (Fang et al., 2020). BEPC via semiartificial photosynthesis integrates the natural biomachineries and functional components of artificial systems (Cestellos-Blanco et al., 2020). In 2008, Marsolek et al. (Marsolek et al., 2008) demonstrated an innovative BEPC system via coupling photocatalysis with microbial biodegradation in a photocatalytic circulating-bed biofilm reactor. In 2012, Lu et al. discovered that the metabolisms and growth of nonphototrophic bacteria could be stimulated by solar light through photocatalysis of semiconducting minerals, attributed to a new type of microbial energy generating metabolisms in BPEC systems, named electrolithoautotrophs (Ishii et al., 2015). Others have also reported the nonphototrophic microorganisms (e.g., *Shewanella oneidensis* MR-1 and *Sporomusa ovata*) as biocatalysts in BPEC systems (Wang et al., 2013; Liu et al., 2015). The pioneering efforts by Sakimoto et al. (2016a), for the first time, realized the self-precipitated clusters of smaller nanoparticles (<10 nm) on the surface of live whole-cell biocatalysts for CO_2 fixation and introduced the concept of biohybrids. Subsequently, BPEC via semiartificial photosynthesis becomes an attractive research topic.

Biocatalysts play a key role in BPEC systems and can either work alone as natural light harvesters or be integrated with light harvesters. Based on the versatile functions of biocatalysts, there are four different types of BPEC systems: (1) Type I: biocatalysts like photoenzymes or photoautotrophic organisms act as the natural light harvesters to trigger the ATP and NADPH regeneration for the redox reaction or electricity production *in vivo* (Figure 1A); (2) Type II: biocatalysts (e.g., heterotrophic microorganisms) conduct the intracellular oxidation of substrates and then the produced electrons are transferred outside the cells

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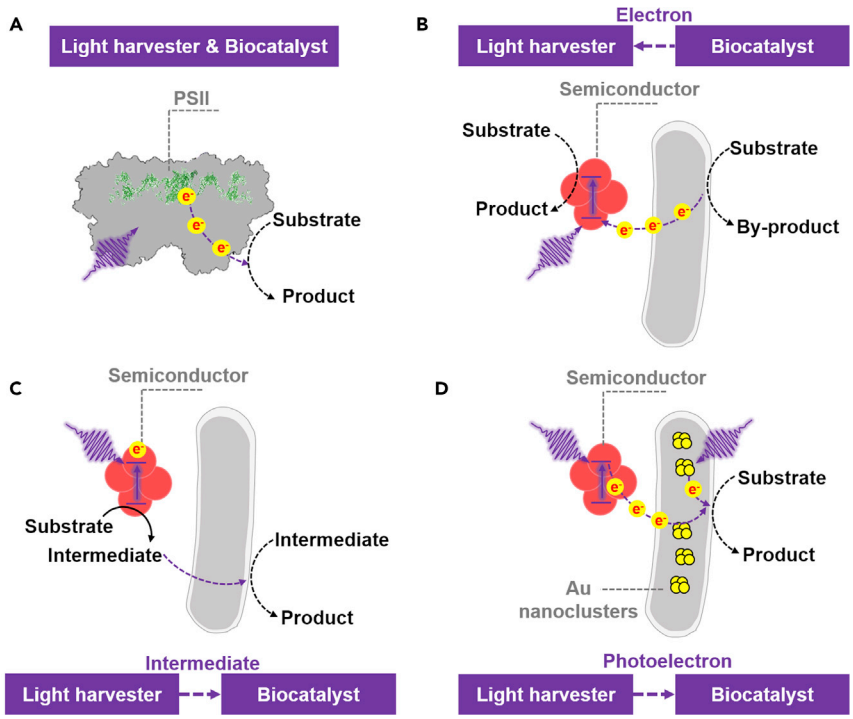

Figure 1. Four types of BPEC systems.

and injected into the energy band of light harvesters to enhance the photocatalytic reaction (Figure 1B); (3) Type III: light harvesters collect solar energy for the photocatalytic degradation of substrates, and then, the produced intermediates are further biodegraded by biocatalysts (Figure 1C); and (4) Type IV: light harvesters adsorb solar energy to drive the generation of photoelectrons, which are then utilized by biocatalysts for the solar-to-chemical conversion (Figure 1D). The performances and metabolic mechanisms of type I, II, and III BPEC systems for energy production and pollution control have been systematically studied (Zhang and Reisner, 2020; Xiao et al., 2019; Yu et al., 2020; Li et al., 2021b; Ding et al., 2021), and type IV system is being studied as an emerging subject.

Type IV BPEC system integrates the board-band light efficiencies of light harvesters for photoelectron (reducing equivalent) generation with the highly specific biocatalytic power of biomachineries for substrate conversion. This phenomenon is widely discovered in both natural and artificial environments. The former can occur in mineral coating (Lu et al., 2012), flooded soils (Chen et al., 2019c, 2019d), and offshore areas (Liu et al., 2020) for the specific biogeochemical redox processes due to the widespread existence of electrotrophs (e.g., *Acidithiobacillus ferrooxidans*, *Alcaligenes faecalis*, *S. oneidensis* and *Geobacter metallireducens*) and natural semiconductor minerals (e.g., rutile [TiO_2], sphalerite [ZnS], and goethite [FeOOH]). The latter holds a great potential for pollutant control and energy production in engineered systems like biological wastewater treatment. Involving BPEC may effectively overcome the limitation of traditional biological treatment through promoting electron donors under light irradiation. Herein, this review focuses on the state-of-the-art of type IV BPEC system (as "BPEC system" below), including configurations, components, photoelectron transfer mechanisms, and the potential applications in energy and environment such as H_2 production, CO_2 reduction, chemical synthesis, pollution control, and the possible biogeochemical cycle of elements.

THE BPEC SYSTEMS

Typical configurations of BPEC systems

BPEC systems can be constructed through integrating light harvesters and biocatalysts within a photoelectrochemical cell (PEC) (Figure 2A). To do so, natural or artificial light harvesters are immobilized on the fluorine-doped tin oxide (FTO) or indium tin oxides (ITO) glass that act as a photoanode in the PEC (more details are in the following sections); this can effectively decrease the energy demand for the production of H^+ and photoelectrons by using solar energy as an energy source (Papageorgiou, 2004). The excited

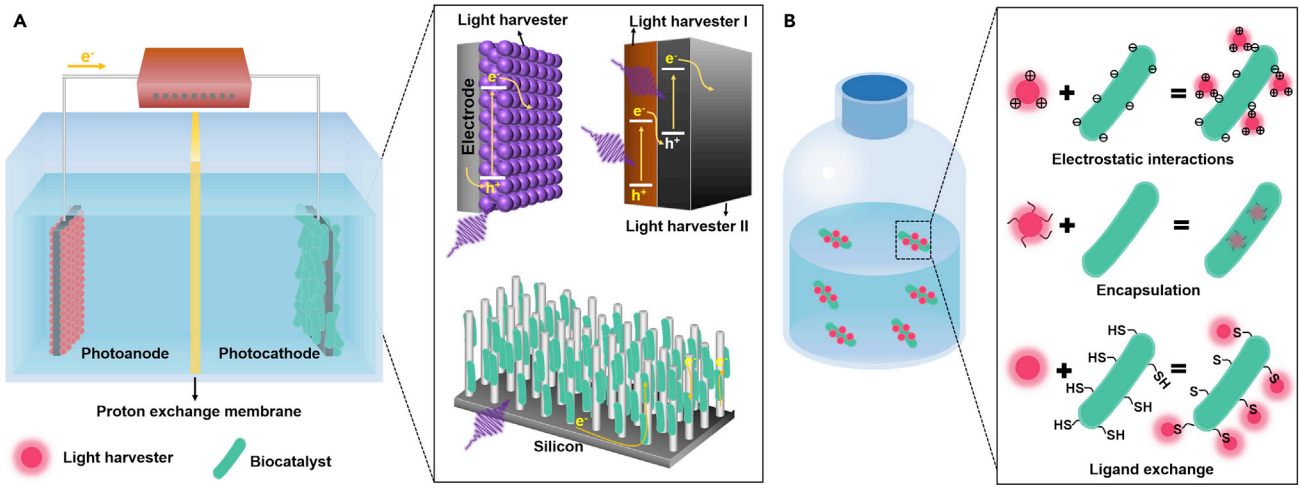

Figure 2. Representative configurations of BPEC systems

(A) a photoelectrochemical cell (PEC) with different photocathodes; and (B) a colloidal system with combined biocatalysts and light harvesters via different interaction mechanisms.

photoelectrons are then transferred to a biocathode via an external circuit. A biocathode should have an excellent biocompatibility with a high surface area, readily diffusion of substrates, and good light transmittance, for example, the hierarchically structured inverse opal mesoporous (IO-meso) electrodes, typically made from ITO (IO-meso ITO electrodes) with the features of 750-nm-diameter chambers interconnected by ~100-nm-diameter channels (Zhang and Reisner, 2020; Kong et al., 2020). To improve the light adsorption efficiency, a biocathode can be decorated with the light harvesters (biophotocathodes) (Kuk et al., 2017), for example, a biocompatible p-type silicon photocathode with a small band gap of 1.1 eV (Lai et al., 2015). However, the utilization of a bare Si surface is limited by the electrode instability in aqueous solution owing to the formation of an insulating SiO_2 layer. To address this issue, TiO_2 is often employed as the charge-separation layer on the biophotocathodes with the dual purposes: protection of light harvesters and enhancement of biocatalyst immobilization (Seger et al., 2013; Lee et al., 2016). More information about the materials for (bio)photocathodes and (bio)photoanodes can be found in a recent review (Gupta et al., 2021). The interaction between light harvesters and biocatalysts in BPEC systems can also be conducted in a colloidal system in which light harvesters are combined with biocatalysts directly (Figure 2B) via mechanisms such as ligand exchange, encapsulation, electrostatic interactions, and hydrophobic interactions (Zhou et al., 2015; Ye et al., 2018a, 2018b).

Light harvesters

Photoenzymes are the important natural biomachineries and have unique advantages for BPEC systems in terms of the product selectivity, reaction rate, and energy efficiency, especially for the complicated chemical transformations with the dual roles of both biocatalysts and light harvesters (Schmermund et al., 2019). As a model photoenzyme, photoexcited photosystem II (PSII), a homodimer complex embedded with the thylakoid of cyanobacteria, algae, and chloroplasts of plants can effectively drive the H_2O oxidation to release $4H^+$, $4e^-$, and O_2 under light irradiation (Yehezkeli et al., 2013). PSII is widely used for the preparation of natural PSII-functionalized photoanode in a PEC (Figure 3A), which can achieve electricity production, H_2 generation, and CO_2 photoreduction with the use of a specific oxidoreductase-functionalized cathode (Zhang and Reisner, 2020). Other natural sub-cellular components such as PSI, sub-chloroplastic components like thylakoid membranes, and the whole chloroplast can also be anchored to an anode for the capture and utilization of solar energy (Figure 3B) (Gerster et al., 2012; Calkins et al., 2013; McCormick et al., 2015). However, the practical application of photoactive proteins and organelles in BPEC systems is challenging due to the rapid photodegradation *in vitro* (e.g., longevity of activity is 30–40 min for PSII and thylakoid membranes, or a few hours for whole chloroplasts), complicated purification processes, and the lack of self-replication ability and oxygen intolerance (McCormick et al., 2011).

Photosynthetic organisms such as the cyanobacteria, algae, and photosynthetic bacteria could be promising alternatives to the purified proteins and organelles in BPEC systems because of their diverse

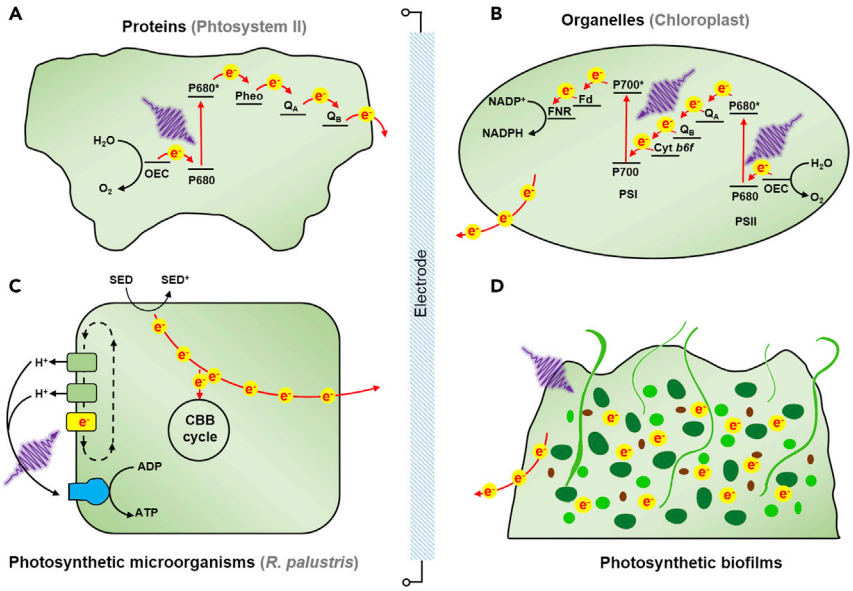

Figure 3. Natural light harvesters-functionalized photoanodes

(A) Photosystem II (the representative of proteins), (B) chloroplast (the representative of organelles), (C) *R. palustris* (the representative of photosynthetic microorganisms), and (D) photosynthetic biofilms are employed as light-harvesters on anodes.

self-repair and self-reproducing mechanisms, high abundances, and the ability to adapt quickly to environmental changes (Yagishita et al., 1998; Torimura et al., 2001). Various wild or gene-modified photosynthetic organisms have been studied in PECs (Figure 3C), including *Rhodospirillum sphaeroides* (Rosenbaum et al., 2005a), modified *S. oneidensis* MR-1 with proteorhodopsin (Johnson et al., 2010), *Rhodopseudomonas palustris* (Xing et al., 2008), and *Chlamydomonas reinhardtii* (Rosenbaum et al., 2005b). Furthermore, the living photosynthetic organisms, either pure culture or mixed culture, can promote the formation of biofilm-functionalized photoelectrodes (Figure 3D). For example, cyanobacteria biofilm-functionalized photoanodes with PSII and PSI complexes *in vivo* showed the superiority of a sustained photocurrent (>5 days) and turnover numbers (>20,000), compared with that with PSII *in vitro* (<6 hours and <7000, respectively) (Zhang et al., 2018b). Microalage *Desmodesmus* sp. A8 as a cathodic microorganism significantly enhanced electricity production under light irradiation, and this was attributed to the substantial increase of DO during the photosynthesis (Wu et al., 2014). However, it should be noted that the load of photosynthetic organisms/biofilms onto electrodes should be optimized for enhanced connection because their large cell sizes usually demand more footprint and thus have a higher requirement for the electrode geometry that need to allow a high loading density without detriment to light penetration (Fang et al., 2020; Ren et al., 2019).

Although BPEC systems with the natural light harvesters could realize the solar-to-chemical conversion, the efficiency is relatively low because of the insufficient adsorption of the incident solar energy and the internal metabolic inefficiencies (Williams and Laurens, 2010; Michel, 2012). A promising strategy for BPEC system construction is to take advantage of the board-band light efficiency of artificial light harvesters, which present distinguished photoelectric characteristics such as the prominent optical performance, a long fluorescence lifetime and a high quantum yield (Medintz et al., 2005; Han et al., 2001; Chan et al., 2002). The commonly used artificial light harvesters include semiconductor quantum dots (SQDs) (Zhou et al., 2015), molecular dyes (Gai et al., 2020), and metal nanoclusters (Zhang et al., 2018a). The main energy band edges of artificial light harvesters are shown in Figure 4A. A typical and well-studied artificial light harvester is SQDs that have the unique advantages of size-controlled luminescence properties. CdS SQDs with a diameter of <10 nm are the most popular choice due to their appropriate band structure for visible light response and the excellent carrier transportation capacity (Zhou et al., 2015). CdS SQDs can be prepared through interacting Cd^{2+} with S^{2-} that originates from the decomposition of cysteine by microorganisms such as *Thiobacillus denitrificans* (Chen et al., 2019a). Then, the prepared CdS SQDs combine with the microorganisms via the surface

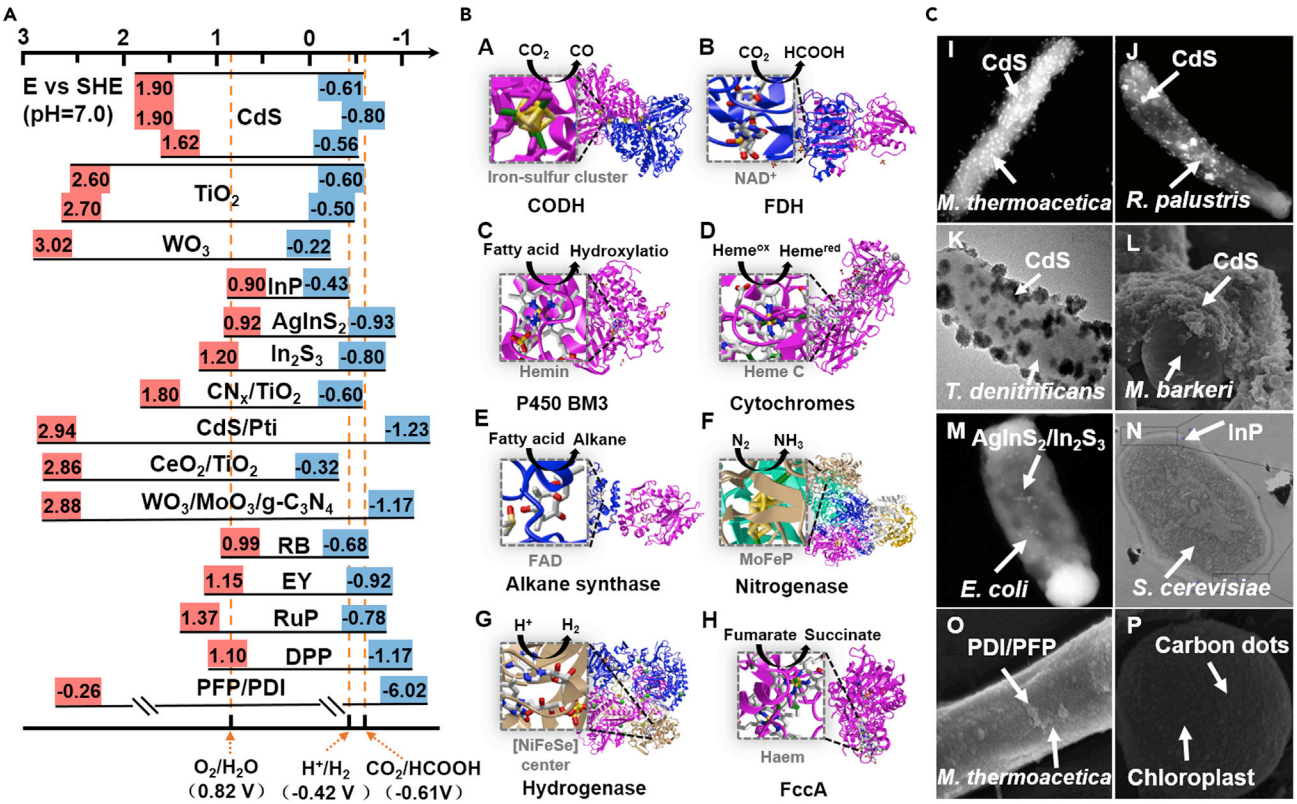

Figure 4. Representative key components of BPEC systems

(A) simplified band diagrams of artificial light harvesters, (B) Commonly used oxidoreductases in BPEC systems, and (C) images of artificial light harvesters bound to biocatalysts. (I) *M. thermoacetica*@CdS (Sakimoto et al., 2016a), (J) *R. palustris*@CdS (Wang et al., 2019a), (K) *T. denitrificans*@CdS (Chen et al., 2019a), (L) *M. barkeri*@CdS (Ye et al., 2019), (M) *E. coli*@$AgInS_2/In_2S_3$ (Jiang et al., 2018), (N) *S. cerevisiae*@Inp (Guo et al., 2018), (O) *M. thermoacetica*@PDI/PFP (Gai et al., 2020), (P) Chloroplast@Carbon dots (Li et al., 2018).

self-precipitation. The biosynthesis of CdS nanoparticles could affect the electrochemical property of yeast cells (e.g., *Saccharomyces cerevisiae*) via the alterations of the protein expression that concerned with electron transfer (Wu et al., 2015). To enhance the electron-hole separation efficiency of SQDs, the strategies like element doping or heterostructure construction can be employed (Ye et al., 2020; Jiang et al., 2018; Ding et al., 2019). However, the toxicity of heavy metals in SQDs and phototoxicity/oxidative stress to biocatalysts could deteriorate the performance of BPEC systems and limit the practical applications (Fang et al., 2020). To address this issue, heavy metals are replaced with carbon materials to form carbon-based SQDs, for example carbon nitride (CN_x), carbon dots, or g-C_3N_4 (Kasap et al., 2016; Martindale et al., 2015; Tremblay et al., 2020). In addition, molecular dyes such as RuP, DPP, and Eosin Y can be used alone or coexisted with the nonmetal semiconductors (e.g., RuP-TiO_2, DPP-TiO_2) as the environmental-friendly light harvesters (Reisner et al., 2009a, 2009b; Warnan et al., 2017), as well as the construction of a p-n heterojunction with perylene diimide derivative and poly (fluorene-co-phenylene) (Gai et al., 2020).

Surface modification could be manipulated to improve the chemical characteristics of light harvesters, such as the ligand length, density, and surface charge, and then enhance their binding with biocatalysts (Ha and Gardella, 2005). For example, the negatively charged surface functionalization of CdTe nanoparticles and CdS nanorods were prepared by capping with 3-mercaptopropionic acid, to trigger the combination of H_2ases with the CdTe/CdS at their positive path (Brown et al., 2010, 2012). The core-shell SQDs can be modified with the cysteine zwitterion to facilitate their affinity attachment to the proteins in microorganisms and thus improve the cell survival (Ding et al., 2019). Similarly, the positively charged ammonium-terminated carbon dots are able to accelerate the electronic communication with the negatively charged H_2ases for H_2 production with excellent efficiency and stability (Rüdiger et al., 2005).

Biocatalysts in BPEC systems

Biocatalysts can harness the photoelectrons from light harvesters and act as the executors of the specific catalytic function in BPEC systems. Various isolated oxidoreductases with the average molecular weights of 10^4–10^6 g mol^{-1} and areal footprints of 50–400 nm^2, such as CODH, FDH, nitrogenase, hydrogenase, FccA, and CbFDH, have been studied to realize the reduction-oxidation reactions via an enzyme cofactor (Figure 4B). Electroactive microorganisms (electrotrophs) are the other type of biocatalysts (Figure 4C) and have evolved special physiological structures – electrically conductive pili (e-pili) and/or conductive membrane structures (Shi et al., 2016) – to accept electrons from external sources for substrate-to-product conversion. The catalytic performance of biocatalysts can be enhanced by the molecular techniques, such as the protein engineering, metabolic engineering, gene engineering, and synthetic biology (Atsumi et al., 2009), through increasing the binding sites and electron flux in biocatalysts. For example, Honda et al. (2016, 2017) constructed a recombinant strain of *Escherichia coli* expressing the genes encoding the [FeFe]-hydrogenase and maturases genes, which significantly improved the photoheterotrophic H_2 metabolism in a BPEC system. Wei et al. (2018) constructed the fusion protein expression plasmid including outer membrane protein A (ompA) and the PbrR protein on *E. coli*, allowing the selective Cd^{2+} adsorption for the CdS formation on the outer membrane of the cells. Specific metabolic pathways can be designed in biocatalysts. For example, Guo et al. (2018) employed the gene engineering to delete the gene *ZWF1* that encoded the glucose-6-phosphate dehydrogenase in yeast strain *S. cerevisiae*, which decreased the cytosolic NADPH generation capacity and enhanced the carbon and energy-efficient production of the metabolite shikimic acid in a BPEC system.

Electron transfer mechanisms

Both natural and artificial light harvesters can adsorb photon energy and extract electrons from H_2O or sacrificial reductants for biocatalysts (e.g., oxidoreductases and electrotrophs). For oxidoreductases, the exogenous electrons can be transferred via specific clusters/relay centers (e.g., [Fe-S] clusters, quinones, and haem cofactors) to the active sites (e.g., [NiFeSe], [MoFe], and flavin) for the electron exchange and the catalytic turnover (Figure 4B). The detailed information about the structure, function, and catalytic mechanisms of the common oxidoreductases has been systematically reviewed (Fang et al., 2020; Zheng et al., 2020). In contrast, electrotrophs can harvest the photoelectrons from the external environment via different pathways (Figure 5). It is well known that the electrical connection between electrotrophs and electron donors could be established through the potential electron carrier like H_2 produced by hydrogenases, similar to the interspecies H_2 transfer (Lovley, 2017b). Furthermore, self-produced redox mediators such as flavin adenine dinucleotide can also function as electron carriers to facilitate the indirect photoelectron transfer at the aid of the intermediate metabolites of flavin mononucleotide (Light et al., 2018; Pan et al., 2021). It is reported that the flavins secreted by *S. oneidensis MR-1* enhanced the electron transfer efficiency by over 3.7 folds while the ATP cost on flavin secretion was negligible compared with the resulting energy benefit (Marsili et al., 2008). The direct electron transfer from electron donors to electrotrophs is conducted through e-pili and/or the membrane-bound proteins such as *c*-type cytochromes (Lovley, 2017b; Summers et al., 2010). Particularly, the flexibility and length of e-pili is beneficial for constructing a highly conductive network and provides a promising opportunity for the long-range electron transfer (Lovley, 2017a), which might have partly contributed to the "electrified" mud up to 5 centimeters in both saltwater and freshwater (Pennisi, 2020). The interfacial photoelectron transfer is further enhanced by the introduction of different liquid-soluble exogenous electron mediators such as diaminodurene and hydroxy-1, 4-naphthoquinone in BEPC systems (Yagishita et al., 1997; Tsujimura et al., 2001). However, the potential toxic effect of liquid-soluble exogenous electron mediators might deteriorate the microbial viability and such an effect could be alleviated with the nonlipid alternatives like conductive polymer (Thorne et al., 2011; McCormick et al., 2013; Kornienko et al., 2018).

Electron transfer in BPEC systems has been studied using spectroscopic and molecular technologies. Kornienko et al. (2016) employed the transient absorption spectroscopy and time-resolved infrared spectroscopy to investigate the charge transfer mechanism from CdS SQDs to *Moorella thermoacetica*. It was found that low H_2ase expression in the first three hours likely favored e^- injection to a membrane-bound e^- acceptor (e.g., ferredoxin, flavoproteins, cytochrome, menaquinones) with a lower quantum efficiency and insufficient energy reducing equivalents, while the increase of H_2ase expression facilitated e^- transfer to a membrane bound H_2ase to generate molecular H_2 with a higher quantum efficiency. Those results were consistent with the untargeted proteome data in which membrane-bound proteins ferredoxin, flavoproteins, and NADH dehydrogenase were upregulated. Those proteins were related to the Wood-Ljungdahl

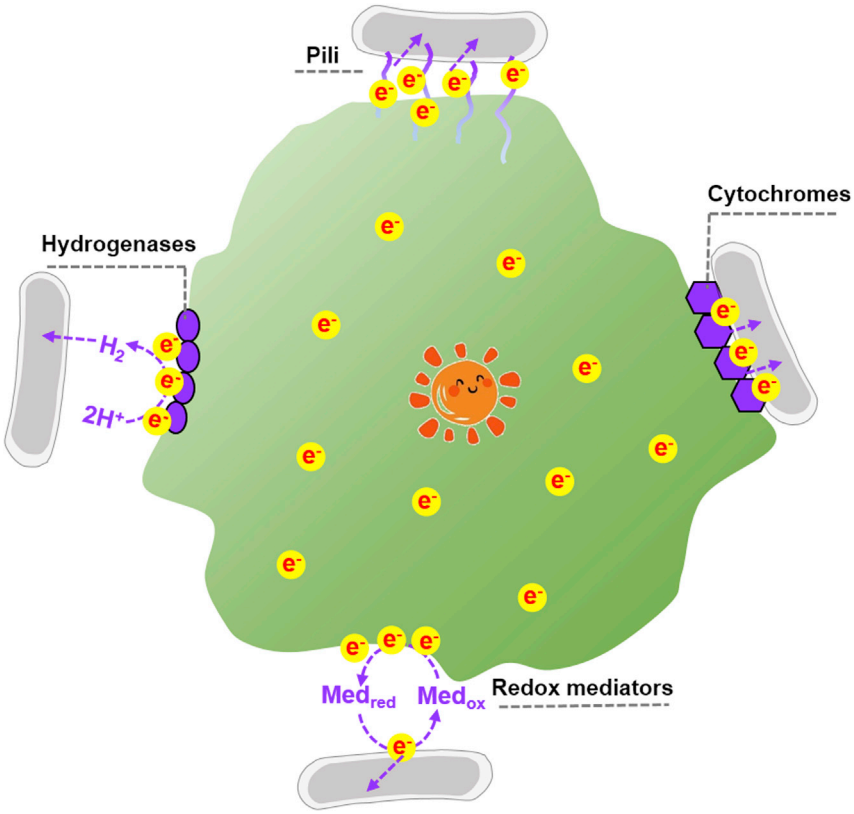

Figure 5. The photoelectron transfer mechanisms in BPEC systems.

pathway, energy-metabolism-associated glycolysis, and the tricarboxylic acid cycle (Zhang et al., 2020). Untargeted proteomic technology was used to investigate the effect of Ni doping on the metabolic status of *Methanosarcina barkeri* in the *M. barkeri*-CdS system. A higher expression of a series of proteins for photoelectron transfer, energy conversion, and CO_2 fixation was detected (Ye et al., 2020). Huang et al. (2019) evaluated the photoelectron-trapped sites on *Geobacter sulfurreducens* PCA via the construction of mutant strains (Δ*omcB*, Δ*omcZ*, Δ*omcS*, Δ*pilA*). Their results showed that *OmcB* was a crucial membrane protein that served as a capacitor to modulate electron transfer in the *G. sulfurreducens*-CdS system. However, it should be recognized that the photoelectron transfer mechanisms in BPEC systems remain in contention and warrant further investigation.

POTENTIAL APPLICATIONS OF BPEC SYSTEMS

As discussed above, BPEC integrates the highly specific biocatalytic power of biomachineries and the board-band light efficiency of light harvesters. The wiring between biocatalysts and light harvesters can be realized in both engineered and natural environments. The former is mainly constructed with the intentionally cultured monoculture/monoenzyme, while the latter is focused on the natural electrotrophic microbial community. In this section, we have described and discussed the potential applications of BPEC systems for energy production and pollution control and as a tool to understand biogeochemical cycle of elements at the water-soil interface.

Hydrogen production

Hydrogen gas (H_2) is considered as a "clean" energy carrier and thus its production is of strong interest to energy sustainability. H_2ases such as [NiFe]- and [FeFe]-H_2ases with the electron relay centers can effectively catalyze the reversible proton reduction to H_2. When H_2ases are immobilized on the ITO as a biocathode (e.g., IO-ITO|H_2ase biocathode) in BPEC systems, they can work with various natural light-harvesters-functionalized photoanodes such as the IO-ITO|PSII photoanode (Mersch et al., 2015) or IO-TiO_2|DPP dye|Os redox polymer|PSII photoanode (Sokol et al., 2018b). The introduction of DPP could enhance

the visible light adsorption with the Os redox polymer acting as a conductive connector during the photoelectron transfer. Such a BPEC system using H_2O as an electron donor resulted in a H_2 production rate of 0.015 μmol h^{-1} with a Faraday efficiency of 76% (Sokol et al., 2018a). Contemporarily, Nam et al. (2018) (Nam et al., 2018) provided a proof of concept for engineered Z-scheme, in which a Si|IO-TiO_2|H_2ase photocathode was connected to a PSII-functionalized photoanode to reduce the thermodynamic barrier needed for the overall water splitting. H_2ases can directly combine with the light harvesters in BPEC systems. For example, the photoelectrons stemmed from different kinds of artificial light harvesters are transferred to the electron relay centers of H_2ases for the proton reduction, such as organic dye Eosin Y (Sakai et al., 2013), RuP-TiO_2 and DPP-TiO_2 particles (Reisner et al., 2009a, 2009b; Warnan et al., 2017), CdS/CdTe semiconductors (Brown et al., 2010, 2012), and robust carbon-based SQDs (e.g., CN_x and carbon dot) (Kasap et al., 2016; Martindale et al., 2015). Particularly, the Eosin Y-H_2ase system showed O_2 tolerance to a certain extent and its photocatalytic performance in the presence of 5% O_2 could be maintained for more than 80% of that under anaerobic conditions (Sakai et al., 2013). Furthermore, natural photosystems can be directly wired with H_2ases to achieve the biological H_2 production with the aid of various conductive materials like molecular wires and redox polymers (Mersch et al., 2015; Lubner et al., 2011). However, it should be pointed out that the biological H_2 production in the aforementioned BPEC systems only lasted for a few hours, possibly due to the instability of materials and weak material-enzyme interaction.

An early attempt of using whole-cell microorganisms for H_2 production in BPEC systems consisted of *Rhodopseudomonas capsulate*, *Rhodospirillum rubrum*, and *E. coli* (biocatalysts), Bi_2O_3 (photosensitizer), and methyl viologen (electron shuttle) (Maruthamuthu et al., 1992). A similar BPEC system using Cu^{2+}/TiO_2 nanoparticles as artificial light harvesters obtained a H_2 production rate of 1.8 mL h^{-1} (Gurunathan, 2000). In recent years, SQDs were coupled with whole-cell microorganisms for H_2 production, e.g., $AgInS_2$/In_2S_3 heterostructure (Jiang et al., 2018), Cu_2O modified with reduced graphene oxide (Shen et al., 2020), ZnO and SiC (Liu et al., 2017a), CdS nanoparticles (Wang et al., 2017), as well as the water-soluble light harvesters such as the proflavine/fluorescein/Eosin Y/RuP/$Ru(bpy)_3^{2+}$ (Rowe et al., 2017). However, the oxygen intolerance of hydrogenases limits the use of whole-cell microorganisms for practical H_2 production in BPEC systems. To this end, a biomimetic silica encapsulation strategy was introduced and enabled the engineered *E. coli* cells to achieve a H_2 yield of 0.52 ± 0.01 μmol/10^8 cells at 36 h under a natural aerobic conduction (Wei et al., 2018).

CO_2 reduction to value-added products

Global warming and climate change have created a strong need for carbon capture. CO_2 capture and utilization can alleviate its negative impact on environment and produce value-added chemicals toward sustainable carbon management. BPEC systems have been studied to reduce and convert CO_2. Both carbon monoxide dehydrogenase (CODH) and formate dehydrogenase (FDH) were used as biocatalysts to drive the two-electron reduction of CO_2 to CO (−0.52 V vs. SHE, pH 7.0) and formate (−0.39 V vs. SHE, pH 7.0), respectively (Appel et al., 2013). CODH was directly wired with the P1 dye-sensitized NiO as a photocathode in a PEC, in which the photoelectrons were transferred from NiO to the excited P1 dye and then injected into the [Ni4Fe-4S] active site of adjacent CODH for CO_2 reduction (Bachmeier et al., 2014). CODH was also combined with RuP-TiO_2 in a colloidal system to realize a CO yield rate of 250 μmol g^{-1} h^{-1} with an average TOF_{CODH} of 0.15 s^{-1} (Woolerton et al., 2010). Likewise, FDH were connected with RuP-TiO_2 directly through electrostatic interaction and chemical sorption, resulting in a formate yield of 2.6 μmol under light irradiation (Miller et al., 2019). Perovskite solar cell based on organometal halides is a promising photovoltaic technology and has been employed in BPEC systems for formate production in recent years. For example, with a $BiVO_4$-FeOOH photoanode, FDH could be loaded on the 3D-structured, electrically conductive titanium nitride nanoshells (3D TiN) and TiO_2-$CuFeO_2$-CuO electrode to yield the formate production rates of 1.06 and 0.098 μmol h^{-1}, respectively (Kuk et al., 2019, 2020). To reduce the cost and environmental risk, precious-metal-free biocathode was prepared with photosystem II, and the constructed PSII-FDH tandem PEC system reached a formate yield of 0.046 μmol h^{-1} (Sokol et al., 2018a). BPEC systems could also be employed for the production of other promising carbon products like methanol via the enzyme cascade dispersed in a cathode chamber or immobilized in a silica matrix (Ji et al., 2016; Kuk et al., 2017; Zhang et al., 2019).

The early study on the utilization of whole-cell microorganisms in BPEC systems for CO_2 reduction was to use the high-surface-area Si nanowire cathode with *S. ovate* for photoelectrochemical production of acetic acid in a PEC. The produced acetate was further used as a substrate by genetically engineered *E. coli* to

synthesize higher value chemicals (Liu et al., 2015). However, the CO_2-reducing current in the constructed *S. ovate*-Si nanowire system was lower than that of electrochemical systems that consisted of purely inorganic catalysts; this could be attributed to the poor bacteria-nanowire interaction resulted from an inhospitable alkaline local environment. This issue could be addressed to some extent by tuning the bulk electrolyte pH and increasing its buffering capacity (Su et al., 2020). The CO_2 reduction to acetate with a solar-to-acetate efficiency of 2.44 $\pm$ 0.62% was innovatively achieved with the self-photosensitized *M. thermoacetica* driven by bioprecipitation of CdS nanoparticles (Sakimoto et al., 2016a). This BPEC system was performed at the expense of thiol amino acid cysteine (Cys) oxidation to the disulfide form cystine (CySS). To realize the quick regeneration of Cys/CySS redox shuttle, TiO_2 modified by cocatalyst Mn(II) phthalocyanine (MnPc) was further prepared and could couple water oxidation with CySS reduction (Sakimoto et al., 2016b). The detrimental effects of the accumulated O_2 and reactive oxygen species (ROS) on CdS and anaerobic *M. thermoacetica* remain to address in those BEPC systems. Rational cytoprotective strategies should be developed for the long-term stability of BPEC systems in oxidative environments. For example, without impacting the cell elongation and separation, the metal-organic framework (MOF) monolayer with 6-connected $Zr_6O_4(OH)_4(\text{-}CO_2)_6$ cluster and trigonal BTB linker effectively reduced the death of strictly anaerobic bacteria by fivefold under an oxidative stress of 21% O_2 (Ji et al., 2018). Gold nanoclusters (AuNCs) were efficient ROS inhibitors and thus could be delivered into the cells with the dual purpose of decreasing the energy loss and overcoming the sluggish kinetics of photoelectron transfer in BEPC systems (Zhang et al., 2018a).

Methane (CH_4) is an important fuel with a calorific value of 890 kJ mol^{-1} and can be produced via CO_2 reduction. Researchers have prepared indium phosphide (InP) photocathode and TiO_2 photoanode in a BPEC system with whole-cell *M. barkeri* as biocatalysts to achieve the CO_2-to-CH_4 conversion with a Faradaic efficiency of 74% (Nichols et al., 2015). This concept was furthered demonstrated by Ye et al. (2019, 2020) that constructed the BPEC systems with CdS/Ni:CdS SQDs and *M. barkeri*. They reported that the suitable Ni dopants were found to serve as an effective electron sink, which not only accelerated the photoelectron transfer in a BPEC system but also changed the metabolic status of *M. barkeri* with the higher expression of a series of proteins for electron transfer, energy conversion, and CO_2 fixation.

Chemical synthesis

Chemical synthesis via "green" pathways can help to meet the environmental and economic goals simultaneously. BPEC systems as a novel and promising tool for synthesis of green chemicals will maximize the desired products and minimize the by-products. Some examples include ammonia (NH_3) synthesis via N_2 reduction and C=C bond hydrogenation. Specifically, N_2-to-NH_3 conversion is crucial for the global nitrogen cycle and agriculture production. Compared with the traditional Haber-Bosch process that must be operated at high temperatures and pressures, a BPEC system containing molybdenum-iron (MoFe) nitrogenase and CdS nanocrystals was demonstrated to achieve the reduction of N_2 into NH_3 with a turnover rate of 75 min^{-1} under an ambient condition (Brown et al., 2016). To maintain the desired energetic coupling of photoelectron production in CdS and the site-selective binding of MoFe nitrogenase with ZnS, CdS@ZnS core-shell quantum dots were designed for efficient NH_3 production catalyzed by MoFe nitrogenase from *Azotobacter vinelandii* (Ding et al., 2019). However, the complexity of enzyme purification and the instability of the cell-free system may hinder the mass production of enzymes and the practical applications of the enzyme-based BPEC systems. The living whole cells (e.g., *R. palustris*) can replace enzymes, for example being integrated with CdS SQDs via a series of facile strategies to accomplish visible-light-driven ambient N_2 fixation (Wang et al., 2019b; Sakpirom et al., 2019). The high performance of N_2-to-NH_3 conversion could be attributed to the increased energy-rich NADPH cofactor that was beneficial for the generation of the Calvin cycle intermediate and solid biomass (Wang et al., 2019b), and the significant upregulation of the key nitrogen-fixation genes including the Mo-Fe nitrogenase gene (*nifH*) and V-Fe nitrogenase gene (*vnfG*) (Sakpirom et al., 2019). Compared with the CdS SQDs, gold nanoclusters have been confirmed with more excellent light absorption properties and biocompatibility and were used to realize efficient biological N_2 fixation by *A. vinelandii* (Bertram et al., 2020). It should be noted that the nitrogen-fixing bacteria may use the produced NH_3 as a substrate for their own growth. To maximize the NH_3 production yield, the effective strategies should be developed to divert more nitrogen from biomass formation to an extracellular NH_3 production such as the addition of a glutamate synthetase inhibitor (Liu et al., 2017b).

Succinate is an important C4 building-block chemical for organic synthesis and can be produced via fumarate reduction that is considered as a model reaction of C=C bond hydrogenation. Flavocytochrome c_3

Table 1. Summary of representative of BPEC systems for solar-to-chemical production

BPEC systems	Substrate/product	Quantum/Faraday/removal efficiency	References
IO- mesoTiO$_2$|Os redox polymer|PSII photoanode and IO- mesoITO|H$_2$ase cathode	H$_2$O/H$_2$	Faraday efficiency of 76% with a H$_2$ production rate of 0.015 μmol h^{-1}	Sokol et al. (2018a)
H$_2$ase@carbon dot-NHMe$_2^+$	H$_2$O/H$_2$	0.36% with an intensity of 1.18 mW cm^{-2}	Hutton et al. (2016)
E. coli@AgInS$_2$/In$_2$S$_3$	H$_2$O/H$_2$	3.3% with an intensity of 1400 mW cm^{-2}	Jiang et al. (2018)
IO-mesoTiO$_2$|DPP dye|Os redox polymer|PSII and IO-mesoTiO$_2$| W- FDHase	CO$_2$/formate	Faraday efficiency of 70 ± 6% with a formate production rate of 0.185 ± 0.017 μmol cm^{-2}	Sokol et al. (2018b)
M. thermoacetica@CdS	CO$_2$/acetate	2.44 ± 0.62% with an intensity of 2 mW cm^{-2}	Sakimoto et al. (2016a)
M. thermoacetica@Au$_{22}$(SG)$_{18}$	CO$_2$/acetate	2.86 ± 0.38% with an intensity of 2 mW cm^{-2}	Zhang et al. (2018a)
M. barkeri@CdS	CO$_2$/CH$_4$	0.34% with an intensity of 1.07 mW cm^{-2}	Ye et al. (2019)
MoFe protein@CdS	N$_2$/NH$_3$	3.3% with an intensity of 3.5 mW cm^{-2}	Brown et al. (2016)
C. necator-CdS@ZnS	N$_2$&H$_2$O/NH$_3$&H$_2$	13.1% with an intensity of 1.6 mW cm^{-2}	Ding et al. (2019)
S. cerevisiae@InP	hexose/shikimic acid	1.58 ± 0.05% with an intensity of 3.0 mW cm^{-2}	Guo et al. (2018)
R. eutropha@g-C$_3$N$_4$	fructose/PHB	6.43 ± 0.97% with an intensity of 4200 lux	Xu et al. (2019)
T. denitrificans@CdS	NO$_3^-$/N$_2$O	2.0 ± 0.2% with an intensity of 3.07 mW cm^{-2}	Chen et al. (2019a)
B. thuringiensis@CdS	Cr^{6+}/Cr^{3+}	Removal efficiency of 92.25% after 24 hours under illumination with visible light	Zuo et al. (2021)
G. sulfurreducens-CdS	Methyl orange	Removal efficiency of 100% after 3 hours with an intensity of 3.07 mW cm^{-2}	Huang et al. (2019)

(fcc$_3$) was innovatively employed to catalyze the fumarate reduction with the aids of RuP-sensitized TiO$_2$ nanoparticles in a colloidal system or a cobalt phosphate-modified BiVO$_4$ photoanode in a PEC (Bachmeier, 2017). However, the used semiconductors exhibited the shortcomings such as the poor aqueous dispersibility and interfacial interaction. By taking advantage of the tunable surface chemistry of carbon dots, the positively charged ammonium-terminated carbon dots (CD-NHMe$_2^+$) were synthesized to be integrated with FccA via electrostatic interactions. Such an enzyme-based BEPC system reached a turnover number of 6000 mol succinate (mol FccA)$^{-1}$ after 24 h (Table 1), and its performance might be further enhanced by optimizing the structure of carbon dots through different strategies such as graphitization or heteroatom doping. To overcome the photoinduced enzyme degradation, the whole-cell *S. oneidensis* was used to achieve the reduction of fumarate with the methylviologen shuttles that transferred the photoenergized electrons from water-soluble photosensitizers (Rowe et al., 2017).

As a biodegradable and biocompatible alternative to plastics synthesized from petroleum, bioplastic polyhydroxybutyrate (PHB) can be produced via the fructose reduction by the *R. palustris*-CdS system (Wang et al., 2019a). Further research has demonstrated that CdS nanorods with the optimized morphology, hexagonal crystal phase, and crystallinity were more suitable for *Cupriavidus necator* than the commercially available CdS, and has increased the PHB production by 1.5 times (Xu et al., 2021). Considering the toxicity of Cd chalcogenides, nonmetallic g-C$_3$N$_4$ was used to couple with *Ralstonia eutropha* for PHB production in the absence of a sacrificial electron donor (Xu et al., 2019). However, such a BPEC system posed serious oxidative stress to *R. eutropha* due to the produced H$_2$O$_2$ from water splitting. To this end, the H$_2$O$_2$-degrading catalase was then introduced to g-C$_3$N$_4$, and the constructed g-C$_3$N$_4$-catalase-*R. eutropha* system triggered an increase of bioplastic PHB yield by 1.84 folds (Tremblay et al., 2020).

Pollution control

The presence of various pollutants exacerbates the shortage of water resources and deteriorates the ecological environment. Thus, pollution control plays a key role in protecting our environment and can be a potential function of BPEC systems. The research on pollutant removal in BPEC systems is still in its infancy and mostly focuses on inorganic pollutants like nitrate and heavy metals. For example, photoelectrotrophic denitrification (PEDeN) is a novel process for nitrate reduction that will help alleviate eutrophication and harmful algal blooms. This process was demonstrated in an engineered BPEC system containing a TiO$_2$ photoanode and a denitrification biocathode (Cheng et al., 2017). Under the illumination intensity of 30 mW cm^{-2} and wavelength of 380 ± 20 nm, the *in situ* nitrate removal efficiency was over 95%. The results were

then verified by the subsequent research in which the periphytic biofilms-TiO_2 system and *T. denitrificans*-CdS system were constructed to promote the nitrate reduction (Zhu et al., 2018a, 2018b; Chen et al., 2019a). The excellent performance could partly be attributed to the increase of humic acid and protein content in EPS, which significantly accelerated the photoelectron transfer by acting as electron mediators (Zhu et al., 2018a). The denitrification performance of the *T. denitrificans*-CdS system was found to be sensitive to the input nitrate and nitrite (NO_2^-), leading to the changes of $N_2O/(N_2/N_2O)$ ratio in the reductive products. This was because that N_2O reduction exhibited greater susceptibility to ROS than NO_3^- reduction during PEDeN. The contributions of hydrogen peroxide (H_2O_2), superoxides ($O_2^{\cdot-}$), and hydroxyl radicals (·OH) to the inhibition of N_2O reduction were >15.0%, >5.4% and 1.3% for a reduction of 13.5 mg/L NO_3^--N, respectively (Chen et al., 2020a). To weaken the inhibiting effect of ROS, a Mn_3O_4 nanozyme-coated BPEC system (*T. denitrificans*-CdS@Mn_3O_4) was constructed and significantly reduced the concentrations of multiple ROS for stable microbial viability, resulting in a 28% higher NO_3^- reduction and 78% lower emission of N_2O than that of the *T. denitrificans*-CdS system (Chen et al., 2020b). Recently, a novel concept of dark photocatalyst was introduced, e.g., cyanamide-functionalized heptazine-based polymer (NCN-CN_x) that could store photoelectrons under irradiation and release them in a dark environment. The NCN-CN_x-based BPEC system with the time-delayed characteristics realized efficient PEDeN process with denitrifiers such as Sphingomonadaceae, Xanthomonadaceae, and Cyclobacteriaceae (Zhou et al., 2020).

BPEC systems may be employed for the treatment of heavy metal pollution. Heavy metal ions (e.g., Mn^{2+}, Cd^{2+}, and Pb^{2+}) can be mineralized to form light harvesters for BPEC systems and the constructed BPEC systems are further used for the detoxification of heavy metal ions (e.g., Cr^{6+} and Se^{4+}) via the intracellular enzymatic reduction (Chaparro-Acuña et al., 2018). Bittencourt et al. (2020) integrated brown algae *Laminaria hyperborean* with TiO_2 to achieve the reduction of Cr^{6+} to Cr^{3+}, although its performance was lower than that of the *L. hyperborean* coated with $FeCl_3$. A biocathode was prepared with *Serratia marcescens* and WO_3/MoO_3/g-C_3N_4 heterojunctions in a BPEC system, which allowed the simultaneous reduction of Cr^{6+} and H^+, and the produced H_2 was further used for acetate production (Huang et al., 2021). Those results provide a potential strategy for efficient removal of toxic heavy metal from wastewater, along with the simultaneous conversion of inorganic carbon to key block chemicals. In addition, BEPC systems were reported to realize the simultaneous detoxification of multiple heavy metal ions such as the Cr^{6+} reduction and As^{3+} oxidation, creating opportunities for the treatment of multiple heavy metal polluted wastewater (Zuo et al., 2021).

Understanding of biogeochemical cycle of elements at the water-sediment interface

Water-sediment interface, the boundary between water and sediments in various nature environments, is one of the important dynamic hot zones that regulate the biogeochemical cycle of elements due to its greatest gradient on the environmental factors such as dissolved oxygen, pH, and redox potential (Santschi et al., 1990; McMahon, 2001). BPEC process may play an important but less recognized role in the biogeochemical redox process at the water-sediment interface. Electrotrophs are active organisms that can conduct extracellular electron uptake and redox reactions at the water-sediment interface (Koch and Harnisch, 2016) and the electrotrophic microbial community can be shaped by human activities like the long-term fertilization in paddy soils (Li et al., 2021a). Meanwhile, the abundant light harvesters as both primary particles and agglomerates/aggregates are observed at the water-sediment interface (Lu et al., 2019; Guo et al., 2019; Ahmed et al., 2010). These light harvesters including Fe oxide, TiO_2, MnO_2, and ZnO can be transported by Brownian motion and gravitational force, and then increase their chance to interact with electrotrophs (Farré et al., 2009). Naturally abundant organic matters (NOMs) such as flavins and humic substances may also serve as the promising light harvesters at the water-sediment interfaces (Chen et al., 2019b). Importantly, these NOM can act as hole scavengers by reacting with other light harvesters via ligand exchange, chelation, cation bridging and H-bonding. Therefore, the co-existence of electrotrophs, light harvesters and hole scavengers would trigger the formation of the natural BPEC systems at the water-sediment interface for the biogeochemical cycle of elements (Figure 6). The study on the natural BPEC systems at the water-sediment interface is at a very early stage and mainly focuses on the metal elements. It was reported that the photo-excited mineral photoelectrons from various SQDs such as ZnS, MnO_2 and TiO_2, participated in the microbial electron transfer chain for As/Fe reduction in flooded soils, and the synchronously excited photoholes could be scavenged by humic/fulvic acids (Dong et al., 2021; Chen et al., 2019c, 2019d). The introduction of these SQDs would increase the electrical conductivities of soil particles and enhance the production of *c*-type cytochrome, thereby enabling a long-distance photoelectron transfer. Accordingly, the abundance of metal-reducing bacteria (e.g., *Anaeromyxobacter*, *Bacillus* and *Geobacter*) would facilitate the metal reduction at the water-sediment interface (Dong et al., 2021).

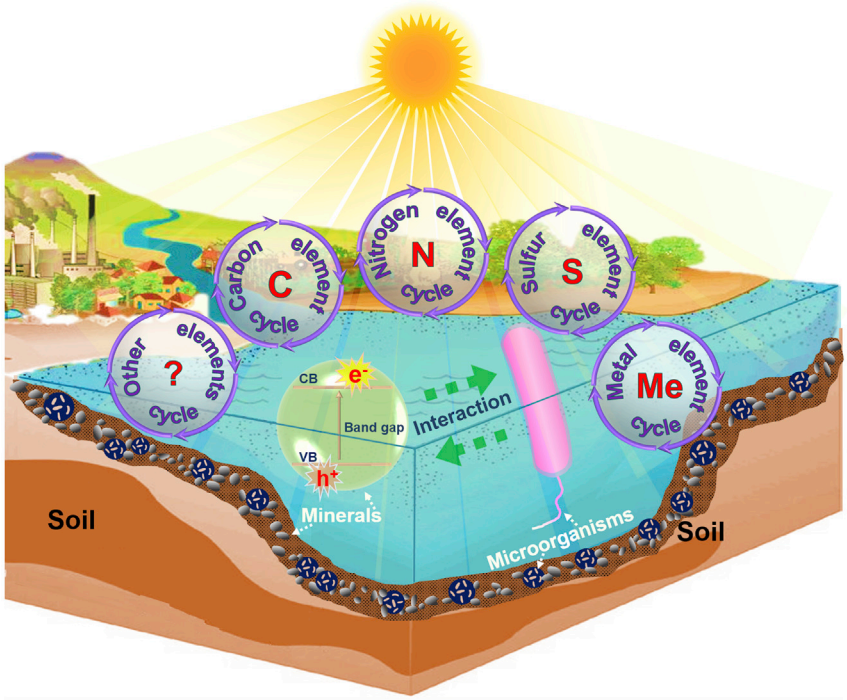

Figure 6. The proposed natural BPEC systems at the water-sediment interface.

CONCLUSIONS AND OUTLOOK

In this paper, we have introduced both BPEC basics and systems and discussed the photoelectron transfer mechanisms via direct and indirect pathways. BPEC takes the advantages of the natural and artificial photosynthesis: the biocatalytic power of biomachineries and the board-band light efficiency of light harvesters. The constructed BPEC system can utilize solar light as an electron pump to drive a wide range of catalytic processes with high product selectivity under mild reaction conditions. BPEC systems have been studied to address the challenges of energy and environment. The system performance could be further optimized via different strategies such as surface modification of light harvesters, molecular engineering for biocatalysts, and cytoprotection. However, the BPEC research for energy and environment requires further work and in the followings several challenges have been proposed and discussed.

Firstly, the biotic-abiotic interface of BPEC system is crucial for overcoming the sluggish kinetics of photoelectron transfer and uptake (Kornienko et al., 2018). Thus, the *in situ* characterization of the electronic and vibrational properties of the functional groups/components on the biotic-abiotic interface should be conducted with the advanced electrochemical methods and spectroelectrochemical technologies such as MALDI mass spectrometry. The obtained information will help develop appropriate strategies to maximize interfacial photoelectron transfer/flux and enhance performance, such as the targeted modification of material morphology and surface of biocatalysts for more efficient connection.

The stability and sustainability are key issues for the BPEC systems. To the best of our knowledge, the reported BPEC systems were mainly constructed by the monoculture/monoenzyme with light harvester, and most of their operations lasted less than 5 days. This phenomenon might be related to the quick depletion of hole scavengers, resulting in the oxidative photodamage of cell (Ye et al., 2019; Sakimoto et al., 2016a). However, a high initial concentration or a second injection of hole scavengers did not significantly prolong the reaction time, indicating the presence of other potential reasons. It is likely that the deposition of light harvesters on the surface of microorganisms might have influenced the proliferation rate and cell viability. A previous study has demonstrated that the wrapping of cells via the interaction between zirconium clusters in the MOF nanosheets and the phosphate residues on the cell surface allowed for cell elongation and separation, including spontaneous covering of the newly grown cell surface (Ji et al., 2018). However, the toxicity of heavy metals in MOF should not be ignored. Although gold nanoclusters as a promising biocompatible light harvester could be

translocated into microorganisms without the influence of the cell division (Zhang et al., 2018a), their high cost, preparation complexity, and potential environmental risk would limit the practical application. Seeking other biocompatible, intracellular light harvesters will be an important research direction. For example, carbon dots (CDs) are considered as a promising alternative and have been demonstrated to accelerate extracellular electron transfer and metabolic rate of CDs-fed *S. oneidensis* (Yang et al., 2020).

Sacrificial reagents play an important role in BPEC systems. They can scavenge holes and serve as the sustainable electron donors. However, the energy/cost for the synthesizing sacrificial reagents could be more than what is provided by the products. Although TiO_2 nanocatalysts could quickly regenerate Cys/CySS redox shuttle (Sakimoto et al., 2016b), the simultaneously produced ROS might affect cell biological activities. Therefore, exploring the natural (waste) materials as sacrificial reagents is critically important to the application and development of BEPC systems. It was found that the widespread wastes such as plastic and lignocellulose can be reformed via the photocatalytic process (Philippe and Schaumann, 2014; Wakerley et al., 2017; Uekert et al., 2018; Tang et al., 2004). These results intrigue the idea of using wastes as sacrificial reagents in BPEC systems via waste oxidation, and the oxidization products can be further used by the microorganisms for metabolism. Such a process will indirectly realize the function of synthetic biology and thus be of interest to research.

Although the feasibility of BPEC systems for the simultaneous synthesis of multiple products has been demonstrated, such as biomass PHB and alcohols (Liu et al., 2016), or the mixture of acetic acid, propanoic acid, butanoic acid, hexonoic acid, methanol, and ethanol (Kumar et al., 2019), it demands further investigation to accurately regulate the formation of target products and then effectively separate and purify these products. For this purpose, advanced molecular techniques will be an important tool to design the specific metabolism pathways and functional gene express pathways. The strategies such as the membrane-based technologies may be used for the downstream product separation. The potential of BPEC systems needs to be further examined with actual wastewaters that would introduce impurities to affect BPEC performance. Microbial strains in a BPEC system for pollution control must have excellent tolerance to multiple pollutants. Cocultured organisms/biofilms can be a method to cultivate the resistance to complicated environment changes via the synergistic effects.

Limitations of the study

A detailed comparison of strengths and limitations of bioelectrochemistry, photoelectrochemistry and BPEC can be further conducted. In addition, the promising potential of BPEC systems as engineering microbial cell factories for biotechnological implications can be explored.

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AUTHOR CONTRIBUTIONS

Conceptualization-J.Y. and M.C.; writing-original draft-J.Y., A.H., and G.R.; writing-review & editing-J.Y., S.Z., and Z.H.; funding acquisition-S.Z.; supervision-S.Z. and Z.H.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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