Recent advances in the roles of minerals for enhanced microbial extracellular electron transfer

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ABSTRACT

Minerals are ubiquitous in the natural environment and have close contact with microorganisms. In various scenarios, microorganisms that harbor extracellular electron transfer (EET) capabilities have evolved a series of beneficial strategies through the mutual exchange of electrons with extracellular minerals to enhance survival and metabolism. These electron exchange interactions are highly relevant to the cycling of elements in the epigeosphere and have a profound significance in bioelectrochemical engineering applications. In this review, we summarize recent advances related to the effects of different minerals that facilitate the EET process and discuss the underlying mechanisms and outlooks for future applications. The promotional effects of minerals arise from their redox-active ability, electrical conductivity and photocatalytic capability. In mineral-promoted EET processes, various responses have concurrently arisen in microorganisms, such as stretching of electrically conductive pili (e-pili), upregulated expression of outer-membrane cytochromes (Cyts) and production of specific enzymes, and secretion of extracellular polymeric substances (EPSs). This review synthesizes the understanding of electron exchange mechanisms between microorganisms and minerals and highlights potential applications in development of renewable energy production and pollutant remediation, which are topics of particular significance to future exploitation of biotechnology.

1. Introduction

The behavior of microbial extracellular electron transfer (EET) processes has attracted considerable attention in recent years because electron exchange processes inevitably influences microbial metabolism, energy conservation, and mineral formation, and contribute to the biogeochemical evolution of the Earth's critical zone – where rock meets life [1–4]. Currently, many alternative approaches are under investigation to improve the electron transfer capacity between microorganisms and electron acceptors, such as induction with conductive materials (*e.g.*, carbon cloth, graphene, and conductive minerals) [5],

exogenous electron shuttles (*e.g.,* quinone compounds) [6], and genetically programmable multistep catalysis [7]. Notably, via long-term evolutionary processes, microorganisms established an intimate relationship with minerals for exchange of electrons to sustain special survival strategies and environmental adaptability [8,9], consequently contributing to the origin and evolution of life [10–12]. Minerals serve as habitats for the formation of biofilms [13], electron donors/acceptors for microbial respiration [8], reservoirs of macro- and micronutrients for sustaining fundamental microbial metabolisms [14], and as electron transfer conduits that favor intercellular interactions [15,16]. Hence, interactions between microorganisms and inorganic minerals are among

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the most colorful and vivid manifestations of the epigeosphere, wherein inorganic and organic materials are mutually biotransformed.

Although the interplay between microorganisms and minerals is complex in subsurface environments, the process of electron transfer and energy flow between minerals and microorganisms has long been considered a fundamental process occurring at the junction between the lithosphere and biosphere [17]. Thus, the electronic response of these interactions and the involved environmental processes are likely to shape the biosphere-lithosphere habitats in which microorganisms live and elements cycle at a variety of temporal and spatial scales [18,19]. Additionally, microorganism-mineral interactions hold promise for exploitation in various bioelectrochemical engineering applications. Previous studies have primarily focused on the behaviors of microbes that harbor EETs coupled with redox-active and/or electrically conductive minerals for mineralization of organic pollutants and methanogenesis [20,21]. In recent years, major advances in microbial EET processes include fixation of carbon dioxide to organic compounds and denitrification via photosynthesis in conjunction with (semi) conductive minerals [22–24]. Therefore, understanding the fundamental mechanisms underlying microbe EETs coupling with minerals is expected to have profound significance in revealing the environmental impact and practical application of minerals.

Microorganisms have developed specific strategies that aid them in sustaining intracellular/extracellular redox balance, such as altering their outer-membrane cytochromes (Cyts) expression patterns and enzyme metabolic pathways, and secreting extracellular polymeric substances (EPSs) in response to shifts in external stimuli [25–27]. Because a diverse range of minerals with various properties is present in the natural environment, substantial uncertainty regarding in electron exchange processes due to the coexistence of different microbial species with multiple mineral phases. Due to these complexities, the molecular mechanisms underlying the abilities of microorganisms to exchange electrons with extracellular minerals or with the same or different microorganism species, such as *c*-Cyts and microbial nanowires, are rarely studied. Particularly, there is a paucity of information regarding pathways involved in electron conduction.

The electrical interplay between minerals and microorganisms is viewed as one of the most complicated, important and dynamic biogeochemical mechanisms on Earth [8,28], and the basic principles might be exploited for various bioelectrochemical engineering applications. In this review, the roles that minerals play in enhancing the microbial EET process were classified into three main categories according to the sites at which they interact within the EET process: redox-active capability, electrical conductivity, and photocatalytic capability. This synthesis addresses current knowledge gaps related to the mechanisms by which minerals mediate EET processes and offers a vision of anticipated future applications in biological engineering.

2. Redox-active minerals

2.1. Redox-active minerals serve as a temporary mediator for electron storage

Several representative minerals containing mixed-valence iron or manganese, *i.e.,* Fe(II)/Fe(III) or Mn(III)/Mn(IV) (*e.g.,* green rust $[Fe_6(OH)_{12}CO_3]$, clay mineral nontronite $[Na_x(H_2O)_4Fe_{3+2}[Al_xSi_{4-x}O_{10}](OH)_2]$ and magnetite $[Fe_3O_4]$), can serve as temporary redox-active mediators or electron storage materials (similar to batteries) in the EET process [8,9,29]. In general, these redox-active minerals function as "naturally occurring batteries" by serving as an environmentally relevant electron sink/source for a vast variety of bacterial communities. These redox-active minerals are commonly used as terminal electron donors and as terminal electron acceptors by specific microbes, correspondingly extending the direct EET distance through multiple redox cycles of mixed-valence metal elements inside these minerals by dissimilatory metal-reducing bacteria (DMRB) and specific phototrophic

bacteria [8,30]. That is, such a redox-active mineral-based "battery" gets "charged" under reducing conditions by DMRB via storing electrons and then undergoes "discharge" to transfer electrons to phototrophic bacteria [30].

For instance, Byrne and coworkers [30] found that efficient direct interspecies electron transfer (DIET) performance was displayed in a co-culture of the dissimilatory Fe(III)-reducing strain of *Geobacter sulfurreducens* and the photosynthetic Fe(II)-oxidizing strain of *Rhodopseudomonas palustris* in the presence of magnetite. In addition, they found that microbial activity did not change the mineral mass [30], indicating that magnetite displayed an effect similar to that of biochar and anthraquinone to confer electron shuttling capability. This redox property of magnetite was used to boost the transient charge storage of the anode in magnetite-amended microbial fuel cells [31,32]. Analogous to magnetite, Zhao et al. [33] found that nontronite could retain its substantial mineral properties even after undergoing up to 3 reversible redox cycles by coupling the Fe(III)-reducing *Shewanella oneidensis* strain and the Fe(II)-oxidizing *Pseudogulbenkiania* sp. strain 2002. Specifically, DMRB delivers electrons to the surface of redox-active minerals for extracellular respiration, resulting in the release of low-valence metal ions that subsequently interact with other oxidizers (*e.g.,* iron-oxidizing phototrophic bacteria and oxidizing substances present at the surface of minerals; Fig. 1a) [34]. In other words, this process can be described as a "redox active mineral-based battery that charges/discharges electrons" process driven by mixed-valence metal ions in redox-active minerals wherein the involved mixed-valence metal ions are repeatedly cycled in a manner similar to that of Fe(II)/Fe(III) redox reactions in magnetite. Although magnetite possesses both redox capability and electrical conductivity (described in section 3), each role is different and may be closely linked to specific microbes in a given bioelectrochemical system. Specifically, participation of Fe(II)-oxidizing microbes in Fe(II) oxidation is a key linkage in maintaining dynamic redox cycles with structural Fe in redox-active minerals, as the resulting product, Fe(III), is an important precursor for accepting electrons.

Considering the ubiquitous existence of redox-active minerals (magnetite, silicate clays and green rust) in natural soils, it is clear that these redox-active minerals are significantly involved in a wide range of biogeochemical cycling processes involving elements and pollutant degradation dynamics. For instance, organic carbon turnover in soils and sediments is closely linked to mineralogical processes via oxidation/reduction, complexation/decomplexation, sorption/desorption and precipitation/dissolution reactions [35]. Because of microbial anaerobic extracellular respiration, sequestered organic fractions that are originally enclosed in redox-active minerals are liberated and available to enhance the secondary EET processes [36]. Additionally, structural Fe in nontronite was able to undergo multiple redox cycles mediated by the Fe (III)-reducing member *Shewanella putrefaciens* CN32 and nitrate-dependent Fe(II)-oxidizing member *Pseudogulbenkiania* sp. strain 2002. This process resulted in continuous removal of nitrate (reduced to nitrogen gas) from aqueous solution [37]. Thus, these mixed-valence iron-/manganese-bearing minerals function as natural batteries for storage and exchange of electrons to support microbial metabolism, which could in turn sustain the redox stability of the mineral. This is especially relevant for biofilms attached to redox-active minerals where *c*-Cyts and e-pili enclosed in biological polymers directly deliver electrons to redox-active minerals. This contact process mediates satisfactory EET efficiency at the interface between the biofilm and crystalline mineral phase with the assistance of the Fe(II)/Fe(III) redox couple [31]. Notably, the prevailing abiotic/biotic reactions occurring in the biogeochemical Fe cycle could be an important mediator for regulating the bioavailability and ultimate fate of several metal pollutants and essential biogenic elements in the epigeosphere (discussed in sections 2.2 and 2.3).
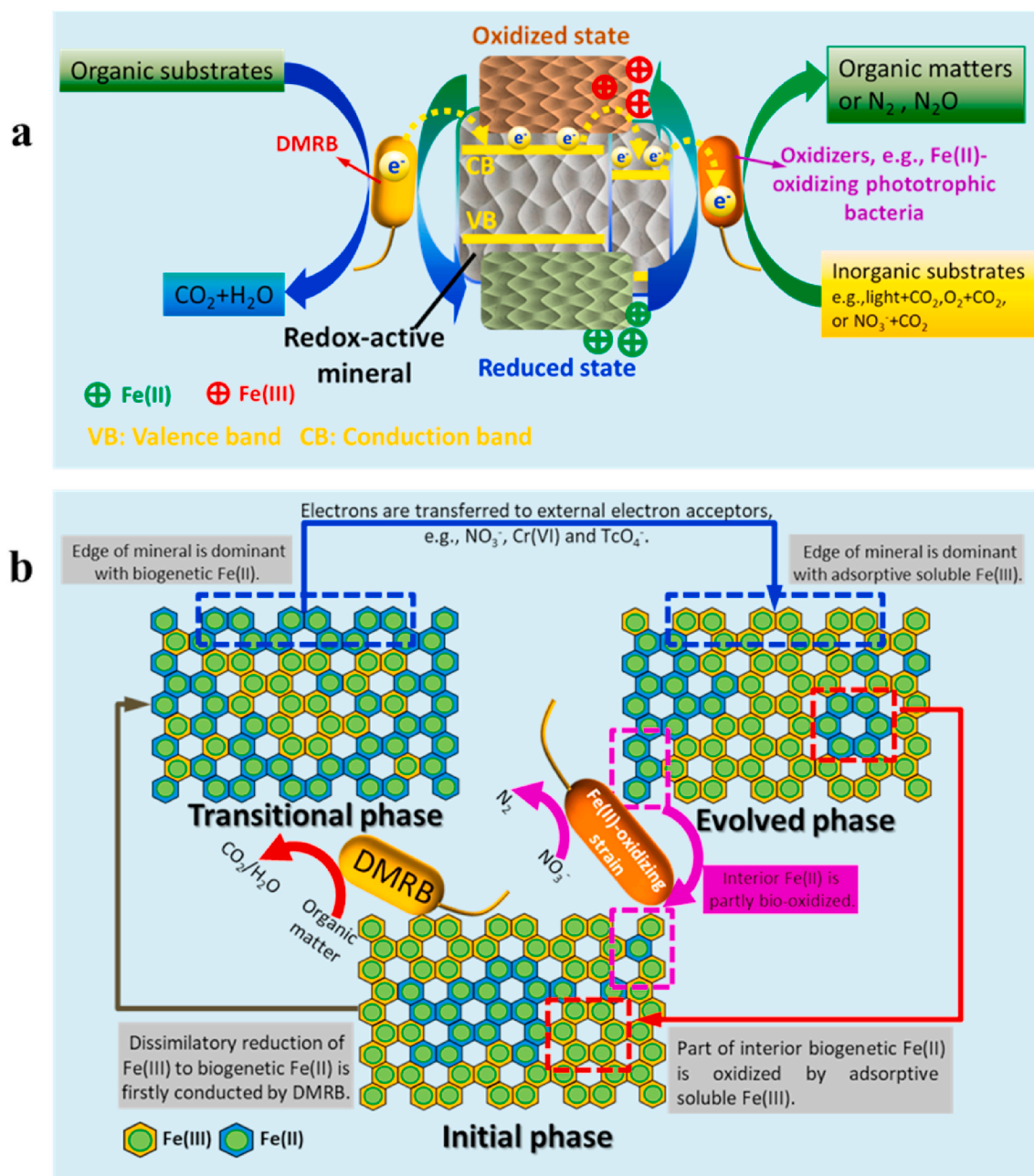
Fig. 1. Redox-active minerals containing mixed-valence iron serve as temporary batteries for electron storage/release and support microbial metabolism (a). Schematic illustration for dynamic redox cycles of structural Fe in redox-active minerals, such as magnetite and nontronite (b). Notably, electrical conduction and reductive dissolution might synchronously occur in magnetite.

2.2. Dynamic redox cycles and recrystallization of structural Fe in redox-active minerals

It is obvious that redox-active minerals such as magnetite and nontronite can exchange electrons through intracrystalline electron hopping between neighboring octahedral Fe^{2+}–Fe^{3+} valence interchanges [38]. The extent and reversibility of these structural changes are commonly determined by the Fe(II)/Fe(III) ratio of the mineral structure [39] (Fig. 1b). Microbial dissimilatory reduction of Fe(III) to biogenetic Fe(II) is first processed from the edges of the minerals to the structural interior phase in a relatively "rigid" environment, creating a reduction front at the Fe(II)–Fe(III) redox boundary [40]. Thereafter, the transiently produced biogenetic Fe(II) in the Fe(II)–Fe(III) domain at the mineral edges directly transfers electrons to the external electron acceptors (*e.g.,* nitrate, pertechnetate, arsenate and hexavalent chromium) to produce adsorptive Fe(III), which can in turn oxidize adjacent biogenetic Fe(II) via intervalence electron transfer [41–43]. Recrystallization of redox-active stable minerals mainly arises through ion exchange occurring as interfacial reactions between mineral phase Fe(III) and aqueous phase Fe(II) [44]. Therein, aqueous Fe(II) is preferentially adsorbed to mineral surfaces while reductive dissolution of structural Fe (III) preferentially occurs at step/defect sites on mineral particles, promoting the recrystallization reaction [45]. Besides, the reaction rate for recrystallization is largely dependent on the pH of the reaction system. Specifically, extensive and rapid recrystallization is most favorable at circumneutral pH conditions in the presence of dissolved Fe(II) [46].

Overall, with such dynamic redox cycling and recrystallization reactions, it is beneficial to certain microorganisms to gain energy for growth from coupled redox cycles with structural Fe, or even to build a syntrophic relationship to mutually support the other partner's growth

by replacing redox-active minerals with an environmental medium. In natural environments, these redox processes mostly thrived in transition zones where a new model of microbial metabolism for energy generation is established at their junctions.

2.3. Significance of redox-active minerals in controlling cycling of major and trace elements

Because of their fine grain size and special chemical structure, reversible oxidation/reduction of structural Fe in clay minerals contributes to organic carbon preservation/degradation [47,48], nitrogen cycling [33,37] and mobility of trace metals and radionuclides (*e.g.,* arsenic [As], chromium [Cr], technetium [Tc] and uranium [U]) [42,43, 49], which have important environmental implications. It could be inferred that alternating oxidation/reduction processes within redox-active minerals potentially occur in sunlight irradiated and anoxic zones (*e.g.,* marsh, shoal area and coastal marine sediment), where dynamic hydrogeological fluctuations drive the metabolic connection with redox-active minerals [50]. For instance, redox conditions are likely to fluctuate due to changes in water depth and oxygen penetration into sediments. In these environments, redox-active minerals may contribute to the bioremediation of pollutants and the fate/transport of several biogenic elements. These results from the biotransformation processes of organic pollutants and the cycling of biogenic elements are closely linked to the reactivity of redox-active minerals [9,47–49]. Additionally, the mobilization/solubilization of As(V) can proceed via microbial dissimilatory reduction/detoxification pathways concomitant with reductive dissolution of Fe(III)-containing minerals in anoxic subsurface environments [35,49]. Subsequently, the dissolved Fe(II) produced as a result of microbial respiration using Fe(III)-bearing minerals can be a powerful reductant to facilitate the reduction of Cr(VI), Tc(VII) and U (VI) [51–53]. Thus, using redox-active minerals to control the biogeochemical fate/transport of trace metals and radionuclides provides alternative remediation strategies.

Considering the diversity of minerals in nature, identifying novel redox-active minerals should be a priority for future research. Additionally, thermodynamic and kinetic prediction models combined with Mössbauer spectroscopy and microscopy methods should be instituted to verify mineral redox reactions and their mechanistic interactions within the epigeosphere.

3. Conductive and semi-conductive minerals

3.1. Enhanced electrical conductivities at the attached interface

Various conductive/semiconductive minerals can serve as electrical conductors to facilitate the EET process, highlighting the importance of the electron transmission mechanism through the conduction band of these minerals. In general, the electrical conductivity of a mineral is primarily determined by the energy level discrepancy required for electrons to jump from the top of the valence band to the bottom of the conduction band. The band gaps are commonly large in insulative minerals, smaller in semiconductive minerals, and smallest in conductive minerals because of the overlap of the valence band and conduction band. In natural soils or sediments, a variety of (semi)conductive minerals are present, such as magnetite, greenockite, rutile and hematite, that are capable of functioning as electrical conduits for transfer of electrons between different microbial species (Table 1) [54–56].

It is known that electron flow between different substances can be thermodynamically permitted due to redox potential discrepancy [67]. Both the Cyt-protein complex in the cytoplasmic membrane of microbial cells and the conduction band of (semi)conductive minerals have wide ranges of redox potentials, electron transfer is theoretically permitted across the microbial cytochrome-protein complex and the conduction band of (semi)conductive minerals. Some (semi)conductive minerals assembled with comparably low resistance can enable improved DIET

Table 1
Selected physicochemical properties of conductive and semiconductive minerals.

Mineral	Chemical formula	Type	Resistivity ($\Omega \cdot m$)	Specific gravity (g/cm^3)	Ref.
Covellite	CuS	Conductive	10^{-4}-10^{-7}	4.59–4.64	[57]
Bornite	Cu_5FeS_4	Conductive	10^{-3}-10^{-5}	4.90–5.01	[58]
Chalcopyrite	$CuFeS_2$	Conductive	10^{-1}-10^{-4}	4.14–4.32	[59]
Magnetite	Fe_3O_4	(Semi)conductive	10^{-2}-10^{-5}	5.16–5.18	[60]
Cassiterite	SnO_2	(Semi)conductive	10^3–10^{-4}	6.06–6.95	[61]
Pyrite	FeS_2	(Semi)conductive	10^0–10^{-5}	4.90–5.27	[62]
Hematite	α-Fe_2O_3	Semiconductive	10^2–10^{-3}	4.91–5.32	[63]
Pyrolusite	MnO_2	Semiconductive	10^2–10^{-3}	4.71–5.23	[64]
Rutile	TiO_2	Semiconductive	10^4–10^{-2}	4.13–4.31	[65]
Sphalerite	ZnS	Semiconductive	10^5–10^{-2}	3.91–4.21	[66]

Note: 1). Mineral resistivity is a function of the purity, geometrical morphology and density of minerals, as well as the temperature. 2). Due to the resistivity ranges reported, several minerals overlap between conductive minerals and semiconductive minerals; herein, we labeled such minerals as "(semi)conductive minerals".

efficiency between different microorganisms in electrical syntrophic cultures. This enhanced effect is prominent when applying (semi) conductive minerals in anaerobic digestion systems to promote methanogenic performance. For example, Kato et al. [20] reported that supplementation with magnetite and hematite accelerated methanogenesis in terms of both lag time and production rate when *Methanosarcina* spp. was grown in co-culture with *Geobacter* spp. Further, genomic analyses by Zhuang et al. [68] even demonstrated that a higher dose of hematite and magnetite increased the higher abundance of *Methanobacterium*, which subsequently accelerated syntrophic cooperation in methanogenic benzoate degradation. These findings emphasize the special roles of magnetite and hematite in boosting methanogenesis via DIET. Overall, these examples demonstrate the efficacy of (semi) conductive minerals for electrical modification of bioelectrochemical systems through decreasing interfacial resistance and promoting charge transfer.

When microorganisms come in direct contact with (semi)conductive minerals, efficient electron transfers occur in electro-syntrophic partners, permitting conductive networks between (semi)conductive minerals, exoelectrogenic bacteria and electrotrophic methanogens. Specifically, large (semi)conductive minerals provide abundant attachment sites for microorganisms to form biofilms on mineral surfaces, whereas submicron-sized minerals are easily aggregated with microorganisms to form floc-like aggregates (Fig. 2). Specifically, biofilm formation on mineral surfaces promotes e-pili and membrane-bound *c*-Cyts
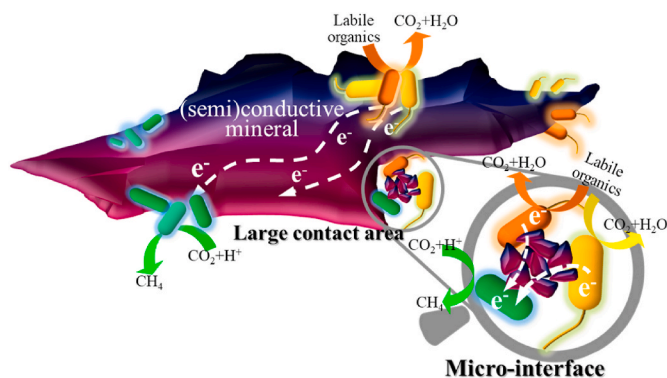

Fig. 2. Schematic of (semi)conductive minerals serving as an electrical conductor to facilitate interspecies electron transfer.

adherence to (semi)conductive minerals. Correspondingly, biofilms form on mineral surfaces by bacterial surface attachment and mono-layer/multilayer growth. Because of suitable conductivity by the (semi)conductive minerals, electron transfer from bacteria to the anode interface is readily facilitated. In this scenario, a conductive network with electron transfer hop might be reconstructed due to coexistence with these (semi)conductive minerals, thereby eliminating sluggish electron transfer in the "blind areas" that lack the relevant electron shuttling matrices. Notably, e-pili and membrane-bound *c*-Cyts serve as

important carriers for electron transfer [69,70], and their direct contact with different nanosized (semi)conductive minerals might exhibit differential physiological responses. The specific mechanisms are further discussed in sections 3.2 and 3.3.

3.2. Nanosized (semi)conductive minerals stimulate the formation and expression of e-pili and c-cyt

In the presence of (semi)conductive minerals, EET efficiency is
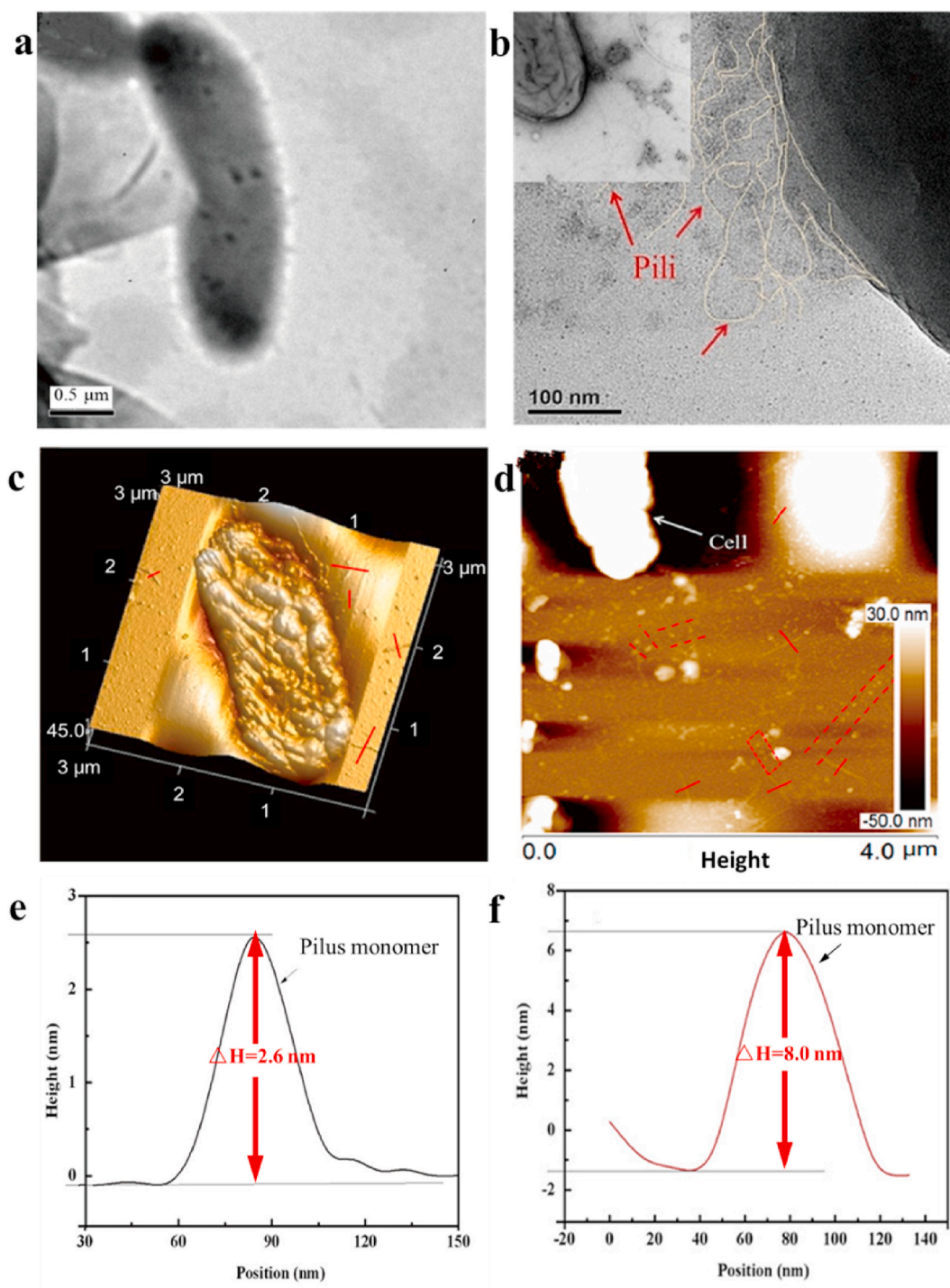

Fig. 3. Comparisons of TEM (a and b) and AFM (c and d) images, as well as heights of pilus monomer (e and f) for *G. sulfurreducens* cells in treatments without maghemite NPs and direct contact with maghemite NPs [77]. In AFM image, red line indicates the existence of pilus. When cells are in direct contact with maghemite NPs, very sparse electrically conductive pili were observed through AFM and TEM observation; the greater heights of pilus monomer were stretched through AFM measurement. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

closely correlated with the degree of crystallinity and crystal size and with the morphology of the minerals [71,72]. Particularly, smaller mineral sizes with larger specific surface areas usually exhibit higher electron transfer performance than large mineral samples [73–75]. Previous investigations conducted using natural or fabricated single mineral crystals, with dimensional scales ranging from nanometer to submicron, confirmed that electroactive species exhibited an apparent recognition towards nanosized minerals. To establish an effective communication between microbes and extracellular electron acceptors, microbes stretch their e-pili in the presence of well-crystalized nano-sized minerals. This physiological response makes microbial assemblages electrically conductive facilitating enhanced respiratory interactions [17]. It was also found that certain *c*-type cytochrome (*c*-Cyt) genes, such as *omcJ*, *pgcA* and *omcK*, were upregulated in the presence of conductive magnetite nanoparticles (NPs) and semi-conductive hematite NPs [25]. Similar observations were reported by Zhou et al. [76] using TiO_2 NPs (a model compound for the semi-conductive mineral of nanosized rutile) to induce the formation of nanowires by upregulating *PilA* expression by 3.1-fold compared to treatments without TiO_2 NPs. It appears that the responses of e-pili and *c*-Cyts might compromise the addition of nanosized semi-conductive/conductive minerals. Notably, our recent finding confirmed that e-pili and *c*-Cyts of *G. sulfurreducens* were stretched through direct contact with a representative nanosized semiconductive mineral, maghemite (γ-Fe_2O_3 NPs) (Fig. 3) [77]. These findings provide strong evidence of the involved biofilm morphologies and electrochemical properties underlying molecular and physiological levels in situations with coexisting nanosized conductive/semiconductive minerals.

Because these nanosized minerals are easily embedded into biofilms, the compacted interfacial system that results from their coexistence can supply more active sites for close contact with the electroactive proteins/cytochromes of microorganisms. These interfaces are particularly beneficial to the direct transport of electrons using multiheme *c*-Cyt (OmcS) associated with the outer membrane [78]. Therefore, a favorable interspecies modification for construction of a "multicultural microbial community-nanosized (semi)conductive mineral" network could be achieved by spatially combining bacterial nanowires with outer-membrane Cyts. This approach offers new insights into selected *c*-Cyts-free microbes for the formation of nanowires to participate in electron transfer. Considering that mixed strains are especially important in systems such as wastewater treatment, environmental remediation and energy production [79,80], interspecies modification is expected to favor the use of nanosized (semi)conductive minerals in bioengineering applications.

3.3. Magnetite stimulates the production of specific enzymes related to electron transfer

Under natural aerobic and anoxic conditions, a variety of microorganisms have an inherent ability to use iron as an essential element for synthesis of cellular components (*e.g.,* metalloenzymes) and energy metabolism [81]. It is well known that processes such as acidogenesis and methanogenesis are mediated by iron-containing enzymes [82]. The active sites derived from the involved mediated enzymes, such as [Fe–Fe] hydrogenase, $F_{420}H_2$ dehydrogenase, F_{420}-reducing hydrogenase, [Fe] hydrogenase, acetyl-coenzyme A synthetase and for-mylmethanofuran dehydrogenase, mostly have iron-containing clusters, which are probably responsive to induction by magnetite. The close mutual contacts between active sites and magnetite (due to the strong attraction by magnetite) might inevitably lead to increased expression of specific enzymes. Therefore, apart from ameliorating interface charge transfer, magnetite supplementation into bioelectrochemical systems is likely to activate the redox enzyme systems related to EET [83,84].

Support for magnetite induced enzyme production follows from magnetite amendment studies that document stimulation of enzymes activities involved in processes such as acidogenesis and methanogenesis [26,85,86]. In early 2005, Eugenii et al. [87] observed improved direct electron transfer performance between a conductive support and enzyme cofactors in a biofuel cell that was surface-reconstituted with magnetite. Further, an anaerobic digestion study revealed that the activities of key enzymes, such as acetate kinase, protease and coenzyme F_{420} that represent the capabilities for acido-genesis, hydrolysis and methanogenesis, were all increased by at least 20% with the assistance of magnetite [86]. These results imply an enhanced direct interspecies electron exchange driven by magnetite resulting in energy conservation. The conserved energy can be used for the production of e-pili or *c*-Cyt in exoelectrogenic bacteria, such as *Geobacter* or *Shewanella* species, and for stimulating key enzymes expression in electrotrophic methanogens.

Addition of magnetite NPs to an acetogens-methanogens syntrophic system for methanogenesis (Fig. 4a) resulted in selective up-regulation for the expression of mRNA encoding several enzymes. These enzymes were involved in CO_2 reduction (in hydrogenotrophic pathway) or ac-etate decarboxylation (in aceticlastic pathway) into the common inter-mediate of 5-Methyl-THMPT [26,86]. Because of stimulation by magnetite NPs, the up-regulated expression of 5,10-methylenetetrahy-dromethanopterin reductase greatly promoted CO_2-dependent meth-anogenesis in the hydrogenotrophic pathway. Further, increased activities of acetate kinase and acetyl-CoA decarbonylase/synthase complex β subunit are beneficial to acetate-dependent methanogenesis in the aceticlastic pathway. Thus, magnetite NPs were involved in the consolidation/establishment of two pathways for final methanogenesis. To profile the expression levels of key enzymes and *c*-Cyts in methane metabolism following magnetite additions to syntrophic cultures, iTRAQ quantitative proteomic analysis was applied by Jing et al. [88]. They revealed a marked increase in production of several chemical compounds (*e.g.,* methylmalonyl-CoA, succinyl-CoA and acetyl-CoA) related to activities of key enzymes involved in aceticlastic methano-genesis of *Methanosaeta* and possible proteins (cytochrome *c* oxidase) related to DIET and associated with the methanation of propionate [88]. This phenomenon is consistent with the results from Wang et al. [26] for syntrophic metabolism of butyric acid in magnetite-supplemented *Geobacter/Methanosaeta* co-cultures. Therefore, magnetite-mediated DIET results from a rapid buildup of the enhanced activities of key enzymes responsible for rapid electron transfer in syntrophic partners and rep-resents an important mechanism for improving the efficiency of methanogenesis.

3.4. Magnetite stimulates EPSs secretion to assist EET

Microorganism production of extracellular secretions is a normal physiological protection response to contact with foreign materials. Until now, up-to-date reviews reporting on EET highlight that EPSs are crucial for facilitating EET [89,90] because most EPSs are dominated by extracellular redox enzymes and electroactive humic substances that are likely to serve as electron shuttles [91]. In addition, the secreted EPSs surrounding microbial cells function as viscous nets that can trap extracellular *c*-Cyts for construction of enlarged conductive biofilms [91]. This observation implies that the EPSs produced by microorgan-isms could serve as a transient media for microbial EET via electron hopping. Thus, magnetite stimulation of EPS secretions might elicit a promotional effect to enhance EET, which is highly relevant for exploitation by microbiology and engineering fields utilizing microbial materials/processes.

Multiple lines of direct evidence show that magnetite stimulates DIET with the support of EPSs. For instance, Yan et al. [92] and Li et al. [93] confirmed that addition of magnetite induced increased EPS se-cretions and correspondingly promoted DIET performance. Insights from anaerobic digestion studies further showed enhanced DIET effects owing to augmented EPSs derived from stimulation by magnetite sup-plementation (Fig. 4b). Magnetite amendment effectively alters EPS composition (especially increased contents of redox enzymes and humic
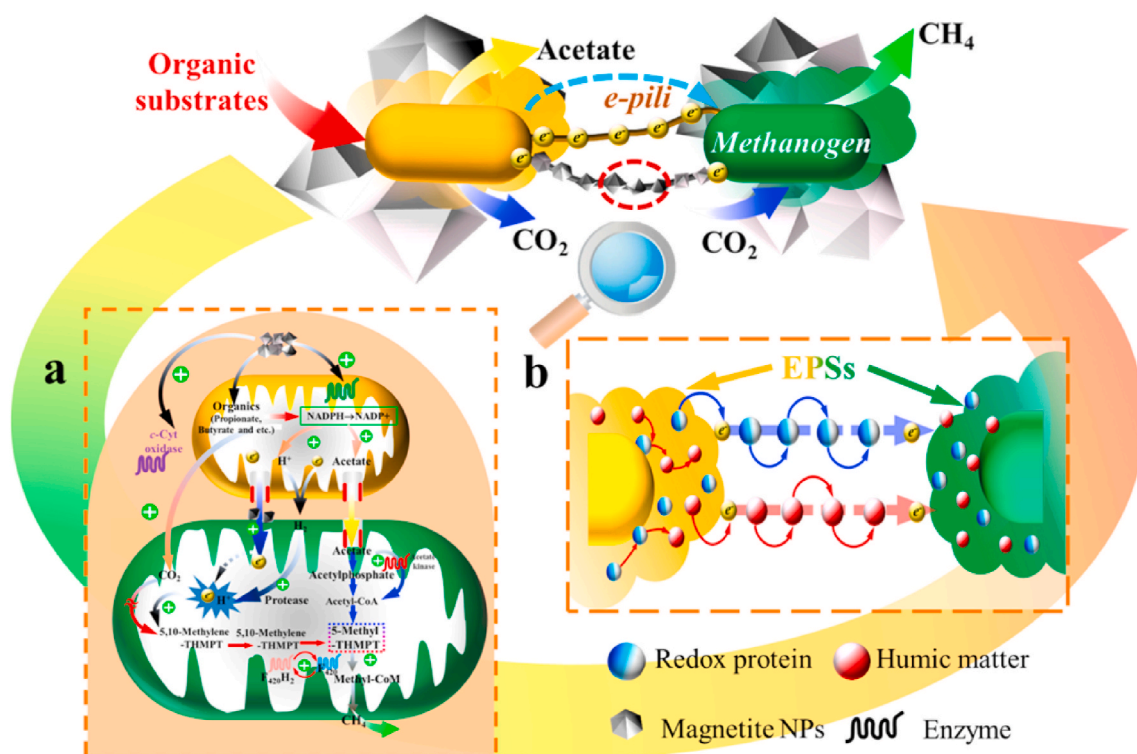
Fig. 4. Mechanisms of syntrophic methanogenesis via stimulating the production of specific enzymes (a) and shuttling electrons in exuberant EPSs (b) stimulated by magnetite.

substances within EPSs [92,94]), contributing to successful establishment of EET conditions. Commonly, magnetite interacts with the EPS layer first to establish direct contact with cells, implying that the secreted EPS preferentially serves as a source of conductive materials to facilitate EET. Hence, in a scenario of augmented EPSs, a magnetite induced EPS diffusion mechanism promotes more efficient long-distance electron transfer through electron multi-hopping relative to the given conductive mechanism alone. Compared with other magnetic materials, magnetite NPs appeared to have superior advantages in stimulating EPS production. Unlike magnetite, more extracellular polysaccharide was secreted around microorganisms in contact with zero-valent iron NPs [93]. In contrast, *Geobacter* species in contact with magnetite NPs developed favorable strategies to secrete more EPSs to enable cell-to-cell connections between microorganisms and/or terminal electron acceptors for methanogenesis through the DIET pathway [93]. In contrast, EPS secretion was comparably limited in the presence of zero-valent iron NPs [93]. This result is ascribed to more exopolysaccharides without redox activity that can serve as circumvolute appendices by attaching to the cell surfaces to form complex networks [95], which potentially decrease the direct contact between cells and the reactive surfaces of zero-valent iron NPs. Indeed, the resulting physiological responses of extracellular secretion and the involved direct interspecies electron transport are closely correlated with the dosages of magnetite amendments, as well as the preferential behavior by microorganisms.

4. Semiconductive mineral-derived photoelectrochemical process

4.1. Alternative photoelectrotrophy microbial metabolism favored by mineral photoelectrons

It is well known that solar-to-chemical energy conversion relies on photosynthetic systems in which phototrophic microorganisms use solar energy via photosynthetic pigments. Previous evolutionary surveys have demonstrated that semiconductive mineral-induced photocatalysis

played a critical role in the origin and early evolution of life on Earth [96–98]. In the photoelectrophy pathway, semiconductive minerals play a similar role together with photosynthetic pigments via conversion of solar energy to chemical or biological energy (in the form of carbohydrates, NADH or NADPH) in the photosynthesis reaction center with the participation of specific proteins and coenzymes [99,100]. Many previous investigations report that mineral photoelectrons are available for the growth of both phototrophic and nonphototrophic microorganisms in sunlight-enriched terrestrial geothermal ecosystems [101–103], particularly in selective zones enriched in iron or manganese-bearing minerals are enriched [104,105].

Photoelectrons have a certain long-range transitivity [106,107], implying that mineral photoelectrons can serve as an alternative available energy source for support of microbial growth and metabolism. Considering the widespread occurrence of semiconductive minerals with sunlight and microorganisms in the epigeosphere, the proliferation of phototrophic microorganisms can be stimulated by mineral photoelectron energy endowed from solar-irradiated semiconductive minerals. Previous investigations provide solid evidence that a typical phototrophic strain (*Rhodopseudomonas palustris* TIE-1) absorb solar energy for its metabolism and growth by coupling microbial phototrophic Fe(II) oxidation to form a nano-scale Fe(III)-bearing mineral [34, 108]. The expressions of *pioABC* operons in *R. palustris* TIE-1 are specifically required for phototrophic Fe(II) oxidation, which are encoded by outer-membrane proteins (Pio-phototrophic iron oxidation ABC) to uptake extracellular electrons [108]. Recently, Wang and coworkers reported that the survivability of CdS-coated *R. palustris* cells incubated without organic carbon under intermittent illumination displayed a survival advantage compared to their natural counterparts [109]. Owing that the key enzyme in the CO_2-reducing Calvin cycle is activated by photo-excited semiconductors [110], NADPH regeneration was promoted via accepting more photoelectrons to consolidate the photosynthetic electron transfer chain [109,111]. This novel energy metabolism of *R. palustris* utilizing photoelectrons provides several competitive advantages for their survivals and biotransformation of inorganic

materials in organic-depleted environments. Moreover, it has been found that Fe(II) oxidation rates driven by an anaerobic anoxygenic phototrophic *Rhodovulum iodosum* were positively correlated with light intensities within an appropriate range [112], contributing to the deposition of banded Fe(III)-mineral formations. Owing to the ultraviolet light absorption capacity of Fe(III)-bearing minerals [113], phototrophic Fe(II)-oxidizing bacteria are partially protected from cellular damage from ultraviolet irradiation [114].

Because microbial community structure can be influenced by ecological destabilization (*e.g.,* biotic interactions, habitat affinities or microbial physiologies) [115], certain individual species might execute a specific evolutionary strategy in response to environmental changes over short and long timescales [116]. These obtained findings offer valuable insight into a typical evolutionary process of phototrophic microorganisms that exhibit good physiological fitness towards photoelectrons for their adaptive evolution.

Compared with phototrophic microorganisms, the pathways through which nonphototrophic microorganisms accept electrons rely on microbial degradation of organic substrates. However, nonphototrophic microbes can also accept mineral photoelectrons delivered from the conduction band of semiconductive minerals to the microbial outer membrane proteins, thus favoring a novel pathway [99]. In a solar-illuminated fuel cell, Lu et al. [117] found that biomass of *Alcaligenes faecalis* in association with natural semiconductive mineral photocatalysis reached up to three orders of magnitudes higher than treatments with no photocatalysis control. This result confirms that phototrophic metabolism can also act as an alternative energy-yielding pathway for nonphototrophic microorganisms, thus overcoming limitations of the conventional chemotrophic metabolism of oxidizing organic or inorganic compounds (Fig. 5). Our recent findings also confirmed that amendments with model compounds for the semiconductive minerals (anatase and sphalerite) resulted in increased in the abundances of several metal-reducing bacteria (*e.g., Bacillus, Geobacter, Clostridium* and etc.) in the soil microbial community under intermittent
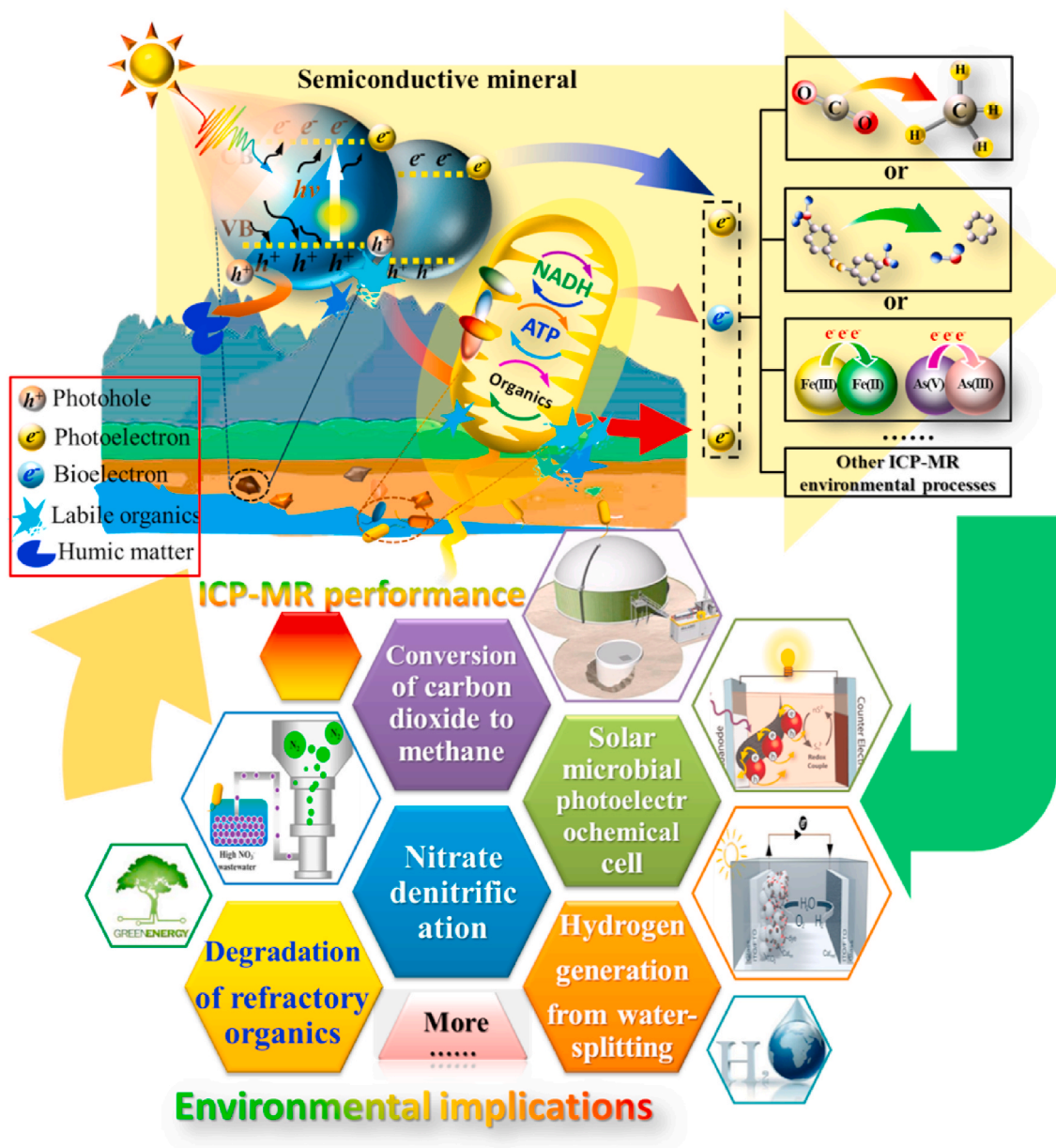

Fig. 5. Interplay within the ternary complex system of "solar radiation-semiconductive minerals-nonphototrophic microorganisms" and its environmental implications.

illumination [118,119]. Notably, there was improved bacterial viability in biofilms and high enrichment of *Geobacteraceae* (a nearly 1.5-fold increase of relative abundance vs. control) in a photobioanode that was equipped with hematite [120]. Because a variety of electricigens that can donate electrons to electrodes without the addition of electron shuttles are affiliated with *Geobacteraceae* [121], enhanced EET performance can be realized with the assistance of semiconductive minerals and visible light. These findings provide compelling evidence for a new microbial energy metabolism pathway that is distinguishable from conventional phototrophy and chemotrophy modes in nature. The novel pathway involves the growth of nonphototrophic microorganisms that are stimulated by a mineral photocatalysis-induced microbial metabolism. This novel energy-utilizing pathway linked to mineral photoelectrons offers opportunities and challenges to satisfy future renewable energy needs (as discussed in sections 4.2 and 4.3).

4.2. Mineral photoelectrons participate in microbial extracellular respiration

Mineralogical and spectroscopic studies confirm the ubiquitous nature of semiconductive minerals in the environment, such as metal oxide and metal sulfide. These minerals can assemble optical band gap energies [122,123], which can excite photoelectron-photohole pairs by solar illumination [124]. Because of crystal defects and surface leakage along the edge of these semiconductive minerals, the excited photoelectron-photohole pairs usually have comparably long lifetimes [124]. In addition, abundant humic substances and reductive inorganic materials (*e.g.,* sulfides) in the biosphere are accessible and can serve as a scavenger for the photoholes. Such alternative administration enables the separation of photoelectron-photohole pairs through the capture of photoholes and guarantees that photoelectrons participate in microbial extracellular electron transfer. Therefore, photoelectrons excited from semiconductive minerals under solar illumination are considered as desirable alternative electron sources for nonphototrophic microorganisms to replace/complement conventional bioelectron sources produced

Table 2
Stimulatory effects of semiconductive mineral model compounds used in improving ICP-MR performance.

Reaction	Inoculum	Substrate	Model compound	Size/area	Remarkable results	Ref.
Reductive dissolution of As(V)/Fe (III)	Tailing soils	Acetate	ZnS (sphalerite)	3×10^3–5×10^3 nm	• Increase in released levels of As(III) and Fe(II) by 2.1- and 1.6-fold • Increase in total abundance of metal-reducing bacteria by 23%	[118]
Reductive dissolution of As(V)/Fe (III)	Tailing soils	Acetate	TiO_2 (rutile) NPs	50–100 nm	• Increase in released levels of As(III) and Fe(II) by 1.3- and 1.7-fold • Decrease in acetate consumption by 1.2-fold	[119]
Conversion of carbon dioxide to methane	Anaerobic activated sludge	Acetate	TiO_2 (rutile) nanowire	Length > 10^4 nm	• Up to 96% of Faradaic efficiency for CO_2 reduction to CH_4 • CH_4 produced at an average rate of 94.6 ± 1.7 μL/cm^2 per day	[23]
Enhance the current production	Anaerobic activated sludge	Acetate	α-Fe_2O_3 (hematite)	UR[a]	• Shortened start-up time from 2.5 days to 1.1 days • Decrease in charge-transfer resistance by 50%	[120]
Solar microbial photoelectrochemical cell	*S. oneidensis* MR-1	Lactate	α-Fe_2O_3 (hematite)	Length: 5×10^3–10^4 nm	• Increase in production of photocurrent by 1.5-fold • 2 weeks of long-term operation for current generation	[137]
Solar microbial photoelectrochemical cell	*S. oneidensis* MR-1	Lactate	p-Cu_2O (cuprite) nanowire	Length: 3×10^3–10^4 nm	• Substantial current generation under white light illumination • Self-sustained operation for more than 50 h	[138]
Denitrification of nitrate by reduction to nitrogen gas	Agrowaste-derived periphyton	Woods Hole culture medium	CdS (greenockite) NPs	UR	• Increase in NO_3^- reduction to N_2 by 1.5-fold • Increase in EPS yield and abundance of electroactive bacteria strains	[139]
Mineralization of tetracycline hydrochloride	Anaerobic activated sludge	Acetate	Ag/TiO_2 (rutile)	UR	• Accelerate of TCH removal by 11% in the first 2 h • Enrichment of genera responsible for scavenging organic substrates	[140]
Degradation of 4-chlorophenol (4-CP)	*G. sulfurreducens*	Acetate	N-doped TiO_2 (anatase type)	8–10 nm	• Increase in degradation efficiency of 4-CP by 3.1-fold • Increase in current generation by 50%	[134]
Conversion of nitrate to nitrogen gas	Anaerobic activated sludge	Acetate	TiO_2 (anatase)/Ti	Surface area: 16 cm^2	• Increase in current efficiency for denitrification by 19% • Increase in denitrification rate constant by 36%	[22]
Phenol degradation	Anaerobic activated sludge	Acetate	Er^{3+}: $YAlO_3$/TiO_2	UR	• Shortened reaction time by at least 6 h • Increase in removal of phenol and DOC by 48.5% and 1.94-fold	[141]
Self-sustaining hydrogen generation	Anaerobic activated sludge	Acetate	$GaInP_2$-TiO_2-MoS_x	Surface area: 0.081–0.09 cm^2	• Up to 93–97% of high current to H_2 conversion recovery efficiency • Produced stable current (0.4 mA/cm^2) for 24 h without any external bias	[142]

[a] UR = Unrecorded in corresponding published article.

from microbial degradation of energetically-expensive organic substrates (*e.g.,* acetate and lactate).

Since the potentials of highly reductive mineral photoelectrons are more negative than those of most of the biological compounds [125], the excited photoelectrons are theoretically accepted by microorganisms to drive specific biogeochemical reactions. Moreover, the conduction bands of many semiconductive minerals are sufficiently negative for excitation of photoelectrons under solar irradiation, thus enabling an intimately coupled photoelectrochemical-microbial reduction (ICP-MR) of protons to hydrogen or reduction of carbon dioxide to methane (Fig. 5) [23,126–128].

Considering that *c*-Cyts are critical for electron transfer [16,129], the

accessibility of *c*-Cyts for photoelectron transfer requires more careful consideration and experimental investigation. In recent studies by Zhou et al. [130–133], markedly higher transcription levels for *c*-Cyts in *G. sulfurreducens* and functional ferredoxin-dependent hydrogenase in *Methanosarcina barkeri* (*M. barkeri*) were all found in response to illuminated cultured systems. This suggests that a *c*-Cyts-mediated mechanism was also important in the photoelectron transfer pathway in a majority of electrogenesis strains. Because the potentials of the conduction band for many semiconductive minerals (*e.g.,* sphalerite, rutile and greenockite) are sufficiently negative [122], the excited photoelectrons are thermodynamically allowed to be transported to enzymes involved in the EET process. Based on this knowledge, various
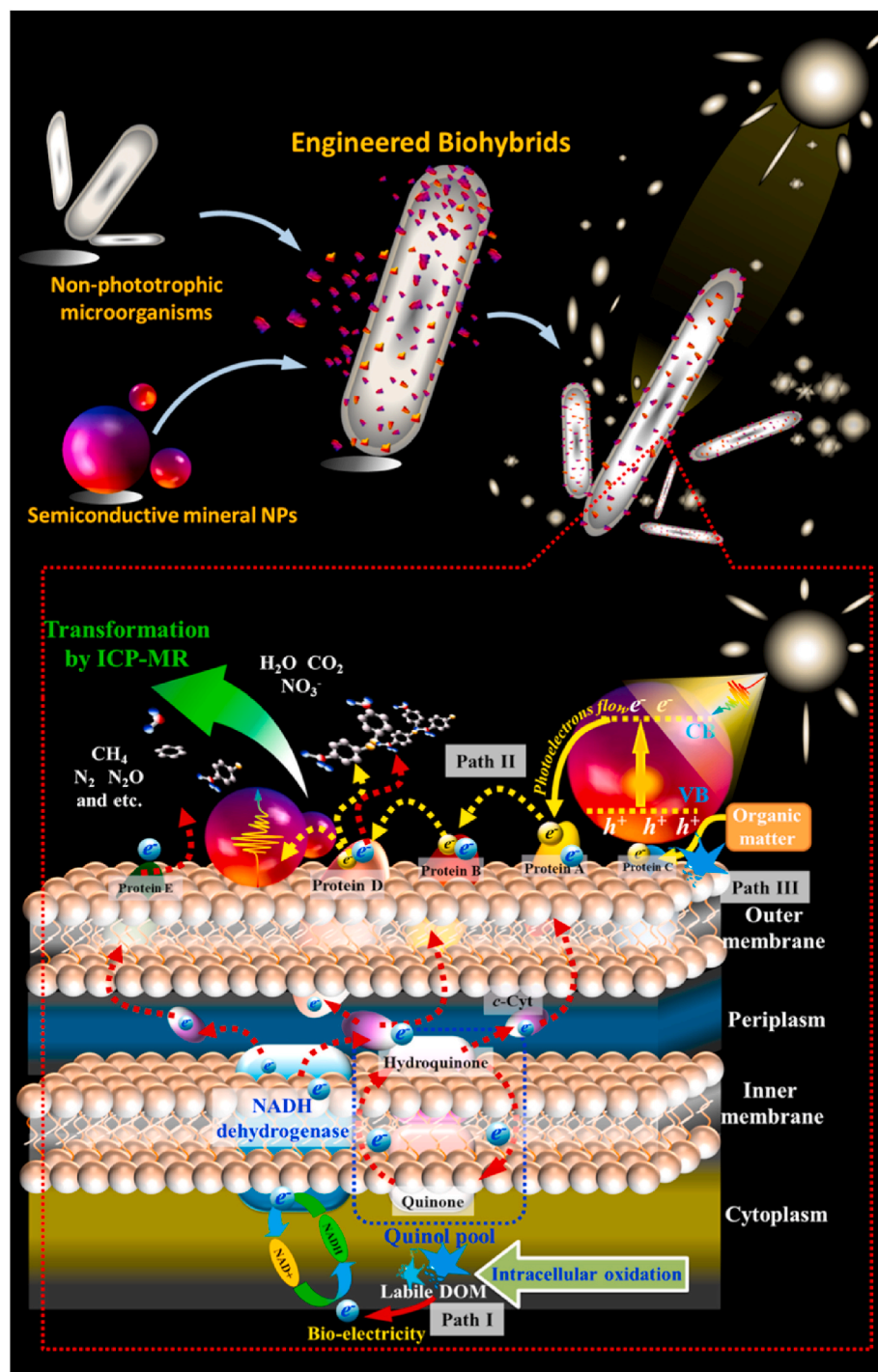

Fig. 6. Schematic illustration for engineering of grafted biohybrids and electron transfer pathways involved in the ICR-MR process. Photoelectron flows are profiled with yellow dashed lines, and bio-electricity derived from microbial degradation of labile DOM is profiled with red dashed lines. Path I, Path II and Path III are denoted as electron transfer pathways derived from microbial degradation of labile DOM, mineral photoelectrons and oxidative decomposition of photoholes, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

proof-of-concept studies have been advocated and their findings demonstrate increasing promise for successful application in several environmental uses, such as decoloration, methane production and organic pollutant degradation (Table 2). Inspired by the above-mentioned observations, a novel methodology was developed using nitrogen doping or in conjunction with a multilayered metal-organic framework (MOF) to construct new ICP-MR systems (Table 2) [134–136]. With the aid of these new modifications, ICP-MR performance is expected to greatly improve making this technology more highly efficient and cost-effective. Overall, the newly constructed ICP-MR systems enhance the light-harvesting wavelength range and overcome the limitations that might result from the weak electronic connection between substitutes for modified mineral compounds and c-Cyts or rapid recombination of photoelectrons and holes.

4.3. Enhanced photoelectric performance in engineered nonphototrophic microorganism-semiconductive mineral biohybrids

Previous research clearly demonstrates that mineral photoelectrons reinforce the EET process and exhibit a distinct advantage from photocatalysis of semiconductive minerals, compensating for deficiencies in pollutant biotransformations by supplying adequate organic substrates. Current efforts are exploring how to integrate mineral photoelectron production into ICP-MR processes to benefit future biochemical engineering applications (Fig. 6). Nonphototrophic microorganisms commonly have higher metabolic activities than those of phototrophic microorganisms and display a superior robustness for loading of semiconductive mineral particle compounds on their cell surfaces. This observation implies the possibility of constructing specific electron transfer agent-free biohybrid systems that can be applied for ICP-MR. Because ICP-MR systems are unavoidably exposed to light, photohole-induced sensitive suppression of microbial activities might make ICP-MR less efficient. Additionally, a suitable photoirradiated mineral energy level is required to enable electron transport across the outer-membrane proteins to ensure efficient electron transfer when loading. Therefore, it is essential to determine which types of photocatalytic semiconductive minerals should be selected to optimize their use in challenging ICP-MR systems and avoid the adverse effects of photocatalytic suppression in grafted biohybrids.

To address the aforementioned limitations of biohybrid systems, the substitutes for semiconductive minerals grafted onto the surface of biohybrids must not only enable light-harvesting energy transfer but also exhibit high biocompatibility and higher electrical conductivity than the microbe alone. Grafting can circumvent restrictions from adverse photoinduced effects and the disadvantages resulting from a charge transfer barrier. Among a variety of mineral substitutes, cadmium sulfide nanoparticles (CdS NPs, a model nanosized compound for semiconductive greenockite) are viewed as a particularly suitable candidate for in situ grafting in engineered biohybrids. The CdS NPs have a high photosensitive coefficient, narrow band gap and stable surface electrostatics that can support the junctions with microbes to overcome the charge transfer barrier [143].

Due to the superior capabilities of CdS NPs in ICP-MR, considerable effort has focused on use of engineered CdS NPs-grafted biohybrids to evaluate their potential for various environmental engineering applications (e.g., methane production, azo dye degradation and denitrification), as shown in Table 3. For instance, Ye et al. [131] revealed that high methane production rates comparable to that of plants or algae when using an innovative biohybrid system consisting of CdS NPs and Methanosarcina barkeri. Similarly, rapid light-driven decolorization of methyl orange was achieved by a G. sulfurreducens-CdS NPs biohybrid [132]. The highest maximum kinetic rate constant (1.441 h^{-1}) was the highest reported in the literature for methyl orange biodecolorization. Notably, the catalytic ability displayed for methyl orange decolorization by the G. sulfurreducens-CdS biohybrid retained its effectiveness after four repeated-use cycles. These results demonstrate that CdS-derived biohybrids display a strong robustness for light harvesting and excellent biocompatibility for electron transfer in ICP-MR systems, as well as long-term durability in practical applications.

Due to interactions between enhanced electrical conductivity and mineral photoelectrons, the produced synergistic effects are conducive to nonphototrophic microorganisms that gain light energy through semiconductive CdS NPs, thereby improving the ICP-MR performance in biohybrids. Outer membrane-bound cytochromes of engineered biohybrids were shown to participate in photoelectron transport by acting as the terminal reductase [131–133], indicating good biocompatibility of CdS NPs for biohybrid construction. Thus, biohybrids constructed through in situ grafting of nanosized semiconductive mineral

Table 3
Selected applications of illuminated engineered biohybrids by superficial precipitation of semiconductive minerals onto nonphototrophic microorganisms.

Application	Biohybrid	Illumination	Remarkable results	Ref.
Decolorization of methyl orange	G. sulfurreducens-CdS biohybrid	LED irradiation 3.07 ± 0.14 mW/cm^2	• The maximum kinetic constant reached 1.441 h^{-1} • Exhibited favorable catalytic ability during 4 repeated recycles	[132]
Conversion of carbon dioxide to methane	M. barkeri-CdS biohybrid	Violet LED irradiation 1.0 ± 0.14 mW/cm^2	• Methanogenesis rate (0.19 μmol/h) was comparable to that of plants or algae • Nearly 1.5-fold increase of mcrA gene copies in biohybrid	[131]
Denitrification of nitrate to generate nitrous oxide	T. denitrificans-CdS biohybrid	Violet LED irradiation 3.07 ± 0.14 mW/cm^2	• More than 72.1% of NO$_3^-$ was converted into N$_2$O • More than 96.4% of N$_2$O dominated in final gaseous products (N$_2$O and N$_2$)	[133]
Hydrogen generation	E. coli-CdS biohybrid	Xenon lamp irradiation 200 mW/cm^2	• 1800 μmol of H$_2$ produced within 3 h under 2000 W/m^2 of visible light irradiation • Higher quantum efficiency (~9.6%) of biohybrid than that of phototrophic bacteria	[144]
Synthesis of acetic acid from carbon dioxide	Moorella thermoacetica-CdS biohybrid	Violet LED irradiation with photon flux of 5 × 10^{18} cm^{-2}· s^{-1}	• Nearly 90% of CO$_2$ was converted into acetic acid in illuminated biohybrid • 10-fold quantum yields vs. that of the averages determined for plants and algae	[101]
Biological nitrogen fixation	Rhodopseudomonas palustris-CdS biohybrid	Visible light irradiation 8 mW/cm^2	• 1.5-fold increase of solid biomass accumulated in biohybrid vs. that of control • Outstanding photosynthetic efficiency (6.73%) and malate usage efficiency (0.06 g/h)	[111]
Conversion of DHS to SA	Saccharomyces cerevisiae-InP biohybrid	Visible light irradiation 5.6 mW/cm^2	• Increased in highest SA/DHS conversion ratio by 35-fold • Increased in total SA production by 24-fold	[24]

Note: LED = light emitting diode.

compounds could serve as an effective approach for enhancing localized energy delivery and shortening the lag phase of electron transport. Further, research findings confirm the desirable capability of CdS-derived biohybrids in reinforcing the electron transfer in ICP-MR systems. However, there is a paucity of information concerning alternative semiconductive mineral compounds for potential use in designing new types of highly functional biohybrids. One promising alternative is the assembly of indium phosphide NPs onto *Saccharomyces cerevisiae* for improved conversion of 3-dehydroshikimic acid (DHS) to shikimic acid (SA) [24]. Therefore, further research evaluating potential alternative semiconductive mineral compounds for construction of biohybrid complexes is among the highest research priorities.

4.4. Significance of semiconductive minerals in assisting ICP-MR systems

Evolutionary surveys confirmed that various natural composite materials are grown by biologically controlled self-assembly processes under ambient conditions [145]. For instance, mineral membranes possessing nanostructure and excellent biocompatibility with attached microorganisms are widely developed on rock/soil surfaces and are highly active upon solar illumination [105]. These naturally self-assembled materials commonly exhibit intimate coupling performance and strong stability. Minerals have a fix chemical composition and highly ordered internal atomic structure, implying that several artificial analogues, like synthetic materials or engineered nanomaterials, may serve as suitable substitutes for semiconductive minerals. Inspired by developments in biomimetic materials, novel semiconductive minerals-based biomaterials are being developed for potential use as solar-driven biocatalysis [146]. Employing synthetic biological approaches of incorporating nanoscale analogues to construct novel biohybrids are expected expand biohybrid designs beyond the traditionally independent microbial EET process. Newly developed mechanistic models for microbial EET will provide a theoretical framework for targeted bioengineering applications incorporating nanosize-mineral analogues and solar illumination in future applications.

Although successful applications derived from familiar semiconductive mineral substituents such as TiO_2, CdS and Fe_2O_3 on ICP-MR have reached a functional level, the potential attributes other highly photosensitive minerals have received little attention. To assess the potential of mineral substituents used in ICP-MR systems, it is essential to evaluate their catalytic capabilities in more complex mixed substrates or under more demanding environmental conditions. Currently, an increasing number of investigations are underway to explore renewable energy production to alleviate the demand on carbon-based fuels in industrial manufacturing is still in great demand [23,147]. Thus, improving the efficiency of semiconductive mineral-mediated hybrid microbial-photoelectrochemical systems for energy conversion (*e.g.,* generation of hydrogen and methane) will hold great promise for meeting future renewable energy goals. Additionally, solar energy is recognized as the most readily available and cost-effective renewable clean energy source for construction of hybrid microbial-photoelectrochemical systems for environmental remediation. Hence, the hybrid systems that integrate microbial catalysts with inorganic semiconductive mineral substituents to harvest sunlight provide a new platform for the future development of renewable energy production and environmental engineering remediation.

5. Applicability of mineral substituents for enhancing bioelectrocatalytic performance

5.1. Production of renewable energy and value-added chemicals

At present, rapid economic expansion and emerging global climate change render an urgent need for production of clean fuel and renewable energy. In microbial electrosynthesis systems, enzymes undertake conformational changes and promote steric effects to aid in reaction selectivity [148]. Armed with the photocatalysis effect by semimineral substituents, energy efficiencies of biohybrid systems using CO_2/H_2O and solar radiation as substrate and an energy source could exceed that of natural photosynthesis. Given the advantage of the abovementioned engineered biohybrids, fuels and chemicals could be synthesized from CO_2 with a high quantum efficiency due to the combination direct enzyme activation and photocatalysis effects in a given biohybrid system [101,109,149]. Thus far, the efficacy of renewable energy, such as hydrogen, methane or other hydrocarbons, has been successfully demonstrated using bioelectro-synthesis from various engineered biohybrids (Table 3).

A previous study demonstrated acetic acid generation from CO_2 reduction in a *Moorella thermoacetica*-CdS NPs biohybrid [101]. We posit the feasibility of more value-added multicarbon products (*e.g.,* ethanol, butanol and polyhydroxybutyrate [PHB]) are theoretically possible to enhance bio-produced acetate using various functional biohybrids. For example, Wang and coworkers demonstrated enhanced CO_2 reduction and valuable C_{2+} chemical production by a *Rhodopseudomonas palustris*-CdS hybrid system [109]. This system increased production of β-PHB, solid biomass and carotenoids by 47%, 48% and 22%, respectively [109]. They further found that the grafted biohybrid exhibited a survival advantage over its natural counterparts under autotrophic conditions. Their findings imply that pairing whole-cell biocatalysts with semiconductive mineral substituent-derived photoelectrochemical systems could decrease energetic barriers to CO_2 activation. Similarly, Ding and coworkers designed novel core-shell nanocomposites by immobilizing ZnS quantum dots to the outer layer of CdS quantum dots to construct a corresponding biohybrid system (*Cupriavidus necator*-CdS@ZnS biohybrid) [150]. Notably, they revealed that prominent light-driven ethylene and PHB production from CO_2 were achieved through energy conversion excited from core-shell nanocomposites coupled with targeted enzymes in *Cupravidus necator* [150]. This implies that optimizing the properties of mineral substituents accentuates the possibility of controllable bioelectrocatalysis for renewable energy production. Hence, engineered biohybrids offer an additional strategy for photocatalysis by upgrading and reconstructing mineral substituents, including opportunities for novel research regarding CO_2 conversion to renewable energy and value-added chemicals.

5.2. Environmental engineering remediation

Inspired by semiconductive mineral-induced photocatalysis, intimate coupling of photocatalysis and biodegradation (ICPB) in conjunction with appropriate mineral analogues provides an opportunity to overcome the limited efficiency of independent processes [151]. Such amendments provide a feasible strategy in environmental engineering applications targeted to degrade/transform bio-refractory organic pollutants. Upon irradiation, oxidative photoholes are produced in semiconductive mineral substituents to promote photocatalytic degradation of bio-refractory organic pollutants into low-molecular-weight byproducts and synchronously separate photoelectrons, hindering the recombination of photoelectron-hole pairs [152]. Subsequently, the resulting byproducts are susceptible to further mineralization to CO_2 and H_2O by microbial degradation. Timely microbial degradation of byproducts effectively circumvents any adverse effects imposed by unfavorable oxidation conditions and interferences with microbial metabolic processes. Recent research reports successful degradation of bio-recalcitrant pollutants, including tetracycline hydrochloride, reactive dyes, phenazopyridine and nitrofurazone, by ICPB reactors configured with specific mineral analogues or their modified substitutes [153–156]. Overall, amendment of ICPB systems with specific mineral substituents offers operational efficiencies and flexibility for application in pollutant control and bioremediation strategies.

6. Conclusions and perspectives

This synthesis provides a large audience with a summary of the unique capabilities of different types of minerals contributing to regulation of EET processes. In most cases, the addition of a specific mineral or appropriate model substituent promotes improved EET performance and fulfills/complements the demand for high bioavailability of carbon in pure-culture systems, syntrophic cultures and microbial-photoelectric coupled cultures. Specifically, supplementation with nanosized-mineral substituents possessing favorable redox activity, suitable conductivity, magnetism or photosensitivity has great potential to improve the electron transfer efficiency. This infers that mineral-boosted EET processes could be manipulated through interfacial modifications, including mineral-electron acceptors, favorable position in the redox boundary, e-pili/c-Cyts-minerals, interspecies modifications and photoinduced electron transitions. Enhanced knowledge concerning optimization of interfacial modifications through supplementation with mineral substituents will greatly advance our understanding of the typical manner of electron transport incorporating contact with specific types of minerals.

Notably, electron transfer is likely mediated by multiple interacting mechanisms rather than a single independent mechanism in bioelectrochemical systems with coexisting mixed strain microbes and specific minerals. Considering the various properties of minerals, electron transfer in the presence of versatile (semi)conductive minerals (particularly magnetite) is more likely instigated by multiple interacting mechanisms in a synergistic manner. Hence, it is important to distinguish the relative influence of each independent mechanism, and the role of positive/negative feedbacks among various mechanisms. Hence, research investigating independent mechanisms and their interactions are of upmost importance. Given the complexity of bioelectrochemical systems, this research requires a multidisciplinary approach incorporating mineralogical, spectroscopy, nano-particle engineering, isotopic, ecological and molecular techniques to tease apart the various mechanisms.

Microorganisms mediate environmental electron transfer through intracellular metabolism that generates electrons and facilitation of charge transfer between external biotic/inorganic interfaces. Thus, to promote renewable energy production and pollutant control/remediation at various scales, research is required to address a number of important microbial biotic/abiotic interactions. (1) To improve bioremediation efficiency, methods to limit cellular damage induced by photoholes are necessary. For example, coating MOF directly onto cell membranes offers a potential shield for cytoprotection, thereby enhancing the adaptability of cells or corresponding biohybrids towards adverse environmental impacts [136]. (2) To promote the conversion of value-added chemicals, exploiting the enzymatic machineries imbedded in native microbial cells might ensure products with exquisite selectivity and circumvent energy/product losses resulting from secondary biomass proliferation [157]. (3) To maximize electron flow in clean fuel synthesis, enhancing the electron flux through engineered microbial strains produced by manipulating genetic materials could greatly enhance efficacy (*e.g.,* employing CRISPR [clustered regularly interspaced short palindromic repeats] and CRISPRi [CRISPR interference] technologies) [158,159]. Following the steady improvements of the past decade, the most salient components responsible for electron transfer are primed for further exploitation in bioelectrochemical system to greatly enhance future applications and operational efficiencies.

Finally, the exploitation of the minerals and engineered nanoparticles mentioned above still faces several challenges. A series of key questions require attention, including questions related to selection of suitable mineral substituents, whether the minerals provide any unexpected beneficial or adverse effects, the effect of the supplemented dosage and particle size of substituents, and whether there are beneficial/detrimental effects resulting from supplementation of two or more substituents in anaerobic digestion systems. Further investigations

should also examine the environmental effects of these materials or their analogues to broaden their future practical application. Moreover, clarifying the electron transduction pathway in a hybrid system and using time-resolved methods to pair biohybrid photochemical complexes will facilitate our understanding of the stepwise processes that underpin these challenging biochemical reactions and will aid in application of this novel biotechnology to larger-scale operations. Overall, it is warranted to make full use of mineral-assisted EET processes to optimize the bioelectrochemical processes because minerals are highly abundant in natural soils and sediments, environmentally benign, and readily/cheaply available in the epigeosphere.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Abbreviations

4-CP: 4-chlorophenol
Cyts: Cytochromes
c-Cyt: c-type cytochrome
CdS NPs: Cadmium sulfide nanoparticles
CRISPR: Clustered regularly interspaced short palindromic repeats
CRISPRi: CRISPR interference
DHS: 3-dehydroshikimic acid
DIET: Direct interspecies electron transfer
DMRB: Dissimilatory metal-reducing bacteria
e-pili: Electrically conductive pili
EET: Extracellular electron transfer
EPSs: Extracellular polymeric substances
ICPB: Intimate coupling of photocatalysis and biodegradation
ICP-MR: Intimately coupled photoelectrochemical-microbial reduction
MOF: Metal-organic framework
NADH: Nicotinamide adenine dinucleotide
NADPH: Nicotinamide adenine dinucleotide phosphate
NPs: Nanoparticles
SA: Shikimic acid