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Review

Electrocatalytic Nanomaterials Improve Microbial Extracellular Electron Transfer: A Review

Xiaopin Wang *, Xu Li and Qisu Zhu

Institute of Science and Technology, Nanchang University, Gongqingcheng 332020, China; lixu@ncuky.edu.cn (X.L.); zhangzilu2000@163.com (Q.Z.)
* Correspondence: xiaowangbi201507@126.com

Abstract: Microbial electrochemical systems that integrate the advantages of inorganic electrocatalysis and microbial catalysis are expected to provide sustainable solutions to the increasing energy shortages, resource depletion, and climate degradation. However, sluggish extracellular electron transfer (EET) at the interface between electroactive microorganisms and inorganic electrode materials is a critical bottleneck that limits the performance of systems. Electrocatalytic nanomaterials are highly competitive in overcoming this obstacle due to their effective association with microbial catalysis. Therefore, this review focuses on the cutting-edge applications and enhancement mechanisms of nanomaterials with electrocatalytic activity in promoting microbial EET. First, the EET mechanism of microbial electrocatalysis in both microbial anodes and cathodes is briefly introduced, and then recent applications of various electrocatalytic nanomaterials in diverse microbial electrochemical systems are summarized, including heteroatom-doped carbons and precious metal, as well as transition metal oxides, sulfides, carbides, and nitrides. The synergistic effects of nanomaterial electrocatalysis and microbial catalysis on enhancing interfacial EET are analyzed. Finally, the challenges and perspectives of realizing high-performance microbial electrochemical systems are also discussed in order to offer some reference for further research.

Keywords: microbial electrochemical system; electrocatalysis; extracellular electron transfer; nanomaterial; electrode; electroactive microorganism

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1. Introduction

The extracellular electron transfer (EET) feature of electroactive microorganisms (EAMs) [1,2] is a widespread natural process in biogeochemical cycles, with significant application potential in various fields such as wastewater treatment, environmental bioremediation, clean electricity generation, biosensing, high-energy fuel conversion, and high-value chemical synthesis [3,4]. EET-based microbial electrocatalysis involves the biocatalytic process of microorganisms and the electrocatalytic process of electrodes [5], both of which play key roles and have tremendous synergistic effects on the fast kinetics of electrodes, making the bioelectrocatalytic process much more complex than either the biocatalytic or electrocatalytic one [6]. Over the past decades, the combination of microbial catalysis and electrocatalysis has led to the construction of microbial electrochemical systems, utilizing microorganisms as catalysts for matter and energy conversion in various applications [7], such as microbial fuel cells (MFCs) for generating electrical energy from wastewater [8], microbial electrolytic cells (MECs) for biological hydrogen production [9], and microbial electrosynthesis (MES) for converting greenhouse gas CO_2 to valuable chemicals [10]. However, the practical application of microbial electrochemical systems is limited by low efficiency, yield, and electron transfer efficiency, hindering their widespread commercial viability. Among them, the weak interfacial electron transfer rate between electroactive microorganisms and electrodes is considered to be the most fundamental bottleneck.

Traditional electrode materials (e.g., graphite rod, graphite plate, carbon cloth, and stainless steel) have limited interaction with microorganisms and electron transfer processes

due to their low specific area and infertile structure. The decoration and functionalization of these conventional electrode materials certainly enhance the performance of microbial electrochemical systems. Many studies have shown that the surface modification of traditional electrodes through various physical or chemical methods (e.g., ammonia treatment, thermal treatment, acidification treatment, and electrochemical modification) could greatly improve their surface chemical properties so as to enhance the performance to varying degrees [11,12]. Notably, nanomaterials with unique properties such as surface effect, volume effect, quantum size, and macroscopic quantum tunneling effect have garnered significant attention in recent years and have been widely used in various fields and industries, including microbial electrochemical systems [13]. With the theme of "nanomaterial*" AND "microbial electrochem* OR microbial electrocatalysis OR extracellular electron transfer", 422 pieces of research literature, published from 2010 to mid-2024, were retrieved from the Web of Science core database. A variety of nanoscale carbon materials (such as graphene [14,15] and carbon nanotubes [16]) have been widely used to improve the conductivity and biocompatibility of microbial electrodes, thereby promoting the growth of electrode biofilms and the electron exchange at the biotic–abiotic interface. Nanosized metal compounds (such as titanium dioxide [17] and molybdenum carbide [18,19]) can greatly improve the surface properties of microbial electrodes with increased interface reactivity. Moreover, some bio-friendly nanomaterials (such as palladium [20] and ferrous sulfide [21]) have been directly used to functionalize microbial cells to improve their EET ability. There is no doubt that nanomaterials have made important progress in promoting the extracellular electron transfer of microorganisms and thus improving the performance of microbial electrochemical systems, and they are still advancing.

As far as we know, there have been some reviews that summarized and discussed the application progress of nanomaterials in microbial electrode materials from the perspectives of performance improvement, nanostructure effect, surface chemistry availability, and promotion of biofilm growth [22,23]. It should be noted that, as mentioned above, the extracellular electron transfer process between microbial cells and electrode materials is a bridge connecting the biocatalysis of EAMs and the electrocatalysis of electrodes and is the cornerstone of microbial electrochemical systems. However, few reviews have been conducted specifically from the perspective of electrocatalytic nanomaterials, although a number of studies have demonstrated that electrocatalytic materials significantly enhance microbial extracellular electron transfer in microbial electrochemical systems through different strategies. To fill this knowledge gap, this review focuses on the cutting-edge applications of electrocatalytic nanomaterials in various microbial electrochemical systems and an in-depth discussion of the mechanisms by which they promote microbial EET enhancement by reviewing the works of literature retrieved above, followed by perspectives for the design and preparation of high-performance electrocatalytic nanomaterials.

2. EET Mechanisms

In general, microbial cells cannot exchange electrons with their extracellular environments because their electron transport chains are closed by nonconductive lipid membranes, peptidoglycans, and lipopolysaccharides [24]. Exceptionally, due to the evolution of special EET pathways across the cellular envelope, EAMs can exchange electrons with extracellular electrodes or insoluble minerals to enable energy flow between living organisms and the external environments [1]. Some of them (termed as exoelectrogens) can export electrons generated from the biological oxidation of organic substrates to extracellular insoluble electron acceptors, such as microbial anodes and iron and manganese oxides, through outward EET pathways, while others, referred to as electrotrophs, can take up electrons from extracellular electron donors, such as the microbial cathode, using inward EET pathways [1]. Meanwhile, the EET pathways between EAMs and electrodes are usually divided into a direct process and an indirect process based on the contact between EAM cells and the electrodes (Figure 1) [25]. The former depends on electron transport carriers on the cell surface, such as *c*-cytochromes (Cyts), vesicles, and nanowires, which can make direct

contact with the electrodes, while the latter generally uses diffused electron shuttles and extracellular enzymes.

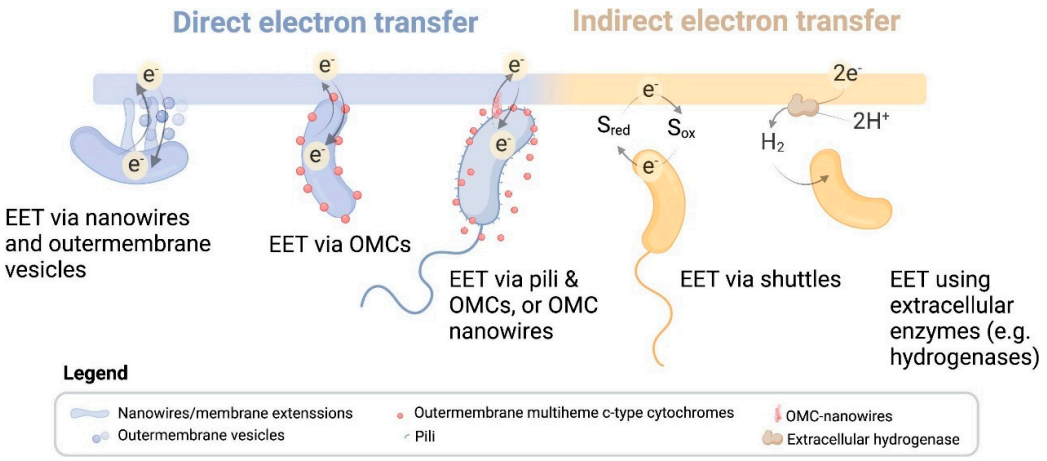


Figure 1. EET mechanism between EAMs and electrodes: the direct process through outer-membrane Cyts, vesicles, and nanowires, and the indirect process via electron shuttles and extracellular enzymes (with permission from [25]).

2.1. Outward EET from EMAs to Anodes

Exoelectrogenic EAMs perform outward EET for electricity production in microbial anodes. Dozens of exoelectrogens have been identified so far [1], and the EET pathways of two typical Gram-negative strains, *Shewanella oneidensis* MR-1 and *Geobacter sulfurreducens* PAC, have been well elucidated. For *S. oneidensis* MR-1, the Mtr pathway that is composed of multiple Cyts (CymA, Fcc_3, MtrA, MtrC, OmcA, and STC) and a porin-like protein MtrB is responsible for efficient direct EET [2,26]. CymA, located at the cytoplasmic membrane, acquires electrons from the quinone pool and transfers them to the periplasmic Cyts of Fcc_3 and STC and then to the ternary complexes of MtrA, MtrB, and MtrC for the transmembrane transport of electrons [27,28]. MtrC and OmcA, located at the cellular outer membrane, interact with each other and deliver electrons to microbial anodes [29]. A similar direct EET pathway, the porin-cytochrome (Pcc) pathway, is present in *G. sulfurreducens* PAC, in which the inner-membrane quinol oxidases ImcH and CbcL link the electron flow from the intracellular electron transport chains to periplasmic Cyts (including PpcA, PpcB, PpcC, PpcD, and PpcE), followed by being transferred to the porin-cytochrome complexes [30]. The complexes consist of periplasmic Cyts OmaB/C, porin-like outer-membrane proteins OmbB/C, and outer-membrane Cyts OmcB/C [30,31]. Moreover, both *S. oneidensis* MR-1 [32] and *G. sulfurreducens* PAC [33–35] can produce bacterial nanowires with electric conductivity to execute direct EET over relatively long distances. In addition, *S. oneidensis* MR-1 can secrete flavins or use natural redox-active molecules (such as humic substrates) as electron shuttles for the indirect EET [36,37]. In recent years, some Gram-positive bacteria have been found to perform EET [1], although the thick and dense peptidoglycan layer in their cell wall is intuitively hostile to EET. However, the EET mechanism of Gram-positive bacteria is currently less well understood, with only a few studies. The multiheme Cyts that localized at the cell wall or cell surface were suggested to take part in the EET of *Thermincola potens* through genomic analysis [38]. In contrast, *Listeria monocytogenes* has been identified to use a distinctive flavin-based EET mechanism to deliver electrons to iron or an electrode [39]. This evidence substantially demonstrates the diversity of EET pathways.

2.2. Inward EET from Cathodes to EAMs

Electrotrophic EAMs utilize the cathode as the electron donor via inward EET pathways [40], which are also divided into direct node and indirect modes. Some EAMs, including *S. oneidensis* MR-1 and *G. sulfurreducens* PAC, exhibit bidirectional EET features.

S. oneidensis MR-1 was reported to use a reverse Mtr pathway to ingest electrons from the cathodes, and the electrons were injected into the menaquinone pool [41]. However, it is controversial whether *G. sulfurreducens* also uses the reversed outward EET pathway to take up electrons from extracellular electron donors. The similar formal potential of acetate oxidation and nitrate reduction of mature electrode biofilms, mainly composed of *Geobacter* sp., seems to support the standpoint of reversal EET [42]. In contrast, *G. sulfurreducens* was found to express much lower levels of genes encoding outer-membrane Cyts and conductive nanowires when receiving electrons from the electrode compared to exporting electrons [43,44], which suggested that the inward EET was not a simple reversal for the outward EET. In addition, flavins or artificial electron shuttles could significantly boost the rate at which they acquire electrons from the cathode [45,46], which indicates the existence of indirect EET. Notably, the transfer of electrons from the cathodes to the bacterial cells has been extensively reported in many strains, such as acetogenic bacterium *Sporomusa ovata* [47], Fe(II)-oxidizing bacterium *Rhodopseudomonas palustris* [48], and sulfur-oxidizing bacterium *Thioclava electrotropha* [49]. However, the specific inward EET mechanism of such electrotrophs is still far from clear. For more details on the EET mechanism, refer to previous reports [2,50–52].

3. Electrocatalytic Nanomaterials for Promoting EET

3.1. Heteroatom-Doped Carbons

Carbon-based electrode materials are widely applied in microbial electrochemical systems due to their low cost, easy availability, and high biocompatibility. However, their electrocatalytic activity is generally limited by the low surface area, inappropriate pore structure, and inert surface chemistry, which severely limits the performance of microbial electrochemical systems. In recent years, non-metallic heteroatom (nitrogen, phosphorus, sulfur, boron, etc.)-doped carbon materials have attracted the attention of researchers. The catalytic ability, current density, cycling stability, and resistance to toxic side effects of carbon materials have been further improved by doping them with N, P, and S elements. This is mainly due to the fact that the geometry and electronegativity of non-metallic heteroatoms are different from those of carbon atoms. When doped into carbon atoms, these non-metallic heteroatoms could cause changes in the properties of surrounding carbon atoms in terms of electron density and spin, thus improving the electrocatalytic performance of carbon nanomaterials. This active effect has been demonstrated in a variety of carbon-based nanomaterials, including graphene [15], carbon nanotubes [53], MOFs [54], and biomass-derived carbon [55].

The element N is adjacent to C in the periodic table, and they have similar atomic radii, but their electronegativity is quite different. Therefore, the electronic structure of carbon nanomaterials will change significantly after N doping. Recently, N doping has been shown to be an effective electrode surface modification method that can enhance the EET process of EAMs, thereby improving the pollutant removal and power generation of MFCs. The preparation of N-doped carbon nanomaterials by pyrolysis of N-containing precursors (such as ammonia [56], polyaniline [53], polypyrrole [57], and natural biomass [55,58]) alone or together with carbon materials is a common and very productive route to improve the performance of microbial electrochemical systems. For example, Yang et al. [56] reported that an N-doped graphene aerogel electrode achieved a then-record power density of milliliter-scale MFCs because of the greatly reduced charge-transfer resistance and internal resistance of the N-doped electrode. Similarly, Wu et al. [53] found that the N-doped MFC anode showed a much higher power density than the counterpart anode without N doping and speculated that the improvement was attributed to the enhanced adsorption of flavins and the biofilm adhesion on the N-doped surface through electrochemical analysis. Natural biomass is an important precursor for the preparation of N-doped carbons due to the presence of N-rich biomolecules. As a case, natural cassava straws were used as a carbon source to prepare activated N-doped porous carbon through a facile process of electrochemical activation; the resulting N-doped carbons, when used as an MFC anode,

achieved a power density almost two times higher than the unmodified counterpart [55]. In addition, the N-doped biomass-derived carbon electrode was found to promote the acetate production from CO_2 and the coulomb efficiency in MES [59]. More interestingly, Hu et al. [60] found that the N-doped carbon dots could be used to modify acetogenic bacteria to enhance their EET and the formation of electroactive biofilm, which subsequently improved the acetate production rate by 57–71% in CO_2-fed MES.

In general, the doped N mainly has three active forms: pyridinic, pyrrolic, and graphitic; the electrocatalytic activity of carbon nanomaterials varies according to the active N form [61–63]. For example, pyridinic N and graphitic N were reported to be the key active sites for activating hydrogen peroxide to generate hydroxyl radicals in electro-Fenton systems [63], while graphitic N was the main working N in nitroaromatic hydrogenation [62]. Wang et al. found that the current density of MFCs showed a positive linear correlation with the pyrrolic N due to the enhancement of both DET and MET of *S. oneidensis* MR-1 [61]. Moreover, they further demonstrated through molecule dynamic simulation that anodic doping with pyrrolic N achieved a more remarkable reduction in the thermodynamic and kinetic resistances of the EET process compared to pyridinic N and graphitic N.

In addition to increasing the electrode biofilm growth and decreasing the interfacial charge resistance, N doping has been found to significantly promote the electrocatalytic reaction of microbial electron mediators, especially flavins. Yuan et al. revealed that a porous N-doped carbon cloth with a high N/C ratio showed an 18 times higher anodic peak current of riboflavin compared to the carbon cloth alone [64]. Wu et al. also demonstrated that both N-doped carbon nanotubes/reduced graphene oxide (N-doped CNTs/rGO) composites [53] and N-doped carbon nanowires [65] could promote a flavin-based interfacial electron transfer in MFC anodes. More importantly, by tuning N doping, the electrode interface could be atomically matched with the flavin molecule, thus achieving strong adsorption and conversion of the diffusive mediators to anchored redox centers (Figure 2). The atomic matching resulted in a short electron transfer pathway in *S. putrefaciens*-inoculated MFCs.

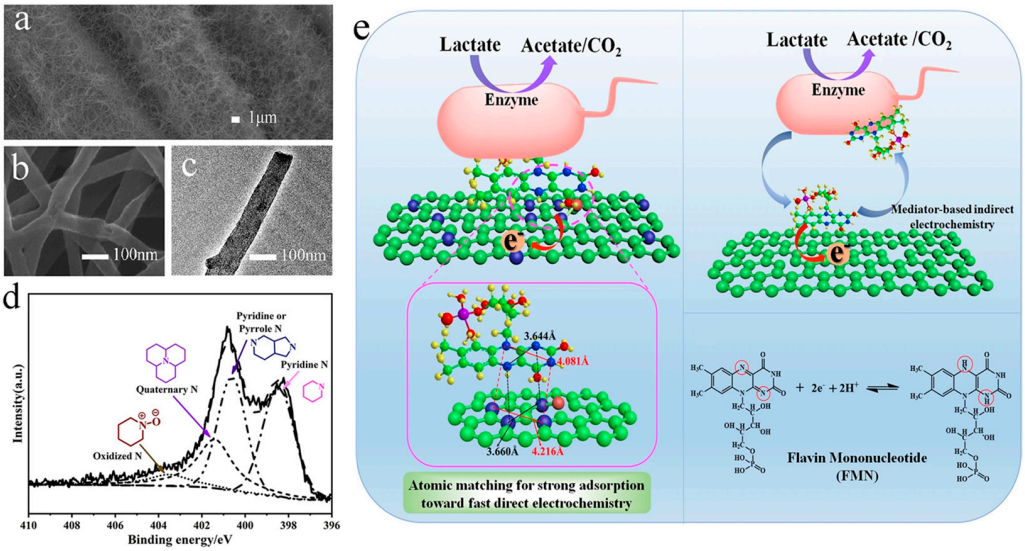


Figure 2. The proposed effect mechanism of N doping on flavins-mediated EET: (**a**,**b**) SEM; (**c**) TEM images and (**d**) XPS N1s spectrum of N-doped carbon nanowires; (**e**) the proposed atomic matching catalysis mechanism (with permission from [65]).

In addition to N doping, S and P doping have been adopted to modify the MFC electrode. Zhang et al. prepared 3D macroporous carbon foam with high N, P, and S contents as an MFC anode electrode through the pyrolysis of bread as the raw material and found that the co-doping of N, P, and S greatly improved the biocompatibility of

the resulting electrode and facilitated the enrichment of bacterial biofilm, which led to a 2.57-fold increase in the power density [66].

3.2. Precious Metals

The application of precious metals, such as platinum (Pt), gold (Au), silver (Ag), and palladium (Pd), in microbial electrodes is an area of interest due to their unique properties, including high electrical conductivity, corrosion resistance, and catalytic activity [67]. In the early stages of research, noble metal nanoparticles were mainly used to modify carbon-based electrodes to improve their electrochemical interaction with EAMs. Both the Pt nanoparticle-decorated graphene [68] and the Pd nanoparticle-coated carbon cloth [69] significantly enhanced the electrochemical dynamics of the microbial anodes, resulting in an increase in MFC power density. However, recent studies have found that directly functionalizing EAM cells with these electrocatalytically active noble metal nanostructures, which can be biosynthesized in situ by the EAM cells, is a more effective and facile route to improve their EET ability [70,71]. It was reported that Au nanoparticles could be precipitated in situ into a *G. sulfurreducens* biofilm through the biological reduction of the Au(III) precursor in a continuous-flow three-electrode MFC, which increased the conductivity of biofilm and the electricity generation [20]. Recently, Cao et al. developed reduced graphene oxide–silver nanoparticle (rGO/Ag) scaffolds for the anode of *Shewanella* MFC and found that the rGO/Ag scaffolds could release silver ions to facilitate *Shewanella* attachment to them and produce the *Shewanella*–Ag hybrids [72]. Particularly, the resulting hybrid species showed the presence of abundant Ag nanoparticles, both inside and throughout the bacterial membrane, which could potentially act as metallic shortcuts to bypass the sluggish electron transfer process mediated by the biological redox centers and make direct contact with the external electrodes to extract the charge more efficiently, thereby contributing to the record-breaking power density of *Shewanella* MFC.

Biologically produced Pd nanoparticles are the most common in bacteria-associated catalytic systems, mainly due to their outstanding catalytic activity and ease of biosynthesis [73]. Back in the early 2010s, the biogenic Pd nanoparticles bound to the cell membrane of *Desulfovibrio desulfuricans* have been demonstrated to participate in EET through the interaction with periplasmic hydrogenases and Cyts, as well as take part in electrocatalysis on an electrode surface [74]. Importantly, a variety of bacteria (e.g., *Enterobacter cloacae* SgZ-5T [75], *Citrobacter freundii* JH [76], *Bacillus megaterium* Y-4 [77], *G. sulfurreducens* [78], *S. loihica* PV-4 [79], and *Escherichia coli* [80]) have been reported to be able to, when in situ, synthesize Pd nanoparticles to improve their electron transport processes for different applications, including the electrochemical hydrogen/oxygen evolution reaction and pollutant degradation. Moreover, the phenotype of biosynthesized Pd nanoparticles could be tailored through by controlling the biological reduction pathways [81], reaction conditions [82] and organic electron donors [83], which provides more opportunities for their practical applications. Particularly, as illustrated in Figure 3, the biosynthetic location and size of the Pd nanoparticles could be modulated through controlling the expression and availability of two key EET-involving components of *S. oneidensis* MR-1—the outer-membrane Cyts (MtrC) and electron shuttles (flavins) [81]—which indicated the possibility of customizing biogenic Pd nanoparticles to, in turn, promote a microbial EET in situ.

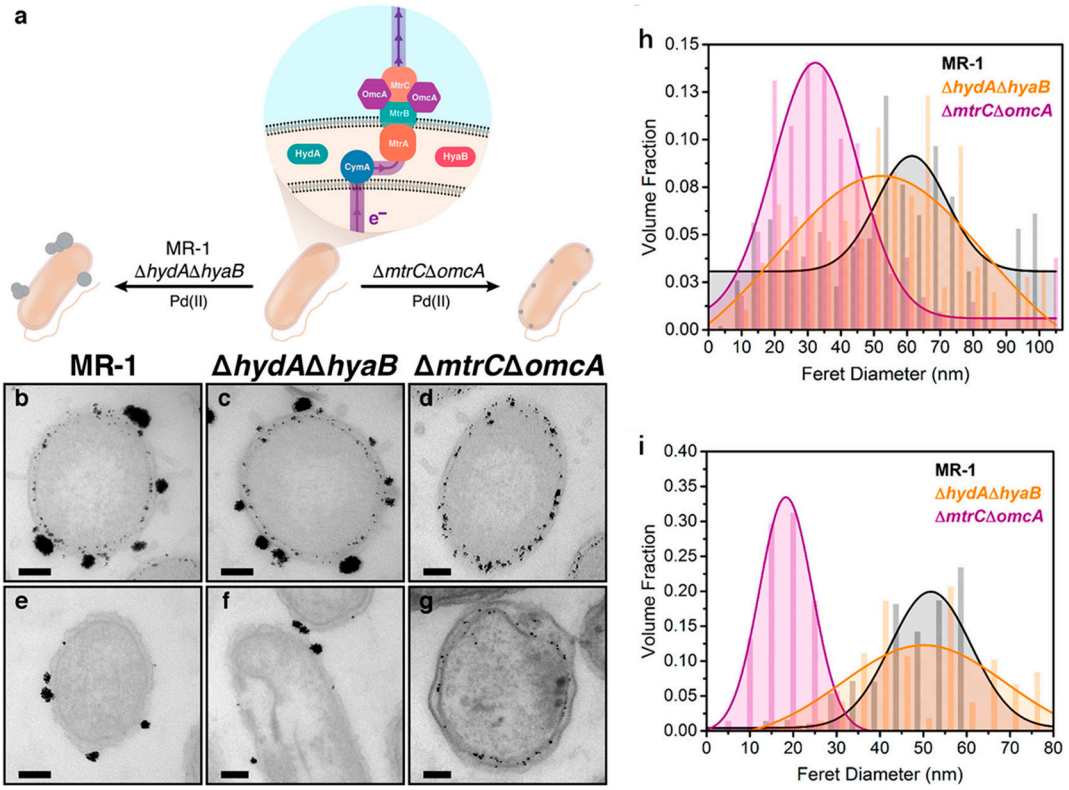


Figure 3. The effect of *S. oneidensis* MR-1 EET components on the location and size of biogenic Pd nanoparticles: (**a**) general diagram of EET and genotypic effect on Pd nanoparticle formation; (**b**–**g**) thin section transmission electron micrographs of *S. oneidensis* MR-1 cells after Pd production under different conditions; and (**h**,**i**) nanoparticle size distributions (with permission from [81]).

3.3. Metal Oxides

Transition metal oxides (TMOs) have gained significant attention in various electrocatalytic reactions [84], such as the oxygen reduction reaction, oxygen evolution reaction, hydrogen evolution reaction, and CO_2 reduction, due to their diverse redox chemistry and electronic properties. The electrochemical and electronic properties of TMOs can be finely tuned through compositional modifications and surface functionalization, allowing for the optimization of their electrocatalytic performance [84]. Without exception, due to their active electrocatalytic activity and high biocompatibility, TMOs (Table 1) have also been widely used as electrode materials for microbial electrochemical systems to enhance the microbial EET process.

Among them, titanium dioxide (TiO_2), with a suitable band structure for efficient charge separation and transfer, is one of the most attractive electrode materials to promote microbial EET. To date, nanoscale TiO_2 with various morphologies and structures (Figure 4), such as nanoparticles [85,86], nanotubes [87,88], nanorods [89], nanosheets [90,91], and nanoclusters [92], have been widely used in microbial electrodes, where a TiO_2 functionalized interface could promote electroactive biofilm formation, substrate diffusion, and the EET rate. Intriguingly, Yin et al. [91], when investigating the electron transfer kinetic from *S. loihica* PY14 to an up-growing TiO_2 nanosheet-modified carbon paper, found that the change in the hydrophobic carbon paper to a super-hydrophilic TiO_2 nanosheet interface not only promoted bacterial adhesion but also altered the redox nature of outer-membrane Cyts. As a consequence, the mid-point potential of Cyts was shifted to a more negative potential, which indicated a higher thermodynamic driving force for the electron release from the bacterial cells. In addition, TiO_2, when with different morphologies, has been shown to stimulate the secretion of electron mediator flavins from the genus *Shewanella*, possibly by enhancing the related biosynthesis pathway, thereby promoting the micro-

bial EET rate [17,93]. Coincidentally, Zhou et al. found that TiO_2 nanoparticles could specifically induce the formation of conductive nanowires by stimulating the *pilA* gene expression in *G. sulfurreducens*, which led to an approximately 5.1-fold increase in microbial electricity production [86]. Obviously, the above results substantially demonstrated the close interaction between highly electrocatalytic TiO_2 and the EET pathways of EMAs. The improvements in nanostructured TiO_2 in electrode biofilm growth and the microbial EET rate could be elaborately tuned by the regulation of its morphology, size, and porous structure [24]. Yin et al. [94] found that N doping could modulate the electronic properties of TiO_2 nanosheets with smaller charge-transfer resistance, more positive flat-band potential, and larger transient-charge storage capacity, which facilitated the interfacial electron transfer from out-membrane Cyts to the TiO_2 nanosheets' modified carbon paper electrode.

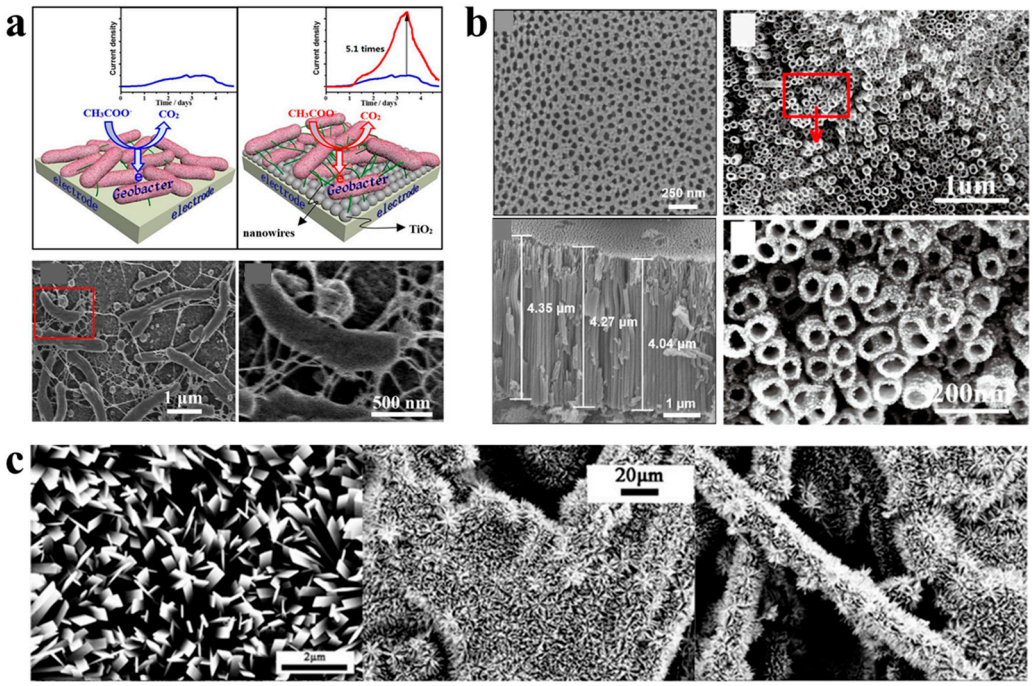


Figure 4. Nanostructured TiO_2 with various morphologies were used to promote microbial EET in microbial electrochemical systems: (**a**) nanoparticles (with permission from [86]), (**b**) nanotubes (with permission from [88,95]), and (**c**) nanosheets (with permission from [90]).

Since iron oxides and manganese oxides are natural electron correlates of typical electroactive microorganisms, they are also often adopted to modify microbial electrodes for the sake of promoting microbial EET. An α-FeOOH nanowhiskers-decorated carbon paper significantly increased the EET of *S. loihica* PV-4 cells, resulting in a 60% increase in current density [96]. The hybrids of Fe_3O_4 nanoparticles and reduced graphene oxide have been shown to dramatically enhance microbial EET for electricity generation in MFCs due to the high affinity between Fe_3O_4 and EAMs [97,98]. In addition, the magnetic Fe_3O_4 could significantly enhance the performance of MES, such as the production of acetate and methane [99,100]. More interestingly, a highly conductive N-doped Fe_3O_4 with a carbon dot shell (Fe_3O_4@CD) could directly hybridize the *G. sulfurreducens* cells, in which the Fe_3O_4@CDs formed an interaction network with intracellular and extracellular conductive proteins for an enhanced EET [101]. As a result, the Fe_3O_4@CDs-fed cells achieved a 6.3 times higher current output compared to the control cells. Recently, the α-Fe_2O_3 nanoarray-modified carbon electrode interface was reported by He et al. to greatly promote the direct EET of *S. putrefaciens* CN32 due to the possible function of the α-Fe_2O_3 nanoarray as an electron mediator [102]. For manganese oxides, they have been reported to improve both the electricity generation of the MFC anode and the chemical biosynthesis of the MES cathode. For example, the reduced graphene oxide/MnO_2 composite increased the

MFC power density by 1.54 folds because of the increased growth of EAM biofilm and the decreased internal resistance [103], while the cauliflower-like polypyrrole/MnO_2 composite increased the power density and real capacitance by 3.58 and 4.84 folds, respectively [104]. A MnO_2-coated felt cathode electrode obtained a 43% increase in the acetate production rate with 2-fold higher current consumption than the non-coated electrode in MES [105]. Similarly, the nanostructured MnO_2/rGO nanohybrid-decorated carbon cloth enhanced the production of isobutyric acid and acetate by 2.09 and 2.91 times, respectively, compared to the bare carbon cloth [106]. Notably, an obviously positive shift of the onset potential was observed in the linear sweep voltammogram of the MnO_2/rGO nanohybrid cathodes under the turnover condition, which indicated more favorable thermodynamics for the EAM cells acquiring electrons from the cathode. In addition, an in situ synthesized biohybrid of amorphous *Geobacter*-Mn_2O_3 was shown to have high electrocatalytic activity for OER due to the synergistic effect, in which the *Geobacter* cells contributed OER-active elements such as Fe and P, while amorphous Mn_2O_3 provided a large electrochemically active surface area and excess catalytic sites for OER [107].

Moreover, other TMOs, including NiO [108,109], CeO_2 [110], WO_3 [111], and SnO_2 [112], have successively been shown to significantly increase the microbial EET in microbial electrochemical systems, despite deviations in the specific enhancement mechanism. It should be noted that since most TMOs with semiconductive properties are relatively poor in electro-conductivity, they are often hybrid with highly conductive polymers (e.g., polyaniline [113] and polypyrrole [104]) and carbon nanomaterials (e.g., graphene [97,98,106], CNTs [112], and carbon dots [101]) when used as microbial electrodes. The above results demonstrated the electrocatalytic interaction between TMOs and EAMs for a high EET rate, which provides great potential for the design and fabrication of high-performance microbial electrodes based on the low-cost and readily available TMOs.

Table 1. Applications of transition metal compounds as electrocatalytic nanomaterials in microbial electrocatalysis and their performances.

Nanomaterials	Applications	Performances	Reference
Transition metal oxides (TMOs)			
TiO_2 nanoparticles	Microbial anode	Approximate 5.1-fold increase in microbial current generation	[86]
TiO_2 nanoparticles	Biophotoelectrode	Four-fold increase in photocurrent generation of *Synechocystis* sp. PCC 6803	[85]
TiO_2 nanotubes	MFC anode	A maximal current density of 12.7 A m^{-2}, 190-fold higher than that of bare Ti electrode	[95]
TiO_2 nanorods	MFC anode	A maximum power density of 2576.3 ± 33 mW m^{-2}, 2.6-fold higher than that of carbon paper electrode	[89]
TiO_2 nanosheets	MFC anode	A maximum power density of 690 mW m^{-3}, 63% higher than that of bare carbon paper electrode	[90]
TiO_2 nanosheets	MFC anode	A maximum power density of 497 mW m^{-2}, 97% higher than that of carbon paper electrode	[91]
N-doped TiO_2 nanosheets	MFC anode	A maximum power density of 747 mW m^{-2}, 196% higher than that of carbon paper electrode	[94]
TiO_2 nanoclusters	MFC anode	A maximum power density of 25.9 ± 6.2 mW m^{-2}, a record-breaking value	[92]
TiO_2/polyaniline	MFC anode	A maximum power density of 813 mW m^{-2}, 63.6% higher than that of TiO_2 electrode	[113]
α-FeOOH nanowhiskers	Microbial anode	A maximal current density of 0.48 A m^{-2}, 60% higher than that of carbon paper electrode	[96]
Fe_3O_4 nanospheres/rGO	MFC anode	A maximum power density of 1837.4 mW m^{-2}, 2.66-fold higher than that of carbon paper electrode	[97]
Magnetite nanoparticles	MES modifier	An 8.5-fold increase in acetate production and 52% decrease in methane production	[99]

Table 1. *Cont.*

Nanomaterials	Applications	Performances	Reference
GO/Fe_3O_4	MES cathode	A CH_4-producing rate of 605 ± 119 mmol m^{-2} d^{-1}, 24.5-fold higher than that of carbon cloth electrode	[100]
N-doped Fe_3O_4@CD	MEC additive	A 6.37-fold increase in maximum current	[101]
α-Fe_2O_3 nanoarray	MFC anode	A maximum power density of 816 mW m^{-2}, 8-fold higher than that of carbon cloth electrode	[102]
rGO/MnO_2	MFC anode	A maximum power density of 2065 mW m^{-2}, 154% higher than that of carbon felt electrode	[103]
MnO_2	MEC cathode	A maximum current density of 3.70 ± 0.5 mA m^{-2}, more than double the non-coated carbon felt cathode, and an acetate production rate of 37.9 mmol L^{-1}, 43.0% higher than that of the bare carbon felt	[105]
MnO_2/rGO	MES cathode	Production of isobutyric acid (15.9 mM) and acetate (3.5 mM), 2.09 and 2.91 folds higher, respectively, than bare carbon cloth	[106]
NiO nanoflakes	MFC anode	A 3-fold increase in maximum power density compared to carbon cloth electrode	[108]
NiO@N-doped carbon nanowires	MFC anode	An 8.5-fold increase in maximum power density compared to carbon cloth electrode	[109]
CeO_2 nanoparticles	MFC anode/cathode	A 4.28 and 3.07-fold increase in maximum power density for cathode and anode, respectively	[110]
CNTs/m-WO_3	MFC anode	A maximum power density of 1.11 ± 0.022 W m^{-2}, comparable to that of Pt anode	[111]
CNTs/SnO_2	MFC anode	A maximum power density of 1421 mW m^{-2}, 3-fold higher than that of bare glassy carbon electrode	[112]
Transition metal sulfides (TMSs)			
FeS	Microbial anode	A 3-fold increase in current density	[114]
FeS_2/graphene	MFC anode	An unprecedented power density of 3220 mW m^{-2} and a remarkable current density of 3.06 A m^{-2}	[115]
FeS@*S. oneidensis*	Biohybrid	An increased interfacial electron transfer rate for ferrihydrite reduction	[116]
FeS@*S. oneidensis*	Biohybrid	A record-high interfacial electron transfer efficiency and BES performance	[117]
FeS@sulfate-reducing bacteria	Biohybrid	An increased extracellular electron transfer rate for Cr(VI) reduction	[118]
FeS@*Dehalococcoides mccartyi*	Biohybrid	Enhanced dechlorination of trichloroethene	[119]
CdS@*Moorella thermoacetica*	Biohybrid	Continuous production of acetate over several days of light/dark cycles	[120]
CdS@*Rhodopseudomonas palustris*	Biohybrid	A 148%, 122%, and 147% increase in production of solid biomass, carotenoids, and poly-β-hydroxybutyrate (PHB), respectively	[121]
CdS@*Clostridium autoethanogenum*	Biohybrid	Production acetate from CO_2 by using only light	[122]
CdS@*Cupriavidus necator*	Biohybrid	Production of 1.41 g PHB from fructose over 120 h and 28 mg from CO_2 over 48 h	[123]
CdS@*Sporomusa ovata*	Biohybrid	Production of acetate from CO_2 with a quantum yield of 16.8 ± 9% over 5 days	[124]
Ni:CdS@*Methanosarcina barkeri*	Biohybrid	A 250% higher CH_4 yield than the CdS@*Methanosarcina barkeri* biohybrid	[125]
Transition metal carbides (TMCs)			
Mo_2C/CNTs	MFC anode	A maximum power density of 1.05 ± 0.0264 W m^{-2}, 13-fold higher than that of carbon felt electrode	[126]
Nanoporous Mo_2C	MFC anode	A maximum power density of 1025 mW m^{-2}, 5-fold higher than that of carbon felt electrode	[19]
Mo_2C/rGO	MFC anode	A maximum power density of 1697 W m^{-2}, 2-fold and 13-fold higher than that of graphene and carbon cloth electrode, respectively	[127]

Table 1. *Cont.*

Nanomaterials	Applications	Performances	Reference
WC	MFC anode	A maximum power density of 3.26 W m^{-2}, chemical oxygen demand removal rate of 95.5%, coulombic efficiency of 83.2%, 2.14-fold, 1.22-fold, and 1.71-fold of that obtained by naked carbon cloth	[128]
Ti_3C_2 MXene	MFC anode	A maximum power density of 3.74 W m^{-2}, 82.4% higher than that of carbon cloth	[129]
Transition metal nitrides (TMNs)			
W_2N-MXene	MFC anode	A 523% increase in power density (548 mW m^{-2}), an 83% decrease in chemical oxygen demand, and a 161% increase in electron transfer efficiency compared to those of plain carbon cloth	[130]
Fe_3N-Fe_3C	MFC anode	A maximum power density increased from 28.57 mW m^{-2} to 58.86 mW m^{-2}	[131]

3.4. Metal Sulfides

Transition metal sulfides (TMSs) are commonly used as highly active electrocatalysts and have also been used in the field of microbial electrocatalysis (Table 1). Back in 2010, Nakamura et al. found, for the first time, that the FeS colloids produced by *S. loihica* PV-4 could self-organize to from electron-conducting networks, resulting in a two orders of magnitude higher electricity production of the *S. loihica* PV-4 cells [132]. Afterward, Jiang et al. further proved the promotion effect of biogenic FeS nanoparticles on the *S. loihica* PV-4 EET through a detailed investigation of the structure and composition of the cell/nanoparticle interface [114]. Similarly, the *S. oneidensis* MR-1 cell strain was also found to generate extracellular FeS nanowires and was used as electron conduits for long-range EET [133]. The decoration of graphene with FeS_2 nanoparticles was demonstrated to not only benefit the enrichment of electrochemically active *Geobacter* species but also promote the EET process, which has given rise to a fast start-up time and an unprecedented power density [115]. Recently, Zhu et al. proved that the biogenic FeS that formed on *S. oneidensis* MR-1 cell surfaces during the ferrihydrite reduction process could significantly increase the EET rate through continuously monitoring the reduction rate of ferrihydrite, and they proposed that the biogenic FeS could act as a solid electron mediator for efficient EET [116]. More significantly, Yu et al. proposed a concept of a single-cell electron collector (Figure 5), which was in situ built with a FeS conductive layer on and across the individual *S. oneidensis* MR-1 cell membrane, and the single electron collector formed intimate contact with the cellular electron transfer route [117]. As a consequence, the in situ synthesized FeS single-cell electron collector efficiently wired living cells with an abiotic electrode surface, which achieved a record-high interfacial EET efficiency and performance of microbial electrochemical systems. In addition to the above-mentioned current production, the enhancement of the FeS nanointerface on microbial EET has also been widely used to accelerate the removal of environmental pollutants, such as the reduction of toxic hexavalent chromium [118] and the dechlorination of trichloroethene [119].

In the last decade, CdS has been another high-profile semiconductor metal sulfide in the field of wiring microbial EET processes due to its excellent light absorption and high photoelectron yield, which has led to a new cutting-edge research frontier of artificial photosynthesis [134,135]. As a pioneering work, Sakimoto et al. developed an artificial photosynthetic hybrid through the self-photosensitization of a non-photosynthetic bacterium *Moorella thermoacetica* with CdS nanoparticles, in which the biological precipitated clusters of small CdS nanoparticles (<10 nm) that were deposited on the bacterial cell surface and in the periplasm could serve as light harvesters with high quantum yields, thus sustaining the cellular metabolism of *M. thermoacetica* for the selective and continuous photosynthesis of acetate from CO_2 over several days of light/dark cycles [120]. Afterward, a series of artificial hybrids for artificial photosynthesis have been developed, such as CdS@*Rhodopseudomonas*

palustris [121], CdS@*Clostridium autoethanogenum* [122], CdS@*Cupriavidus necator* [123], CdS@*Sporomusa ovata* [124], and CdS@*Methanosarcina barkeri* [125] for the production of various chemicals. These works demonstrate a promising future for artificial photosynthetic systems to combat global warming and resource depletion.

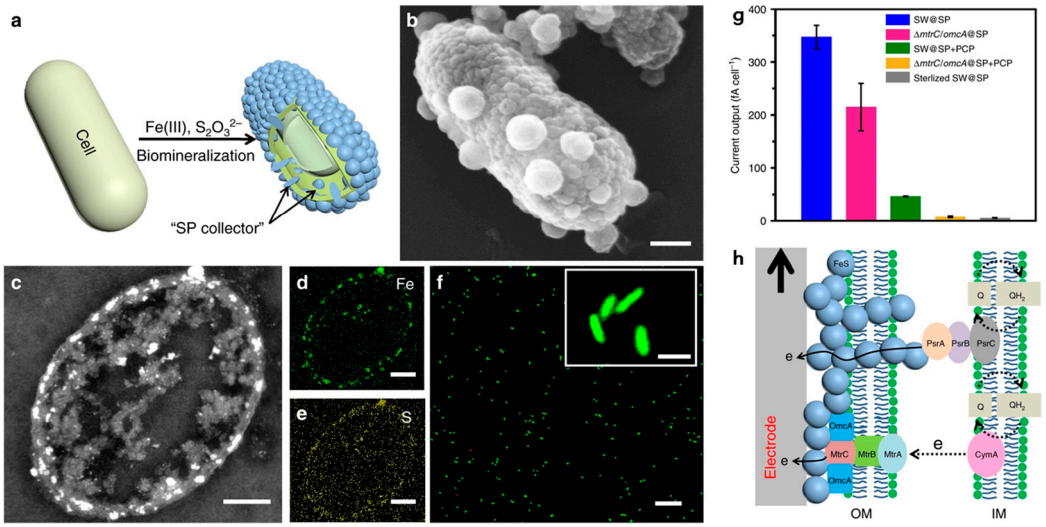


Figure 5. The FeS single-cell electron collector on individual *S. oneidensis* MR-1 cell: (**a**) schematic illustration of collector assembly; (**b**) scanning electron micrograph; (**c**) transmission electron micrograph; (**d**,**e**) EDS mapping; (**f**) fluorescence microscopy image; (**g**) current output under different conditions; and (**h**) proposed electron transfer pathway (with permission from [117]).

3.5. Metal Carbides

Transition metal carbides (TMCs), such as Mo_2C and WC, are also widely used in diverse electrocatalytic reactions, including microbial electrocatalysis (Table 1), due to their Pt-like electric and catalytic characteristics. As early as 2010, Zeng et al. found that the MFC power density delivered by the Mo_2C anodic catalyst could be compared to that obtained by the Pt anodic catalyst [136]. A possible contribution of nano Mo_2C catalyst to microbial electricity production was its electrocatalytic activity towards the oxidation of hydrogen, a common electron-rich metabolite of microorganisms [126]. In addition, Zou et al. proved that the nanoporous Mo_2C catalyst, grown on carbon fibers, showed significant electrocatalytic activity towards endogenous electron shuttle flavins with an obvious negative shift of formal redox potential, which indicated a more favorable thermodynamic driving force for anodic indirect EET [19]. To further improve the EET at the *S. oneidensis* MR-1/anode interface, they introduced the highly conductive rGO to overcome the insufficient conductivity of Mo_2C nanoparticles, which produced a record-high MFC power density [127]. Considering that pure Mo_2C nanoparticles are difficult to synthesize and easy to aggregate, Zeng et al. prepared a highly dispersed polydopamine-modified Mo_2C/MoO_2 nanoparticle as an anode electrocatalyst by using polydopamine that contained amine and phenol groups as the soft template, which achieved an obvious increase in MFC power density compared to the unmodified Mo_2C/MoO_2 catalyst [137]. Recently, nanostructured Mo_2C has also been shown to increase the electrocatalytic activity of microbial cathodes greatly. For example, a three-dimensional macroporous carbon co-decorated with polydopamine and Mo_2C (Mo_2C/N-doped LS), when used as an MES cathode, achieved an increased acetate production rate by 2.5 times compared with carbon felt, resulting in a maximum acetate concentration of 6.08 g L^{-1} and a 64% coulomb efficiency [59]. Recently, the Mo_2C-modified carbon cloth cathode was found to greatly promote the electric-driven fumarate reduction by *S. oneidensis* MR-1 due to the increased interfacial EET [18].

In addition to Mo_2C, WC also showed electrocatalytic activity towards microbial metabolites (e.g., hydrogen and formate), thus enabling a high MFC power and current

density when used as an anodic catalyst [138]. The carbon cloth decorated with WC nanoparticles was found to not only promote the attachment of dense biofilm but also enrich the exoelectrogens of *Geobacter*, *Geothrix*, and *Pseudomonas*, which led to an enhanced MFC power density, chemical oxygen demand removal rate, and coulombic efficiency by 2.14, 1.22, and 1.71 folds, respectively, compared with the naked carbon cloth anode [128]. A two-dimensional Ti_3C_2 MXene anode was also found to greatly improve the MFC output voltage and power density, which benefited from its multilayer structure, high surface area, good conductivity for fast microbial growth, mass transfer, and more active sites for biological electrocatalytic redox reactions [129]. The above reports substantially demonstrated the significant benefits of the electrocatalytic activity of TMCs in boosting microbial EET in microbial electrochemical systems.

3.6. Metal Nitrides

Similar to TMCs, transition metal nitrides (TMNs) have also shown great potential for electrochemical energy conversion and storage (e.g., supercapacitors, batteries, and electrocatalytic reactions) due to their unique electronic structure, high electrical conductivity, good chemical stability, large volumetric energy density, and excellent electrocatalytic activity [139,140]. However, the application of TMNs in promoting microbial EET in microbial electrochemical systems is relatively rare, with only two recent cases to our knowledge (Table 1). Kolubah et al. prepared a W_2N-MXene composite catalyst through the introduction of W_2N nanoparticles into the Ti_3C_2Tx MXene for the purpose of improving the wettability, electrical conductivity, electron transfer efficiency, and microorganism attachment capability [130]. As a consequence, the MFC power density obtained by the W_2N-Ti_3C_2Tx-decorated carbon cloth anode was, respectively, 52% and 84% higher than that obtained by the Ti_3C_2Tx-decorated carbon cloth anode and plain carbon cloth anode, with an obviously increased chemical oxygen demand removal and coulombic efficiency. Cheng et al. investigated the effect of the carbon felt anode modified with Fe_3N and Fe_3C nanoparticles on the MFC's electrical performance and found a significantly increased output voltage and maximum power density [131]. Although the cases are limited, it is also proved that TMNs can promote microbial EET. Of course, the specific effect mechanism needs to be further clarified.

4. Conclusion and Perspectives

With the concept that microbial electrochemical systems are collaborative systems of microbial catalysis and electrocatalysis, this tutorial review presents a summary of electrocatalytic nanomaterials used for promoting the microbial EET process and a discussion on the underlying effect mechanisms. A series of nanostructured catalysts with highly electrocatalytic activity, including heteroatom-doped nanocarbons, precious metals, and transition metal compounds (TMOs, TMSs, TMCs, and TMNs), have been demonstrated to show great merits in boosting both the outward and inward EET through diverse enhancement mechanisms. The functionalization of microbial electrodes with nanomaterials generally offers advantages in reducing interfacial electron exchange resistance, promoting EAM cell adhesion and biofilm growth, and providing more active sites for electrochemical redox reactions. More impressively, these electrocatalytic nanomaterials showed unique features that improve the microbial EET kinetics by tuning the redox potential of outer-membrane Cyts and electron shuttles and heightening the amounts of available EET components by stimulating the related biosynthetic metabolism. These pieces of evidence not only further demonstrate the inherent bridge between the biocatalysis of EAMs and electrocatalysis of electrodes but also show a promising avenue for the realization of high-performance microbial electrochemical systems through rational electrode design and fabrication.

Of course, in order to achieve the above goals at an early date, we believe that more efforts need to be made in the following areas in the future. Firstly, the application of electrocatalytic nanomaterials is still mainly concentrated in the MFC anodes with outward EET and relatively little in the MES cathodes with inward EET. However, given the deteriorating

climate and depleting resources, MESs that convert CO_2 to highly valuable chemicals using electricity as electron donors should be more competitive in future practical applications. Therefore, more efforts need to be devoted to the design and use of electrocatalytic nanomaterials to strengthen the performance of MES cathodes and to comprehensively investigate the underlying mechanisms. Meanwhile, the construction of an artificial photosynthesis system by the direct hybridization of EAMs with nanocatalysts with semiconductor properties is emerging and deserves rapid development. Secondly, electrocatalytic nanomaterials can directly impact the microbial EET components and even the intracellular metabolism. Thus, the biological modification of EAMs by means of systematic and synthetic biology is a new and promising direction to realize the adaptive connection between biocatalysis and electrocatalysis. Thirdly, the microbial EET pathway at the bio–abiotic interface is a highly complex process, and the specific mechanisms, especially inward EET, are not well understood. This is a key obstacle to the rational design of electrocatalytic materials and the modification of biocatalytic cells. In addition, the phylogenetical diversity of EAMs further complicates the EET pathways. Therefore, it is not only necessary to use various multidisciplinary techniques to clarify the EET mechanism of specific EAM strains deeply but also to use artificial intelligence technologies for big data analyses and simulation, which is expected to accelerate the development and commercialization of microbial electrochemical systems.

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