Carbon material-based anodes in the microbial fuel cells

Xiaoqi Fan | Yun Zhou | Xueke Jin | Rong-Bin Song | Zhaohui Li | Qichun Zhang

1 Henan Joint International Research Laboratory of Green Construction of Functional Molecules and their Bioanalytical Applications, School of Ecology and Environment, Zhengzhou University, Zhengzhou, China
2 Department of Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong, China

Correspondence
Rong-Bin Song and Zhaohui Li, Henan Joint International Research Laboratory of Green Construction of Functional Molecules and their Bioanalytical Applications, School of Ecology and Environment, Zhengzhou University, 450001 Zhengzhou, China.
Email: rbsong@zzu.edu.cn and zhaohui.li@zzu.edu.cn
Qichun Zhang, Department of Materials Science and Engineering, City University of Hong Kong, Kowloon, 999077 Hong Kong, China.
Email: qiczhang@cityu.edu.hk

Abstract
For the performance improvement of microbial fuel cells (MFCs), the anode becomes a breakthrough point due to its influence on bacterial attachment and extracellular electron transfer (EET). On other level, carbon materials possess the following features: low cost, rich natural abundance, good thermal and chemical stability, as well as tunable surface properties and spatial structure. Therefore, the development of carbon materials and carbon-based composites has flourished in the anode of MFCs during the past years. In this review, the major carbon materials used to decorate MFC anodes have been systematically summarized, based on the differences in composition and structure. Moreover, we have also outlined the carbon material-based hybrid biofilms and carbon material-modified exoelectrogens in MFCs, along with the discussion of known strategies and mechanisms to enhance the bacteria-hosting capabilities of carbon material-based anodes, EET efficiencies, and MFC performances. Finally, the main challenges coupled with some exploratory proposals are also expounded for providing some guidance on the future development of carbon material-based anodes in MFCs.

KEYWORDS
carbon materials, cell surface modification, extracellular electron transfer, hybrid biofilm, microbial fuel cells

1 | INTRODUCTION

The sustainable development of the economy strongly depends on energy support, where fossil fuels continue to provide dominant contribution in the presented energy structure. Therefore, the ever-increasing demand for energy has not only caused the global energy crisis, but also brought many environmental problems such as serious water pollution.1–3 Microbial fuel cells (MFCs) are a type of bioelectrochemical system, in which the exoelectrogens are harnessed to produce electrical energy from chemical energy in fuels.4–7 The clean by-products (H2O and CO2) and the renewable exoelectrogens endow MFCs with the great potential to become a green energy source. Moreover, due to their ability to use organic wastes as fuels, MFCs are regarded as a promising wastewater treatment technology, which is superior to the traditional physical and chemical methods for treating wastewater in terms of cost, reusability, and secondary pollution.8–11 These features ingratiated the trend of renewable energy development and environmental governance, making them particularly appealing in the past decades.
The origin of MFC technology could be dated back to 1911 when Potter used the microbes to produce electricity. As the direct transfer of electrons from bacteria to anode is easily hampered by the non-conductive lipid membrane of bacterial cells, the electron mediators have usually been involved in the earlier MFCs, which can accelerate electron transfer through the capture of electrons from the interior of bacterial cells and their release to anode. Considering the cost, toxicity, and the need for constant replenishment, the addition of mediators seems not to be sustainable. Therefore, the MFC technology was found to be stagnant until 1999, when the exoelectrogens that directly transfer electrons to electrodes were gradually revealed. After that period, the MFC technology entered a high-speed development period, resulting in the diversity of research activities. The research, which is focused on MFC, now covers anode materials, cathode materials, separator materials, configuration, and so on. Among them, the anode material is the most frequently investigated object. On the one hand, MFC anodes provide the space for bacterial attachment and affect the microbial extracellular electron transfer (EET), which is highly associated with MFC performance. On the other hand, the theories and experiences from the investigations of traditional fuel cells can offer abundant importuned reframes for the development of cathode materials and the configuration in MFCs; however, these theories and experiences about the anode of traditional fuel cell are not suitable for the MFC anodes, thus requiring intensive research studies.

Carbon is an Earth-abundant element in nature, which possesses the following features: low cost and high chemical and thermal stability. Moreover, the surface morphologies and structural forms of carbon materials can be adjusted in an unusually broad range, leading to the presentation of the desired physicochemical properties for any particular application. Naturally, carbon materials have become an intrinsic part of the anode materials in MFCs. The classical carbon materials used in MFC anodes mainly refer to commercially available carbon electrodes, including carbon paper (CP), carbon cloth (CC), carbon felt (CF), graphite rod, and flake graphite. These commercially available carbon electrodes are posited in the anodic chamber, and then the exoelectrogens attach to them for the formation of natural biofilm. Although these carbon electrodes inherit the abovementioned characteristics of carbon element, they usually exhibit relatively poor performance when used in MFC anodes. The deficiencies in the biofilm formation and EET between carbon electrodes and exoelectrogens are counted as the main contributing factors.
With the advancement of nanotechnology, extensive efforts have been devoted to the creation of various novel carbon-based nanomaterials for offsetting the aforementioned deficiencies (Scheme 1). The modification of these carbon-based nanomaterials can enlarge the surface area of commercial carbon electrodes, leading to the increased spatial positions for bacterial attachment and biofilm formation. Besides, the surface properties can be regulated to increase the anode/bacteria interactions, thus enhancing the EET and the formation of biofilm.49–52 Most of the commercial carbon electrodes belong to planar electrodes, where the biofilm formation and electron transfer are confined to the outer surface. To accelerate the diffusion of self-secreted mediators and even the formation of natural biofilm on the interior space of anode, the freestanding carbon materials with tailored porous structures are also developed as candidates for commercial carbon electrodes.43,44 As a consequence of these research studies on carbon material-based anodes, the MFCs show improvement in the performance by nearly an order of magnitude. However, the EET efficiencies inside the natural biofilm formed on these carbon material-based anodes with a natural biofilm are still unsatisfactory, because only the bacterial cells nearby the carbon materials can transfer the electrons effectively, whereas these bacterial cells, located far away from the material interfaces, inject electrons into anode through an inefficient path (adjacent non-conductive bacterial cells).45,46 Therefore, the concept of hybrid biofilm has been employed, in which carbon materials and bacterial cells are previously mixed and then transferred to the substrate electrode for the formation of hybrid biofilms.47,48 In this case, the inserted carbon materials in the hybrid biofilms can serve as conductive electron transfer paths to enhance the EET efficiency. Moreover, the cell densities in these hybrid biofilms can be improved by changing the ratio between carbon materials and bacterial cells or optimizing the transportation technologies. However, the simple mixing mode between bacterial cells and carbon materials cannot ensure that every bacterial cell in the hybrid biofilms could make direct contact with the carbon materials. To further improve the EET efficiency, cell surface modification has recently been employed to develop novel hybrid biofilms. In this new mode, the carbon materials are modified on the cell surface, and then the modified bacterial cells are transferred to the substrate electrode for the formation of hybrid biofilms, which integrate every exoelectrogen with carbon materials to expand their contact interface for further optimizing the EET and the performance.49–51

To date, the progresses on the different subfields of MFCs have been comprehensively summarized.52–54 As to the anode materials, the presented reviews only focus on the design of materials but neglect the difference with regard to the type of biofilms. In this review, considering the biofilm types and anode materials, we first divide the carbon material-based bioanodes on the basis of the difference in the types of biofilms. Then, we outline important strides in the creation of each type of carbon material-based anodes in MFCs and highlight the enhancement strategies used in the design of these carbon material-based anodes. We hope that this review will provide a comprehensive grasp of the main development line of carbon material-based anodes in MFCs, as well as offer valuable guidance to future research focuses on relevant subjects for pushing the practical application of MFCs.

2 | CARBON MATERIAL-BASED ANODES WITH NATURAL BIOFILMS

2.1 | Pure carbon materials

As mentioned above, MFC anode provides active sites for bacterial attachment and electron transfer. This function drives the anode materials to set high requirements concerning conductivity, biocompatibility, and anti-corrosive ability. As the pure carbon materials can satisfy the aforementioned demands, they have been employed as substrate materials for the growth of natural biofilms in the bioanode of MFC. More importantly, the morphologies and structures of pure carbon materials play important roles in the bacteria-hosting capability of anode and the EET efficiency between anode and natural biofilm. For example, pure carbon materials with macro-porous structures (>$\mu$m) allow bacterial colonization in the interior of anode, whereas microporous pure carbon materials can promote the diffusion of endogenous mediators (e.g., riboflavin) for improving the EET efficiency.55–57 Therefore, we summarize the part of pure carbon materials based on their different dimensions, to understand the dependencies between MFC performance and material structure.

2.1.1 | One-dimensional (1D) carbon materials

As one kind of famous 1D carbon materials, carbon nanotubes (CNTs) emerge as substrate materials in MFC anode due to their large specific surface area, high mechanical strength, excellent conductivity as well as specific fiber structure.58 Peng et al.59 investigated the
voltammetric behavior and current generation capability of *Shewanella oneidensis* on CNT-modified glassy carbon electrode (GCE). The cyclic voltammetry curves showed a reduced oxidative/reductive peak separation with CNTs modification, indicating that the good conductivity of CNTs enhanced the kinetics of direct electron transfer between outer membrane cytochrome c and CNT-modified GCE electrode. As a result, the current generation capability of this modified electrode exhibited an 82-fold increase as compared with that of bare GCE electrode in the *Shewanella oneidensis*-involved electrochemical cells. However, the performance of MFCs with CNT-modified GCE electrode has not been provided in this study. To disclose the real application of CNT modification in MFC anode, a CNT-modified CC electrode has been fabricated in a single-chamber MFC. The MFC displayed a maximum power density of 65 mW·m⁻², whereas the maximum power density was only 26 mW·m⁻² in the case of MFC with unmodified CC, confirming the positive function of CNT modification toward MFC performance. Mohanakrishna et al. also fabricated the multiwalled carbon nanotube (MWCNT)-impregnated plain graphite anode by using conductive epoxy adhesive for MFC. They found that the microbial mediator-involved charge transfer between the anolyte and the modified anode was more effective due to the facilitated surface area after the impregnation of MWCNT. Therefore, we can conclude that the CNTs modification can accelerate both the direct and indirect electron transfer for optimizing the MFC output, which may be attributed to their high conductivity, large surface area, and the fiber structure that connects the anode and cytochrome c on bacterial outer membrane.

Although the above research studies have deeply explored the effect of CNTs on anode performance, the information of this material on long-term stability is rarely mentioned. In this case, Zhang et al. fabricated the CNT-modified graphite felt (GF) through a dipping–drying process, and they evaluated the long-term stability of the MFC with this CNT-modified anode. Unlike the MFC with CF anode, which represented a reduced performance, the MFC with CNT-modified anode exhibited a constant performance during the whole testing time (13 months). The author attributed this enhanced stability to the better growth of electrochemically active biofilms (EABs), the enhanced interaction between anode and EABs, as well as the increased EET after the modification of CNTs. The 1D carbon materials include the CNTs, carbon nanowires, and carbon nanofibers (CNFs); however, the latter two kinds of carbon materials have not been found to be used in MFCs. It is encouraged to probe the performances of MFCs with these carbon materials as anode modifier. With these efforts, we can further understand the influence of slight distinction in anode materials with respect to MFC performance, thus improving the level of finesse of the anode material designs.

### 2.1.2 Two-dimensional carbon materials

Compared with 1D carbon materials, the plane structure of two-dimensional carbon materials can offer an enlarged contacting area for bacterial attachment and EET. Thus, some of the two-dimensional carbon materials have been put on the domain of MFC anode. Among them, graphene is one most important representatives, which possesses good conductivity, stability, and biocompatibility as well as high specific surface area. In a typical example, graphene was used to modify the stainless-steel mesh (SSM), which served as the anode for MFC with *Escherichia coli* as the biocatalyst. As the modification of graphene can increase the surface area and thus the number of attached bacteria, the modification of graphene on SSM has resulted in an 18-fold increase in the maximum power density of MFC. It is noted that the potential toxicity of materials should be taken into consideration for MFC anode, as it will affect bacterial growth. In most cases, reduced graphene oxide (rGO) is obtained by the chemical reduction of graphene oxide (GO), and the residual reducing agents (e.g., hydrazine monohydrate) possibly poison bacteria. To remove the potential toxic hazards, the electrochemical reduction method was used to prepare graphene for MFC anode. Similar to the chemically reduced graphene, the electrochemically reduced graphene could also improve the MFC performance. Another biocompatible and sustainable approach is the bioreduction of GO. Zhou et al. developed a biosynthesized graphene by using *Eucalyptus* leave extract as reducing agent (Figure 1A). When using the biosynthesized graphene as anode materials in MFC, they found that the maximum power density was 70% higher than that of MFC with anode modified with electrochemically reduced graphene. Such enhancement could be explained by the biomolecules coating-induced surface hydrophilization and biocompatibility of biosynthesized graphene, which made the anode surface less harmful and more available for bacterial attachment and growth.

Although the graphene nanosheet possesses large surface area, the π–π stacking between graphene nanosheets will sacrifice this superiority. In this regard, the reduced graphene particles, which seem like crumpled paper balls (Figure 1B), have been developed as anodic materials for the MFCs. Due to the aggregation-resistant property and open structure, the reduced
graphene particles enhanced the surface area of anode, the electrochemical kinetics, as well as the mass transfer. As a result of these enhancements, the reduced graphene particle-modified anode delivered a maximum power density of 3.6 W·m$^{-3}$ in the MFC test, which signified a 1.3-fold increase as compared with those of MFC with reduced graphene nanosheet-modified anode (Figure 1C). The MWCNT-derived graphene oxide nanoribbons (GONRs) are another kind of two-dimensional carbon materials, which not only inherit conductive cellular pili-like feature from MWCNTs, but also offer large electrochemical active surface area as graphene. Thus, the use of GONRs has been demonstrated to make the EET process on MFC anode more effective.\(^6\)\(^3\)

### 2.1.3 Three-dimensional (3D) carbon materials

The porous structures of 3D carbon materials can accelerate the mass transfer of fuel and the diffusion of self-secreted mediator. Moreover, the penetration of bacterial cells into the interior surface of the anode is also permitted if the pore sizes or channel sizes are larger than those of bacterial cells. On the basis of these advantages, the 3D carbon materials have attracted much scientific interest in the field of MFC anode. By taking advantage of the chemical vapor deposition (CVD) method, Erbay et al.\(^6\)\(^9\) developed a novel 3D MFC anode, in which the MWCNTs were directly grown on the wires of SSMs in the radial direction. Apart from the large 3D surface, the minimal Ohmic loss between MWCNTs and substrate electrode, caused by the use of direct growth strategy, was also conducive to performance improvement. They also optimized the 3D structure from the aspects of length, packing densities, and surface conditions, and concluded that the 3D anode with long and loosely packed MWCNTs exhibited the highest performance in MFC. The CVD method is available to fabricate the 3D self-standing materials for increasing the applicability of MFCs. As a typical example, a 3D CNTs sponge has been developed for MFC by using a three-zone furnace coupled with a quartz tube (Figure 2A).\(^7\)\(^0\) The 3D CNTs sponge showed a length of 10 cm without base materials (Figure 2B). Moreover, the scanning electron microscopy (SEM) image revealed that the sponge possessed a high porous structure (Figure 2C), which was ideal for microbial penetration and growth on the exposed surface. Thus, the MFC with this 3D CNTs sponge produced a maximum power density of 2150 W·m$^{-3}$. Undoubtedly, the CVD method is widely used for the fabrication of various 3D materials; however, this method is expensive and also complicated. In this context, the carbon material-doped chitosan hydrogel has become an attractive choice for MFC anode. Liu et al.\(^7\)\(^1\) fabricated a CNT hydrogel by electrochemical deposition of CP in a CNT–chitosan solution at $-3$ V (Figure 2D,E). The results demonstrated that the CNT hydrogel was a more effective MFC anode, compared with CP, which could be attributed to the enhanced electrochemical surface area and large content of functional groups on the surface. Nevertheless, the pore size of this CNT hydrogel is about hundreds of nanometers; thus, bacterial penetration into the interior of CNT hydrogel is not feasible. To solve this issue, the ice segregation-induced self-assembly technology was used to unidirectionally freeze the
MWCNT/chitosan dispersion. After freeze-drying, a 3D MWCNT scaffold was obtained, which possessed a micro-channeled structure with a channel size of about 16 μm (Figure 2F–H). Thus, this 3D MWCNT scaffold could permit the interior bacterial colonization, which finally produced a maximum volumetric power density as high as 2.0 kW·m⁻³; however, the operation conditions of the used flow MFC configuration were not optimized. On the basis of the same method, the hierarchically porous chitosan/vacuum-stripped graphene scaffold has also been successfully obtained, which was an effective anode for MFC.

The abovementioned methods are universal for the fabrication of 3D CNT or graphene. Besides them, there existed some special strategies for CNTs or graphene, due to their different structures and properties. For example, the fiber-like structure of CNTs allows them to become a precursor for fabrics. Inspired by this, Delord et al. used the wet-spinning process to assemble MWCNTs into long filaments, which could be manually woven to obtain a CNT fiber textile (CNTex). The CNTex showed similar macroscopic and microscopic scales as CP (Figure 3A,B), but it possessed a much large...
macropore scale (200–700 μm) than that of CP (100 μm). As this large-scale porosity and nanostructuration promoted bacterial colonization, the CNTex anode was superior to CP anode in the maximal current density of MFC. Similarly, GO nanosheets have been found to form graphene hydrogel during the hydrothermal treatment process. By freeze-drying the hydrogel, a 3D porous graphene aerogel with a pore size of some 10 μm was fabricated (Figure 3C).\textsuperscript{74} Benefiting from these porous structures, a maximum power density of 5 mW·m\textsuperscript{-3} was realized when using it as an MFC anode.

As some natural substrates possess 3D porous structures, modifying carbon materials on their surfaces is a simple but an effective way to obtain 3D carbon material-based anodes for MFC. Xie et al.\textsuperscript{75} developed a two-scale porous anode by conformally coating CNTs on textile (Figure 3D). The macroscale porous structure of textile provided open 3D channels to guarantee the internal colonization of bacterial cells and efficient substrate transport, whereas the microscale porous CNT layer strongly interacted with bacterial cells to accelerate the EET, which finally resulted in a 68% higher maximum power density as compared with that of CC anode. On the basis of this study, the same group changed the 3D substrate from textile to sponge, and the as-prepared CNT sponge still retained the 3D porous structure of the sponge with a pore size range of 300–500 μm (Figure 3E,F).\textsuperscript{44} Compared with the previous CNT–textile anode, the CNT-sponge anode exhibited better conductivity, stability, and continuous 3D CNT surface, resulting in a 48% increase in the maximum areal power density of MFCs. The graphene sponges have also been demonstrated as a high-performance 3D anode for MFC, further confirming the superiority of 3D sponge

**FIGURE 3** (A, B) Photograph and schema of carbon nanotube (CNT) fiber textile. Reproduced with permission: Copyright 2017, Elsevier.\textsuperscript{73} (C) Scanning electron microscopy (SEM) image of three-dimensional porous graphene aerogel. Reproduced with permission: Copyright 2018, Elsevier.\textsuperscript{74} (D) SEM image of CNT–textile composite. Reproduced with permission: Copyright 2011, American Chemical Society.\textsuperscript{75} (E) SEM image of CNT sponge. (F) Photograph of CNT-sponge electrode. Reproduced with permission: Copyright 2012, Royal Society of Chemistry.\textsuperscript{44} (G–J) SEM images of stainless steel fiber felts (G, H) and carboxyl graphene-modified stainless steel fiber felts (I, K) at different magnifications. Reproduced with permission: Copyright 2014, Elsevier\textsuperscript{76}
substrate. However, the nonconductivity of these two 3D substrates may have some adverse effects on the MFC performance to some extent. In this context, Hou et al. employed the conductive stainless steel fiber felts (SSFFs) with an open macroporous structure (Figure 3G,H) as the substrate for the fabrication of 3D MFC anode. The modification of graphene on the SSFFs made the surface much rougher but preserved the macroporous structure (Figure 3I,K), which further increased the contact area between anode and bacterial cells. Thus, the MFC with graphene-modified SSFFs anode delivered a remarkably increased maximum power density as compared with that of MFC with SSFFs anode (2142 vs. 0.8 mW·m⁻²).

2.2 | Heteroatom-doped carbon materials

The modification of pure carbon materials has been demonstrated to be efficient for enhancing the performance of MFCs. However, the pure carbon materials possess a hydrophobic nature theoretically, which will affect the biocompatibility for bacterial adhesion and biofilm formation on the anode. In general, the acid treatment can introduce some functional groups to make the pure carbon materials hydrophilic, but the electrical conductivity will become poor at the same time. Thus, doping heteroatoms into carbon materials has been proposed as a useful strategy. On the one hand, heteroatom doping can break the chemical inertness of pure carbon materials to improve the hydrophilicity and biocompatibility for bacterial adhesion. On the other hand, the hydrophilic defects created by the doping of heteroatoms are conducive to the EET between anode and cytochrome c on outer membranes of bacterial cells. To date, various heteroatom-doped carbon materials have been developed for MFC anode. In this part, we will classify them according to the use of exogenous or endogenous sources of heteroatoms.

2.2.1 | Exogenous sources of heteroatom

Among various heteroatoms, the most common case is nitrogen (N-) doped carbon materials for the MFC anode. As a typical example, Ci et al. developed a kind of special N-doped CNT (bamboo-like NCNTs) that displayed a bamboo-like structure (Figure 4A) as modifying material for MFC. The high-resolution N 1s X-ray photoelectron spectra (XPS) of bamboo-like NCNTs revealed the presence of three types of N atoms, confirming the successful doping of N into this material (Figure 4B). Benefiting from the N-doping and bamboo-like structure, the bamboo-like NCNTs provided better biocompatibility and enlarged active area for EET, ultimately leading to a 1.6-fold increase in the peak current density of MFC when compared with CNT. By changing the external N sources from ethylenediamine to the concentrated ammonium hydroxide and N₂, some other kinds of N-doped carbon materials have also been developed, which were proven to largely improve the MFC anode. Nevertheless, whether the type of N sources would affect the performance of MFC is an undisclosed issue. To make this clear, Iftimie and Dumitru utilized two procedures for the fabrication of two kinds of N-doped CNTs and compared their application potentials in MFC anode. The N-doped CNT with 4-nitroaniline was indexed as CNT1, whereas the other one with 4-nitrobenzenediazonium tetrafluoroborate was indexed as CNT2. As shown in Figure 4C, the peak intensities at 400 and 405.8 eV in the XPS pattern of CNT2 are much higher than those of CNT1, indicating higher contents of the nitro group of 4-nitrophenyl layer and partially reduced nitro groups, such as −NH₂ and −NH₂OH. Such high contents of these N-contained groups can help to improve the surface hydrophilicity and bacterial adhesion, so the maximum power density of MFC with CNT2 as an electrode is higher than that of MFC with CNT1 as an electrode (Figure 4D).

The carbon material doped by dual heteroatoms has also been used as MFC anode. The in-situ formation of N, S-doped graphene on the graphite plates by using electrolysis in (NH₄)₂SO₄ solution has increased the maximum power density of MFC from 0.39 ± 0.020 to 0.67 ± 0.034 W·m⁻². This result can be explained by the doping of heteroatoms, the improved electron transfer, and the microporous structure. Although the XPS characteristics have revealed the doping of S atom into graphene, its effect on the MFC performance has not been mentioned. Therefore, relevant investigations should be performed to confirm whether the doping of S atom has a positive effect on the MFC performance in future research studies.

2.2.2 | Endogenous sources of heteroatoms

The use of exogenous sources of heteroatoms for the fabrication of heteroatom-doped carbon materials will result in increased cost, inconvenient fabrication process, and additional toxic hazards. Thus, research studies on the fabrication of heteroatom-doped carbon materials have begun to flourish in the use of precursors that can serve as carbon and heteroatom sources simultaneously. The first one is melamine, which can afford abundant N
atoms for N doping due to the high N content (66.7%) in the molecular structure. By using porous melamine foam as the precursor, You et al. developed a 3D macroporous N-enriched graphitic carbon (NGC) scaffold for MFC anode. The N content in this NGC scaffold is as high as 10.89%. Such high N content could accelerate the EET, as the density-functional theory (DFT) calculations revealed that the interactions between pyrrolic N structure and active center of cytochrome c on the outer membrane of bacterial cells were enhanced. Moreover, the existing 3D macroporous structure maximized the space for bacterial attachment and facilitated mass transport. On the basis of these advantages, the MFC with this NGC anode delivered a maximum power density of 750 mW·m⁻².

Natural biomass is another kind of the precursor integrating the functions of carbon and heteroatoms sources. For example, the biomass carbon with N doping derived from mango wood has been prepared as anode material for MFC, which obtained a maximum power density of 589.8 mW·m⁻². As the presence of porous structure in the anode will upgrade the MFC performance, some of N-doped porous carbon materials derived from candle soot, almond shell, and silver grass have also been created as anode materials for MFC. Although these anode materials possessed improved MFC performance, the effects of pore types on the MFC performance are confusing. In this case, Zou et al. prepared the porous N-doped CNF aerogel for MFC anode by the pyrolysis of freeze-dried bacterial cellulose pellicles. The porous structure of CNF aerogel can be tuned by the alteration of pyrolytic temperature. With the increased pyrolytic temperature (600–1000°C), the micropores gradually disappeared, whereas the content of mesopores in the structure of CNF aerogel was found to be increased (Figure 5A). The mesopores not only behaved as bags with a suitable size to trap and release flavin molecules, but they also offered curvature or kink surfaces to increase the contacting opportunities toward electroactive sites for effective surface absorption and two-electron transfer electrochemistry (Figure 5B). As a result, the CNF obtained at a pyrolysis temperature of 1000°C showed the highest content of mesopores and the best performance in MFC. In another work, the

**FIGURE 4** (A,B) Transmission electron microscopy image and N 1s X-ray photoelectron spectra (XPS) of bamboo-like NCNTs. Reproduced with permission: Copyright 2012, Elsevier. (C) N 1s XPS of different N-doped carbon nanotubes (CNTs). (D) Polarization and power density curves of different microbial fuel cells (MFCs). MFC1, MFC2, and MFC3 were respectively fabricated with pure CNT, CNT1, and CNT2. Reproduced with permission: Copyright 2019, Elsevier.
FIGURE 5  (See caption on next page)
researchers have adjusted the pore sizes of the coffee waste-derived N-doped activated carbons (CWACs) for optimizing the MFC performance. Unlike the mesopores converted from micropores in previous work, the mesopores here originated from macropores. However, the same conclusion was obtained, that is, the increase in the mesopores content of CWACs favored the performance of MFC. It is worth noting that the sizes of those discussed pores are in the range of several to dozens of nanometers, allowing the access of mediators or substrate. However, for the macropores that can serve as the channels for bacterial penetration, their appearances in the structures of biomass-derived N-doped carbon materials are still valuable for the performance improvements of MFCs. Silk cocoon is an abundant natural material that possesses an intrinsically 3D nonwoven structure. By directly heating it at high temperatures (Figure 5C), Lu et al. obtained a N-enriched 3D pseudographitic anode with multiple layers and pores (Figure 5D) as anode for MFC, which produced a 3.1-fold maximum power density compared with that of MFC with CC anode. This result can be attributed to the fact that the enriched N content and hierarchical 3D microstructure improve the biocompatibility and habitat for the formation of biofilm on anode. To further improve the application potential of biomass-derived 3D macroporous N-doped carbon materials in MFC anode, the N-dopant states have been optimized by the integration of exogenous N sources biomass. As the N-dopant states and their corresponding contents were highly associated with the added precursors, the polyaniline (PANI) and polypyrrole (PPy) were, respectively, added during the pyrolysis of naturally abundant nitrogenous corncobs to obtained 3D N-doped macroporous carbon foams (NMCF) with different N-dopant states (Figure 5E). The primary N component was graphitic N for the NMCFs prepared at 1000°C with the addition of PANI and without an external N source (Figure 5F). In contrast, the pyrrolic N was the dominant N component in the structure of NMCF prepared at 1000°C with the addition of pyrrole (PPy@NMCF-1000). The DFT calculations indicated that the pyrrolic N was the key component to promote the EET process; thus, the MFC with the PPy@NMCF-1000 anode achieved the best performances among all tested MFC with different NMCF anodes. Certainly, this high performance also originated from the bacterial attachment in the 3D macroporous structure of PPy@NMCF-1000 anode.

The carbonization or pyrolysis of natural biomass not only can produce the N-doped carbon materials but also generate carbon materials doped with other heteroatoms. By taking the advantage of bread as the raw material, a 3D macroporous carbon foam with high content of N, P, and S (NPS-CF) has been created as MFC anode. The doping of N, P, and S has largely improved the biocompatibility of NPS-CF for favoring the enrichment of bacterial cells on the surface as compared with CC (Figure 5G–J), ultimately leading to a 2.57-fold maximum areal power density. Unfortunately, the individual functions of S- and P-doping have also not been revealed in this study. Another example was the porous carbon–silica (PC/Si) composite, which was prepared by the carbonization of the distiller’s grains. The PC/Si exhibited a honeycomb-like porous structure with abundant macropores and mesopores, which were in the size range of 2–15 μm and 3–4 nm, respectively (Figure 5K). These porous structures can increase the active area for bacterial adhesion and flavin-mediated electron transfer. More importantly, the presence of Si was found to largely increase the number of bacterial cells on the electrode surface (Figure 5L,M). These factors guaranteed that the maximum power density of MFC with PC/Si anode was 4.5-fold higher than that of MFC with CC anode.

2.3 Carbon-based composites

The carbon-based composites can reinforce and enrich the surface properties of the corresponding pure carbon materials or even adjust their space structure to further increase the power density. Thus, various carbon-based binary composites have been widely developed as anode materials for MFC. On the basis of the types of introduced components, these binary composites can be divided into...
three categories: carbon/carbon composites, carbon/metal composites, and carbon/conducting polymer composites. The defined carbon/metal binary composites cover the carbon/pure metal composites and carbon/inorganic metal compounds. Considering the effectiveness of binary composites toward performance improvement of MFCs, the carbon-based ternary composites that exhibited more abundant surface properties and delicate structures have also been created to improve the anode/bacteria interactions, EET efficiency, and bacterial adhesion. Thus, we review these carbon-based composites in this section and highlight the enhancement strategies.

2.3.1 Carbon/carbon binary composites

As previously reported, the 1D fiber structure of CNT is not beneficial for bacterial adhesion, whereas the π–π stacking-induced aggregation of graphene nanosheets during the reduction of graphite oxide will reduce the superiority of graphene in the surface area. However, when we integrate these two kinds of carbon materials together, the graphene can retain its suitable plane structure for bacterial attachment, and the CNT can be inserted between the graphene nanosheets to reduce the aggregation degree for extending the electrochemical active sites. Therefore, graphene/CNT composite has become a kind of classic carbon/carbon binary composite for MFC anode. In a typical example, Zou et al. created a hierarchically porous MWCNT@rGO composite (the input ratio of MWCNT to GO was 1:2) for MFC anode through a solvent-processed method. As shown in Figure 6A–F, the layered aggregation observed on the SEM image of rGO sample has not occurred for MWCNT@rGO, which displayed obvious porous network architecture. This result implies that the insertion of MWCNTs effectively protects the rGO nanosheets from aggregation and bridges the separated rGO nanosheets. The extended surface area enriched the bacterial cells on the anode, whereas the improved multidirectional connections between rGO sheets ensured a high electron transfer rate, therefore leading to a sixfold increase in the MFC performance.

N-doped carbon/carbon binary composites, which not only preserve the advantages of carbon carbon/carbon binary composite but also possess the positive effects of N doping, are highly appealing to MFC anode. Wu et al. fabricated a hierarchically porous N-doped CNTs/rGO composite by using PANI as an N source for MFC anode. The performance of MFC with N-doped CNTs/rGO anode was superior to those of MFCs with N-CNTs, N-rGO, and CNTs/rGO anodes, confirming that both the fabrication of composites and the doping of N were effective for the performance improvement. The former one allowed the formation of 3D hierarchically porous structure for enriching the bacterial biofilm, whereas the latter one provided an N-doped surface to adsorb flavin for improving EET efficiency. Besides rGO, the GONR has also been integrated with N-doped CNT. Liu et al. synthesized an N-doped MWCNT@GONR composite with core/shell structure by a microwave-assisted unzipping process and used it as anode for MFC. The encapsulation of the MWCNT core with GONR improved the hydrophilicity and surface area of MWCNT, enriching the bacterial adhesion. Thus, the MFC with MWCNT@GONR anode delivered higher power density than that of MFC with MWCNT anode (970 vs. 3291 mW·m⁻²). The doping of N to MWCNT@GONR further enhanced the electrical conductivity and surface roughness, resulting in an additional improvement in the power density of MFC with N-doped MWCNT@GONR (3444 mW·m⁻²). Taken together, the synergistic effect between individual components can be coupled with the strategy of doping heteroatom to further upgrade the MFC performance.

2.3.2 Carbon/metal binary composites

In general, the noble metal nanoparticles can be used to fabricate carbon/metal binary composites for MFC anode, because their good biocompatibility and the excellent electrocatalytic activity favor the bacterial attachment and enhance the EET efficiency between anode and bacterial cells. For example, the MFC with biogenic gold nanoparticles/MWCNT composite anode exhibited a better performance as compared with that of MWCNT anode, whereas the 3D graphene aerogel anode produced a 1.8-fold increase in the power density of MFC after decorating with platinum nanoparticles. However, the high cost of these noble metal nanoparticles will limit their application. In this context, the inorganic metal compounds naturally become the candidates to construct carbon/metal binary composites. Song et al. developed a graphene/Fe₃O₄ composite as anode material for MFC. They found that the presence of Fe₃O₄ component in this composite largely increased the bacteria-hosting capability of anode (Figure 6G,H), due to the high affinity between Fe₃O₄ nanoparticles and Shewanella species. Thus, the maximum power output of MFC with graphene/Fe₃O₄ composite anode was 2.8 times that of graphene anode. The usage of SnO₂ nanoparticles to decorate CNT anode was also demonstrated to improve the MFC performance, and the research studies explained that the electrostatic binding between SnO₂ nanoparticles and cytochrome c on the outer membrane of bacterial cells facilitated the EET.
FIGURE 6  (See caption on next page)
Compared with the abovementioned metal oxides, TiO$_2$ nanoparticles were more frequently used to prepare various carbon/TiO$_2$ composites anodes for improving the MFC performance due to their good biocompatibility and high resistance to corrosion.$^{107,108}$ Subsequently, the researchers explored the preferred crystallinity of TiO$_2$ nanoparticles for MFC performance, and they concluded that the presence of amorphous TiO$_2$ instead of TiO$_2$ nanoparticles on the surface of rGO produced better performance in MFC anode due to the enhanced specific surface area for contacting with bacterial cells and accepting electrons from self-secreted mediators.$^{55}$

Besides metal oxides, the metal sulfide and metal carbide have also been integrated with carbon materials to develop efficient anodes for MFC. Wang et al.$^{100}$ used FeS$_2$ nanoparticles to decorate rGO for improving the application potential of rGO in MFC anode. They disclosed that the FeS$_2$/rGO anode had better interaction with microbial film and enhanced EET efficiency as compared with those of rGO (Figure 6I–K), ultimately resulting in obvious improvements in the start-up rate, voltage, and power of MFC. In another research, the decoration of rGO anode with Mo$_2$C nanoparticles was proven to increase the maximum power density of MFC from 812 to 1697 mW·m$^{-2}$. This result is due to the excellent electrocatalytic activity of Mo$_2$C nanoparticles toward the electron shuttle (riboflavin) and several microbial fermentation metabolites (e.g., hydrogen and formate), which are conducive to the acceleration in anodic bioelectrocatalysis reaction and electron transfer between biofilm and anode. Even replacing the rGO anode with CNT anode, the introduction of Mo$_2$C nanoparticles on the surface of rGO (Figure 6L–N, ultimately resulting in obvious improvements in the start-up rate, voltage, and power of MFC.

In another research, the decoration of rGO anode with Mo$_2$C nanoparticles was proven to increase the maximum power density of MFC from 812 to 1697 mW·m$^{-2}$. This result is due to the excellent electrocatalytic activity of Mo$_2$C nanoparticles toward the electron shuttle (riboflavin) and several microbial fermentation metabolites (e.g., hydrogen and formate), which are conducive to the acceleration in anodic bioelectrocatalysis reaction and electron transfer between biofilm and anode. Even replacing the rGO anode with CNT anode, the introduction of Mo$_2$C nanoparticles still has a positive effect on MFC performance.$^{110}$

2.3.3 Carbon/conducting polymer binary composites

Owing to the good conductivity and environmental durability of conducting polymers, their application as the components to construct carbon/conducting polymer composites is appealing for MFC anode. Among various conducting materials, PPy can exhibit outstanding conductivity in neutral pH condition,$^{111}$ which is more compatible with the MFC. In this context, Zou et al.$^{112}$ constructed a PPy-coated CNTs composite anode for MFC with E. coli as the biocatalyst. They found that the MFC with this anode delivered a maximum power density of 228 mW·m$^{-2}$. In another research, the power density of MFC with PPy/rGO composites anode was evaluated to be 1068 mW·m$^{-2}$. However, we cannot have direct knowledge of the PPy contribution from these works, due to the lack of information about MFCs with CNT or rGO. To make it clear, a PPy/GO composite was uniformly coated on the CF anode for MFC anode through the in situ electropolymerization of Py with GO as the anionic dopant in the presence of substrate electrode.$^{114}$ The PPy/GO anode had a 37% higher cell voltage than GO anode. Moreover, the PPy/GO anode also exhibited better stability during 120 cycles of lactate feeding. These results can be attributed to the improved electronic conductivity, the enhanced bacterial adhesion, and the increased EET efficiency caused by the synergistic effect between PPy and GO.

PANI is another attractive choice to fabricate the carbon/conducting polymer anode in MFC, as its intrinsic positive charge can improve the adhesion of negatively charged bacterial cell on the anode.$^{115–117}$ As a typical research, Qiao et al.$^{118}$ fabricated a CNT/PANI composite anode with a networked-rod nanostructure for MFC, which delivered a maximum power density of 42 mW·m$^{-2}$. The integration of PANI with graphene$^{119,120}$ and graphene nanoribbons$^{121}$ has also been proven to improve the MFC performance with these carbon material-based anodes. Moreover, PANI has also been extended to integrate with one 3D carbon material-based anode. Yong et al.$^{101}$ developed a PANI-decorated graphene foam with 3D macroporous structure as an anode for MFC. The PANI has been demonstrated to have an important role in recruiting bacteria on electrode, as the bacterial cells can densely adhere to the external and interior surfaces of 3D graphene/PANI foam instead of 3D graphene foam (Figure 6L–N). On the other level, the synergistic integration between PANI and 3D graphene promoted the direct EET between bacteria and anode. Thus, the MFC with 3D graphene/PANI foam.
produced a maximum power density of 768 mW·m⁻², whereas this value for MFC with graphene foam was only 12.8 mW·m⁻². Besides the abovementioned PPy and PANI, some other conducting polymers including polydopamine and poly(diallyldimethylammonium chloride) have also been used to combine with carbon material-based MFC anode.¹²²,¹²³ These two kinds of conducting polymers possess positive charge as PANI, thus enriching the bacterial cells on the carbon material-based anodes for the performance improvement of MFCs.

2.3.4 Carbon-based ternary composites

The more components in the composites, the more properties can be integrated.¹²⁴ In this case, some carbon-based ternary composites have been created for MFC anode. The 3D graphene with macroporous structure allows bacterial penetration, and the presence of MWCNTs can prevent graphene nanosheet from re-stacking and bridge the separated nanosheets. Moreover, the high affinity between Fe₃O₄ nanoparticles and bacterial cells can accelerate bacterial attachment. In this case, a 3D graphene/MWCNTs/Fe₃O₄ anode has been developed with the purpose of combining all abovementioned enhanced strategies.¹²⁵ The graphene/MWCNTs/Fe₃O₄ anode exhibited excellent bacteria-hosting capability and high EET efficiency. Therefore, the MFC with this anode delivered a maximum power density of 882 W·m⁻³, which was obviously higher than those of corresponding binary composites. However, the poor conductivity of Fe₃O₄ nanoparticles has a negative impact on the electron transfer to some extent. The same group employed the core/satellite structured Fe₃O₄/Au nanoparticles to replace the Fe₃O₄ nanoparticles in the design.¹²⁶ In the devised 3D macroporous graphene foam decorated with Fe₃O₄/Au nanoparticles (Fe₃O₄/Au-3DGF), the electrons produced by bacterial cells could transfer through Au satellites instead of Fe₃O₄ core, further promoting the EET. Moreover, the advantages of 3D macroporous graphene foam and Fe₃O₄ nanoparticles for the bacteria-hosting ability were well preserved. Consequently, the maximum power density of MFC with Fe₃O₄/Au-3DGF anode was 2980 mW·m⁻², which was much higher than the value obtained from the previous work using the graphene/MWCNTs/Fe₃O₄ anode. The N-doping strategy was also used for carbon-based ternary composites for further improving the MFC performance. The developed anode materials including N-CNT/PANI/MnO₂ and S/N-CNT/PANI/MnO₂ displayed better MFC performance, compared with the corresponding binary counterparts, strongly confirming their better synergistic effects.¹²⁷,¹²⁸

3 CARBON MATERIAL-BASED ANODE WITH ARTIFICIAL BIOFILM

3.1 Carbon material-based hybrid biofilm

For the above investigations of MFC anodes, the carbon-based materials were modified on the substrate electrode for the natural growth of biofilm. However, the electron transfer inside these naturally formed biofilms is inefficient when the thicknesses of biofilm exceed a certain limit.¹²⁹ Furthermore, even for the carbon-based materials with macroporous structures, it is still difficult to make full use of their interior surfaces, as the bacterial colonization will block the channels over time.⁴⁷ In an early work, Liang et al.¹³⁰ found that the simultaneous addition of CNT powders and bacterial cells into the anode chamber of MFC resulted in the formation of a composite biofilm on the anode, which increased the output voltage of MFC. Although this study initiated the application of hybrid biofilm in MFC anode, there was no significant increase in the biomass on anode. The improved performance of MFC was only attributed to the fact that the inserted CNT reduced the anodic resistance. In this regard, researchers have fabricated the bacteria/CNT suspension and filtered this suspension by a cellulose acetate filter for creating the bacteria/CNT composite films (Figure 7A).⁴⁵ The SEM images revealed a densely packed biofilm on the exterior surface of this composite film (Figure 7B). More importantly, the CNT and bacteria interpenetrated throughout the interior space of films (Figure 7C). In contrast, less cell density was found on the exterior surface of CNT anode with a natural biofilm growth manner, whereas no cell was observed on the interior surface of this control anode. Thus, the application of hybrid biofilm can improve both the EET and cell density on the bioanode of MFC, making it a better replacement for traditional bacteria-colonized carbon material-based anodes. Besides the pure CNT, the CNT-based nanocomposite was also used to fabricate hybrid biofilm in MFC anode. Park et al.¹³² developed an Fe₃O₄/CNT/E. coli hybrid biofilm for MFC, which also produced a better power density as compared with that of natural biofilm. Apart from the enhanced EET by inserting CNT into biofilm, the intrinsic magnetic property allowed the fixation of hybrid biofilm on the substrate electrode under an external magnetic field, which helped to form a multilayered biofilm and increase the cell density of the anode. Obviously, this study provides a universal strategy to replace the traditional suction filter process for the fixation of hybrid biofilm to substrate electrode, which can eliminate the possible metabolic activity loss or bacterial shedding, but the poor conductivity of Fe₃O₄ that can affect the
FIGURE 7  (A–C) Schematic presentation of the fabrication process of bacteria/CNT composite film and its SEM images at top and side views. Reproduced with permission: Copyright 2018, Wiley.45 (D–F) Proposed bidirectional EET mechanism in the rGO/bacteria hybrid biofilm and its SEM images at side and top views. Reproduced with permission: Copyright 2014, Wiley.131 (G) Schematic illustration of the preparation of G-CNT hybrid biofilm anode. (H) The current generation capabilities of anodes with different hybrid biofilms in an MFC using an external resistor of 1000 Ω. Reproduced with permission: Copyright 2015, Wiley.129 CNT, carbon nanotube; EET, extracellular electron transfer; MESy, microbial electrosynthesis system; G-CNT, graphene–carbon nanotube; GO, graphene oxide; MFC, microbial fuel cell; rGO, reduced graphene oxide
EET should be considered for a further improvement in the MFC performance.

Graphene is another good precursor for the fabrication of hybrid films, as its planar structure can provide the suitable habitat for bacterial attachment. Encouraged by this, Yong et al.\textsuperscript{131} developed a 3D rGO/bacteria hybrid biofilm by the self-assembly of bacterial cells and the GO. During the fabrication process, the water-soluble GO nanosheets behaved like fishing nets to capture the bacterial cells. Meanwhile, the GO nanosheets were reduced to rGO by the captured bacterial cells, which self-assembled to form the hybrid biofilm due to the π−π stacking between nanosheets (Figure 7D). The SEM images confirmed that the rGO/bacteria hybrid biofilm delivered a 3D macroporous network with a large amount of bacteria on the surface of graphene nanosheets (Figure 7E,F), ensuring the high cell density in the MFC anode and unobstructed substrate transport. Moreover, the multiplexed conductive pathways could be formed (Figure 7D) due to the good conductivity of rGO in this hybrid biofilm, accelerating the electron transfer between bacterial cells and substrate electrode. As a result, this hybrid biofilm outperformed the natural biofilm in the MFC performance. On the basis of this study, the same group replaced the native bacterial cells with the engineered bacterial cells, which displayed the enhanced flavin biosynthesis and transportation.\textsuperscript{131} In this case, the local concentration of flavins was increased, ultimately enhancing the electron shuttle-mediated EET rate in the rGO/engineered bacteria hybrid biofilm and the MFC performance. Moreover, the graphene-based composite was also used to construct hybrid biofilm for further optimizing MFC performance. Zhao et al.\textsuperscript{129} integrated CNT into 3D rGO/bacteria hybrid biofilm for improving the EET and thus the MFC performance. The fabrication process of graphene–carbon nanotube (G-CNT) hybrid biofilm was similar to that of 3D rGO/bacteria hybrid biofilm, except for the use of a GO–CNT composite as a substitute for GO (Figure 7G). The current density of MFC with G-CNT hybrid biofilm was higher than that of rGO hybrid biofilm (Figure 7H), confirming the effectiveness of inserting CNT into rGO hybrid biofilm.

### 3.2 Carbon material-modified individual bacterial cell

The abovementioned hybrid biofilms were developed by mixing the nanomaterials with the bacterial cells. During this process, the bacterial cells may aggregate together, owing to which the bacterial cells inside the aggregations cannot make direct contact with the nanomaterials.\textsuperscript{134} In this regard, the EET efficiency in the hybrid biofilm still has the space to be improved. Recently, cell surface modification technology has received much attention, through which various function materials can be coated on the surface of individual living systems.\textsuperscript{135–137} Thus, the cell surface modification technology has become an effective strategy for further improving the EET between anode and bacterial cells, because it allows every bacterial cell in hybrid biofilm to intimately make contact with nanomaterials.\textsuperscript{138,139}

The use of carbon materials as surface modifiers for exoelectrogens is still in its infancy, and only carbon dots (CDs) have yet been used as a surface modifier. Yang et al.\textsuperscript{140} have exploited CD-fed bacterial cells for MFC. As shown in Figure 8A–D, unlike the rare bacterial cell with a smooth profile, the black spots that could be assigned to CDs were found on the surface of CD-fed bacterial cell. The TEM images from cryo-electron tomography further revealed that the CDs penetrated into the CD-fed bacterial cell and were found in the cytoplasm, periplasm, and inner membrane of the bacterial cell (Figure 8E,F). These CDs not only favored the EET and cellular adhesion but also accelerated the metabolic rate, ultimately leading to an increased maximum current density of MFC. Apart from the good conductivity, CDs also possess good photoelectrical responsive capability. Inspired by this, the CDs have been used as a dual-functional modifier to boost the performance of photo-assisted MFC.\textsuperscript{141} The bacterial cells modified with N,S-doped CDs were fabricated by an electrostatic attraction strategy, in which the bacterial cells carried a negative charge, whereas the N,S-doped CDs were previously modified with amine-terminated ionic liquid to show a positively charged surface. The laser confocal scanning microscopy images of functional bacterial cells showed a green fluorescence from CDs, and the TEM images revealed that the CDs were coated on bacterial surfaces (Figure 8G–I). The differential pulse voltammetry spectra displayed that the oxidation and reduction peak potentials of cytochrome c on the N,S-doped CD-modified electrode in the dark condition were negatively and positively shifted, compared with those of unmodified bacterial cells, respectively. Moreover, the shift degrees were increased under light illumination (Figure 8J,K). These results indicated that the good conductivity and photoelectrical responsive capability together promoted the EET efficiency. As a result, the MFC with functional bacterial cells generated a maximum power density of 1697.9 mW·m\textsuperscript{2} under light illumination, which is 2.6-fold higher than that of the MFC with unmodified bacterial cells. These successes achieved by using CD-modified bacterial cells will encourage us to intensify the investigation of carbon material-modified bacterial cells in MFCs.
FIGURE 8 (See caption on next page)
4 | CONCLUSIONS AND PERSPECTIVES

In this review, we focused on the carbon material-based anodes that have been used in MFCs for improving performance. On the one hand, carbon materials have been used as anodic materials for bacterial habitat. In this type, the CNTs and graphene are the most commonly investigated carbon materials. Then, some enhancement strategies, including the introduction of 3D porous structures, heteroatoms, and other kinds of nanomaterials (metals, metal organic compounds, and conducting materials), have been employed to enlarge the surface area and enrich the surface properties of carbon materials for increasing their bacteria-hosting capabilities and the EET efficiencies. Moreover, these enhancement strategies were also integrated together to develop novel carbon materials with better performance, such as 3D macroporous heteroatom-doped carbon materials, carbon-based ternary composites. On the other hand, in view of the low cell density on anodic materials, the concept of hybrid biofilm has been proposed as MFC anode. The hybrid biofilm involving CNT and graphene and their composites was created, which improved EET efficiency expect for the higher cell density. Moreover, the single-cell surface modification technology has been used to ensure that each bacterial cell in the hybrid biofilm can form good contact with the carbon material for the best EET efficiency.

Although these sophisticated carbon materials and delicate hybrid biofilms have brought enormous strides in the performance of MFCs, the research studies on carbon-based anode of MFC still have not dealt with a number of aspects. In the future, the research studies can focus more on the following aspects:

(1) Intensifying the investigation on the carbon-based hybrid biofilms for MFC. Unlike the extensive research studies on the development of novel carbon materials as anode materials for MFC, only several groups have paid their attention to the carbon-based hybrid biofilms. However, these reported works strongly proved that these carbon-based hybrid biofilms outperform the same carbon materials but with a natural biofilm. Thus, the fabrication of novel carbon-based hybrid biofilm is promising for MFC.

In the future, the enhancing strategies used in the traditional anode with a natural biofilm can be further introduced for the fabrication of novel hybrid biofilms. For example, the doping of heteroatoms can improve the performance of carbon material-based anode with natural biofilms; however, the question whether it could provide a better performance in the manner of hybrid biofilms and cell surface modification still remains unanswered. Moreover, the optimization of space structure has been demonstrated to display positive effects on the performance of carbon material-based anode with natural biofilm, because it is conducive to the diffusion of substrate and mediators. However, most of the current hybrid biofilms are randomly formed. Thus, it is believed that the regulation of spatial structure of these hybrid biofilms would extend their application potentials in MFCs.

(2) Exploring the new generation of carbon-based anodes to integrate MFCs with other energy-related systems. Up to now, the carbon material-based anodes have been demonstrated to obviously improve the MFC performance. However, the maximum open-circuit voltage of MFC cannot exceed 1.1 V in theory. Except for the cascading of multi-anodes in series, the sole use of MFC still has its limitation. In this case, developing dual-functional anodes to integrate MFC with some other energy systems seems to be a good choice. On the one hand, much more effort should be dedicated to endowing the carbon-based anodes of MFC with photoelectrically responsive ability. The chemical-to-electrical conversion can be coupled with solar-to-electrical conversion for improved electricity production. On the other hand, the carbon-based anodes of MFC can be offered capacitive property, which can also realize the higher output. Certainly, it is worth to input strong effort in probing into the combinational use of these three technologies or the integration of MFC with other kinds of energy-related systems.

(3) Revealing the relationships between carbon material-based anode and the long-time stability of MFC. After

FIGURE 8 (A–D) Transmission electron microscopy (TEM) images of carbon dot (CD)-fed bacterial cells (A,B) and pristine bacterial cells (C,D) at different magnifications. (E,F) TEM images constructed by cryo-electron tomography for CD-fed bacterial cells. Reproduced with permission: Copyright 2020, Springer Nature.140 (G,H) Bright and fluorescence field images of the functioned bacterial cells. (I) High-resolution TEM images of the functioned bacterial cells. (J,K) Differential pulse voltammogram of cytochrome c on the unmodified electrode and CD-modified electrode in the dark or light conditions. (L) Polarization and power density curves of MFC with pristine and functional bacterial cells under dark or light conditions. Reproduced with permission: Copyright 2019, Elsevier141
the output of MFC reaches a new elevated level, the researchers inevitably face the issue of its lifetime. Several carbon-based anodes have demonstrated to improve the long-time stability of MFC \(^{62,115}\); however, the underlying mechanisms have not been clarified due to lack of powerful pieces of evidence. Some advanced in situ or in operando analysis methods that can accurately grasp the information of biofilm formation, metabolic rate, and secretion compositions would be required. By coupling the as-obtained information with advanced microbiology theories and high-level modeling tools, expedient properties of anode for MFC lifetime can be summarized, ultimately pushing the practical process.

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**ORCID**

Qichun Zhang @ http://orcid.org/0000-0003-1854-8659

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**AUTHOR BIOGRAPHIES**

**Xiaoqi Fan** received his BS degree from the College of Chemical Engineering at Zhengzhou University in 2020. Currently, he is a master’s candidate under the supervision of full Prof. Zhaohui Li and associate Prof. Rong-Bin Song at Zhengzhou University. His research interests focus on single-cell surface modifications and their applications in microbial fuel cells.

**Rong-Bin Song** received his PhD degree from the School of Chemistry and Chemical Engineering at Nanjing University in 2017. He continued his postdoctoral research at Nanjing University from 2017 to 2020. Currently, he joined Zhengzhou University as an associate professor. His recent research interests focus on the novel electrode materials for microbial fuel cell, single-cell surface modification, and biofuel cell-based self-powered biosensor.

**Zhaohui Li** received his PhD degree from the State Key Laboratory of Chemo/Biosensing and Chemometrics at Hunan University in 2007. He did his postdoctoral training in Walt Group at Tufts University from 2007 to 2009 and in Pacific Northwest National Laboratory from 2009 to 2011. At present, he is a full professor at Zhengzhou University. His research interests mainly focus on nanomaterial preparation and its applications in chemo/biosensing.

**Qichun Zhang** is a professor at the City University of Hong Kong. His research interests include carbon-rich conjugated materials and their applications in optoelectronic and semiconductor devices as well as microbial fuel cells. Dr. Zhang is a fellow of the Royal Society of Chemistry. He has published more than 400 papers, with >21,800 total citations and an H-index of 81. From 2018 to 2020, he is a highly cited researcher in cross-field (top 1%) on Clarivate Analytics’s lists.

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