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Graphene-based electrode materials for microbial fuel cells

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Microbial fuel cells (MFCs) are environmentally friendly technology capable of converting chemical energy stored in wastewaters directly into electrical energy by using microorganisms as biocatalysts. However, the overall low power density of the MFC and the high cost of its components are two major barriers for its commercialization. Among all the factors, the electrodes (cathode and anode) materials play the significant role in affecting the performance of MFCs. Recently, the performance of MFCs has been improved by using graphene-based electrodes that are more conductive and mechanically stable with larger surface area and higher electrocatalytic activity compared to the conventional carbon materials. This paper provides an overview of recent research progress in graphene-based materials as electrodes for MFCs, which will be the promising candidates for developing MFCs and other bioelectrochemical systems to achieve sustainable water/wastewater treatment and bioenergy production.

INTRODUCTION

In the past decade, microbial fuel cells (MFCs) have been emerging as one of the promising alternative technologies for harvesting renewable energy through wastewater treatment [1–3]. The traditional two chamber-MFCs typically have an anode and a cathode separated by a proton exchange membrane in a two chamber setup (Fig. 1). When organic compounds (e.g., organic wastes in wastewater) are infused into the anode chamber, electrochemically active bacteria oxidize the substrates with producing protons and electrons. The protons pass through the proton exchange membrane to the cathode. Electrons are transferred through an external circuit from the anode to the cathode, driving an external load and reducing the electron acceptor (e.g., oxygen) at the cathode. As the electrodes are the sites for electron transfer, excellent electrical conductivity is the favorite properties for the potential electrode material. Besides this, a desirable anode material should be biocompatible so that bacteria introduced into the system will form a biofilm on the anode, while a favorable cathode material should have a highly electrocatalytic activity toward oxidants (e.g., oxygen) reduction reaction. However, high cost of cathode catalysts and low charge transfer efficiency of electrodes restrict the development of MFC technology [4].

To address these issues, a variety of materials and their modifications, including carbon/graphite materials, carbon nanotubes (CNTs), nanostructured materials and non-precious metals, have been studied, as reviewed in detail elsewhere [1,5]. While some traditional materials have shown certain promise in MFCs, their applications are still limited by their intrinsic issues, such as low specific surface area, low conductivity, poor biocompatibility, and/or complicated synthesis procedures. For instance, the synthesis of multiwall CNTs (MWCNTs) is normally carried out at a higher temperature (>500°C) in the presence of metal catalyst using the chemical vapour deposition (CVD) technique [6]. The presence of metal catalyst in the MWCNTs-based cathode can also have negative effects on the performance of MFC. Graphene, as a newly developed material, can be synthesized at room temperature using simple solution chemistry at a much lower cost than that of MWCNTs, during which toxic metal catalysts are not used. In this prospect, graphene is a desired alternative to MWCNTs for application in the MFCs [7].

So far, graphene based materials have been extensively investigated and envisaged as potential electrode materials for lithium ion batteries, supercapacitors, biosensors, photovoltaic cells, and catalysis due to its attractive properties, including high surface area (theoretical value 2630 $m^2 g^{-1}$), high conductivity, and easy synthesis process [8,9]. Recent studies show the maximum power density of the MFCs has been significantly improved by using the graphene as the catalyst support due to the better dispersion of the metal

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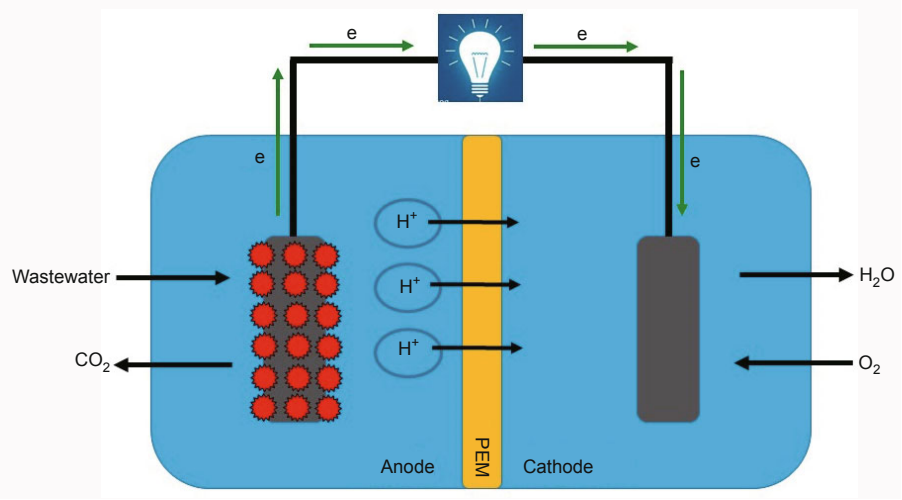

Figure 1 A dual-chamber MFC in which a proton exchange membrane (PEM) separates anode and cathode chambers.

catalysts on the graphene surface [10–12]. In addition to being an excellent catalyst support, the potential of using graphene-based cathode/anode electrode in MFCs has also been demonstrated in some studies [13–19]. All studies revealed the great potential of using graphene to improve the electrode performance in MFCs.

This review summarizes the recent developments using graphene as either catalysts or supports of electrode for MFCs, which consists of two major sections: 1) the progress regarding graphene as the cathode catalysts of MFCs, and 2) the modification of graphene as the anode electrode for improving MFC performance.

GRAPHENE-BASED CATHODE MATERIALS

Like conventional fuel cells, electrons produced on the anode side of MFCs pass through an external electric circuit and then are consumed on the cathode side (Fig. 1). Therefore, a proper electron acceptor, e.g., potassium ferricyanide ($K_3[Fe(CN)_6]$) or oxygen (O_2), should be present in the cathode chamber to accept the electrons through a reduction reaction. Nowadays, O_2 is the most popular oxidant applied in MFCs due to its ubiquity and high oxidation potential. The oxygen reduction reaction (ORR) may take place by inserting the cathode into an aqueous solution and allowing O_2 to diffuse to the cathode (aqueous-cathode) or by placing the cathode in direct contact with the air (air-cathode) [8–10]. However, the development of the O_2 cathode-based MFCs still faces daunting challenges, such as the slow rate due to the sluggish kinetics of ORR and the high overpotential of oxygen reduction on the surface of the cathode at neutral pH, as well as poor contact between O_2 and the cathode electrode. A variety of approaches have been proposed to improve the performance of the cathode by lowering the reaction overpotential, including the use of mediators, electrode modification with catalysts, and optimizing operational conditions within the cathodic compartment [11,12].

The ORR involves a series of electron transfer processes depending on the type of catalysts used at the cathode of the fuel cells. Generally, the electroreduction of O_2 may proceed either directly to water by a 4-electron reaction (Reaction 1) or by a two-step reaction via hydrogen peroxide (H_2O_2) as the intermediate (Reactions 2 and 3).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (3)$$

Certainly, a direct 4-electron transfer in ORR is the most favorable pathway for an MFC system. Whereas some catalysts are incapable of oxidizing H_2O_2 at sufficient rates, the reduction will terminate after the first two electron reduction steps. In this case, the 2-electron pathway produces H_2O_2 as an intermediate or the end product of the oxygen reduction, causing degradation of the cathode catalysts and leading to a high overpotential [13]. So far, the main problems with practical applications of the MFC are the low power output and the high cost of platinum (Pt), a conventional cathode catalyst. Therefore, it is highly desirable to explore alternative materials to Pt-based catalysts. Recently, breakthrough has been achieved in developing new materials as inexpensive alternative to the costly Pt. In the following section, we outline the highlights of the last decade of progress in the field of cathode catalysts for MFCs,

mainly focusing on graphene-based cathode catalysts that may be proved to be useful for MFCs.

Platinum cathode catalysts

Pt or Pt based binary alloy is often used as the oxygen reduction catalyst on the cathodes of MFCs [20,21]. The catalytic activity of Pt-based materials is influenced by their structure, metal particle size and shape, and supporting material used on the electrode. For example, the dendrimer encapsulated Pt-based cathodes resulted in a higher power production with 129.1% as compared to cathode with electrodeposited Pt [22]. The supporting materials for electrodes also affect the performance and stability of the catalysts. Carbon black-supported Pt catalyst hinders its use as the electrode catalyst due to its vulnerability toward oxidation of carbon black support [23]. However, some other nano-structured carbon supports show oxygen reduction activities and their application can reduce the quantity of noble metals catalyst required. For example, CNT/Pt composite electrodes would increase MFC power output by 8.7–32.2% [24]. Xie *et al.* [25] reported an MFC equipped with a CNT-textile-Pt cathode demonstrating a 2.14-fold maximum power density with only 19.3% Pt loading, compared to that with a commercial Pt coated carbon cloth cathode. The subsequent study of them revealed that the CNT-sponge electrodes had lower internal resistance, greater stability, more tunable and uniform macroporous structure (pores up to 1 mm in diameter), and improved mechanical properties in comparison with the CNT-coated textile electrodes [25,26]. Graphene (G), a two-dimensional ultrathin material, has become the focus of intense fundamental research due to its extraordinary properties, such as good electronic conductivity, large surface area, high mechanical and/or thermal stability and durability. Graphene has become a promising support material for the ORR catalyst [27,28]. Yan *et al.* [11] proved that the maximum power density of the MFC with a Pt-Co/G cathode was 1378 mW m^{-2}, which was a little lower than that with a Pt/C cathode (1406 mW m^{-2}). Moreover, compared with carbon black or carbon nanotubes, graphene not only possesses similar physical properties but also larger surface areas. Additionally, production cost of graphene sheets in large quantities is much lower than that of CNTs [29]. Thus, intensive effort has focused on using graphene as the catalyst support for fuel cell applications. However, the practical application of Pt has been limited greatly due to its relatively high cost and sensitivity to poisoning. Therefore, the following two approaches are usually adopted to reduce the catalyst cost: to reduce Pt loading through enhancing the utilization efficiency for ORR, and to develop noble metal-free electrocatalysts of ORR. In the short-term, catalysts loading small amounts of Pt are the priority and are also practical, but in the long term, precious metal-free catalysts should be a better solution.

Precious metal-free cathode catalysts

Metal oxide

The application of cheap transition metal oxides as ORR catalysts of MFCs has attracted great attention, especially in the use of manganese dioxide (MnO_2), which has been studied extensively by researchers worldwide owing to its low cost and low toxicity, environmental benignity, and high chemical stability and catalytic activity [30–32]. The studies of MnO_2 applied in MFCs demonstrate that the crystal structure, particle size, synthesis method and the support material can significantly affect the catalytic activity of MnO_2. For example, MnO_2 materials with different crystal structures (α-MnO_2, β-MnO_2, and γ-MnO_2) have been investigated extensively as the cathode catalysts in MFCs. β-MnO_2 was proved to be the most effective catalyst with a maximum power density of 3773 ± 347 mW m^{-3} [31]. However, the electrochemical performance of pure MnO_2 is still unsatisfactory due to poor dispersion and electrical conductivity. As an effective eletrocatalyst, MnO_2 can be incorporated into the electron-conductive materials (such as nanocarbon) to improve its catalytic activity for ORR. Previous reports demonstrated that the electrochemical performance of β-MnO_2/CNT mixtures or *in situ* MnO_2/CNTs was partly affected by the structure of the carbon substrate [6,33]. Graphene nanosheet (GNS) is a kind of two-dimensional layer of sp^2 hybridized carbon, which has significant advantages for catalyst support material compared with the conventional carbon materials such as activated carbon and CNTs. Wen *et al.* [10] proved that the nano-structured MnO_2/GNS composite exhibited an excellent catalytic activity for ORR due to MnO_2 nanoparticles closely anchored on the excellent conductive graphene nanosheets. As shown in Fig. 2a, oxygen reduction peak of the electrode with MnO_2/GNS catalyst is clearly observed at −0.43 V, which is more positive than that of MnO_2 catalyst (−0.71 V) and even a little more positive than that of Pt/C catalyst (−0.44 V), indicating that MnO_2/GNS could catalyze ORR at a more positive potential. Additionally, the oxygen reduction peak current of MnO_2/GNS catalyst is larger than that of Pt/C catalyst. As a result, MFC with MnO_2/GNS as air cathode catalyst generated a maximum power density of 2083 mW m^{-2} (Fig. 2b), which was higher than that of MFC with pure MnO_2 catalyst (1470 mW m^{-2}) [10]. Moreover, a maximum volumetric power density of 4.68 W m^{-3} was achieved from the MFC with manganese diox-

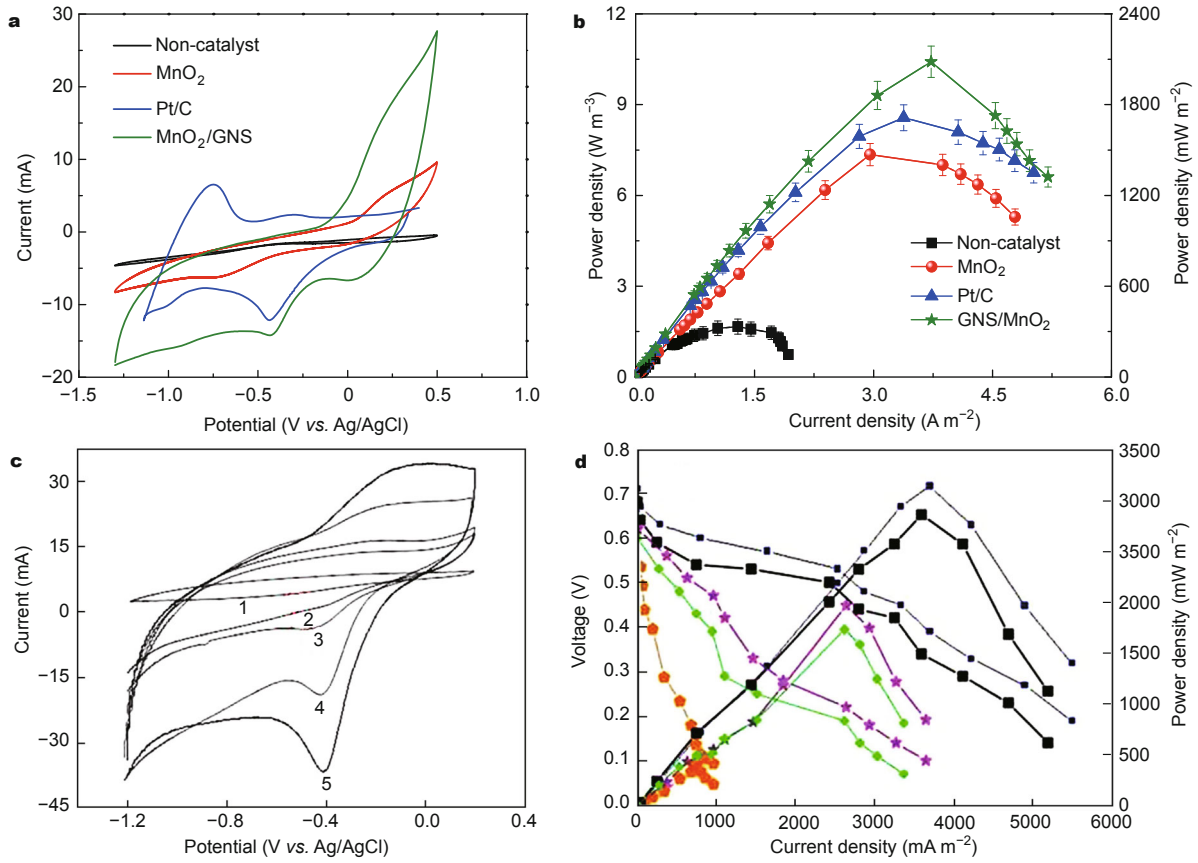

Figure 2 (a) Cyclic voltammogramsof the electrodes with different catalysts at scan rate of 10 mV s^{-1} in 50 mM phosphate buffered solution (pH 7.0). (b) Power density curves of MFC equipped with non-catalyst cathode, MnO_2 cathode, Pt/C cathode and MnO_2/GNS cathode (Reproduced with permission from Ref. [10], Copyright 2012, Elsevier). (c) Cyclic voltammograms and (d) power generation of air cathode MFC equipped with unmodified (curve 1, ●), α-MnO_2 nanorods (curve 2, ♦), α-MnO_2 nanotubes (curve 3, ★), Pt/C (curve 4, ■), and α-MnO_2 nanotubes/GO nanocomposite carbon cloth electrode (curve 5, ▪) (Reproduced with permission from Ref. [12], Copyright 2014, Elsevier).

ide nanotubes (MnO_2-NTs) as the catalyst and graphene as the support in the cathode, which is higher than that of MnO_2-NTs/MWCNTs (3.94 W m^{-3}) and MnO_2-NTs/Vulcan XC (2.2 W m^{-3}) composite cathodes [34]. Gnana Kumar *et al.* [12] revealed that hollow structured MnO_2 nanotubes exhibited excellent catalytic activity towards the ORR over the rod structure and was further enhanced with the effective carbon support graphene oxide. At the potential of –0.4 V, a higher current of –0.35 mA was observed for the MnO_2/GO composite modified electrode, which was the highest among the studied electrodes (Fig. 2c). The MnO_2/GO composite modified electrode achieved a maximum power density of 3359 mW m^{-2}, which was 7.8 fold higher than that of unmodified electrode and comparable with the Pt/C modified electrode (Fig. 2d) [12]. All in all, the larger surface area, better electronic conductivity and lower production-cost of graphene than that of MWCNTs make it a suitable candidate among different forms of carbon. Additionally, electrochemical measurements revealed that the as-prepared Co_3O_4/N-G nanocomposite exhibited a high catalytic activity and long-term stability for ORR in neutral electrolyte. Using Co_3O_4/N-G as the cathode catalyst in MFCs, the obtained maximum power density was 1340 ± 10 mW m^{-2}, which was as high as almost four times that of the plain cathode (340 ± 10 mW m^{-2}), and only slightly lower than that of a commercial Pt/C catalyst (1470 ± 10 mW m^{-2}) [35]. It should be noted that, another work conducted by Song *et al.* [36] revealed that the performance of MFC with Co_3O_4/NCNT cathode was better than that of the MFC with Co_3O_4/NGO. The maximum power density achieved from the Co_3O_4/NCNT cathode was 469 ± 17 mW m^{-2}, which is 1.1 times larger than that of the Co_3O_4/NGO cathode.

M-N/C catalysts

Transition metal nitrogen-containing complexes support-

ed on carbon materials (M-N/C, M = Fe, Co, Ni, etc.) have been considered to be efficient non-precious metal ORR catalysts [16,37,38]. Among these M-N/C electrocatalysts, metal-N_4 macrocycles, such as Fe- and Co-N_4 macrocycles, have been gaining popularity as cathodic electrocatalysts in MFCs due to the abundance and high electroactivity of transition metals [39,40]. For example, Fe-N*x*/C derived from pyrolysis of Fe(II) phthalocyanine (FePc) was tested as cathodic electrocatalyst for ORR in a two-chamber MFC system [41]. It should be noted that the performance of the FePc cathode in MFCs also strongly depended on the carbon support materials. The FePc/graphene electrode had a more positive peak potential and a larger peak current for ORR in comparison with the FePc electrode. The maximum power density of 817 mW m^{-2} has been obtained from the MFC with a FePc-G cathode, which is close to that of a Pt/C cathode of 856 mW m^{-2} [41,42]. Fe-N*x* composites, was considered as the active centers of Fe-N*x*/C for ORR. In early time, Fe-N*x* composites were produced through high-temperature pyrolysis of metals containing macrocyclic compounds, such as FePc compounds [43]. However, the high price of porphyrin or Pc, and the sophisticated preparation procedure, especially the heat-treatment strategies, inhibit large-scale synthesis of these catalysts. A significant breakthrough was achieved by Yeager and coworkers when they replaced expensive macrocyclic compounds with cheap nitrogen-containing polymer and transition metal precursors [44]. Meanwhile, recent studies suggested that nitrogen-doped graphene (N-G) can enhance the conductivity of graphene and its electrocatalytic activity [45,46]. Thus, functionalized graphene with iron/colbalt and nitrogen can be a promising candidate for ORR in neutral pH condition. For example, linear sweep voltammetry (LSV) tests showed that Fe-N/G catalyst had more positive onset potential and increased reduction current densities as compared to the pristine graphene catalyst (Fig. 3a). More importantly, the Fe-N/G-MFC achieves the highest power density of 1149.8 mW m^{-2}, which is 2.1 times of that generated with the Pt/C-MFC (561.1 mW m^{-2}) and much higher than that of the G-MFC (109 mW m^{-2}, Fig. 3b) [15]. Moreover, Liu *et al.* [47] proposed a novel strategy to improve the loading and distribution of the Fe-N*x* com-

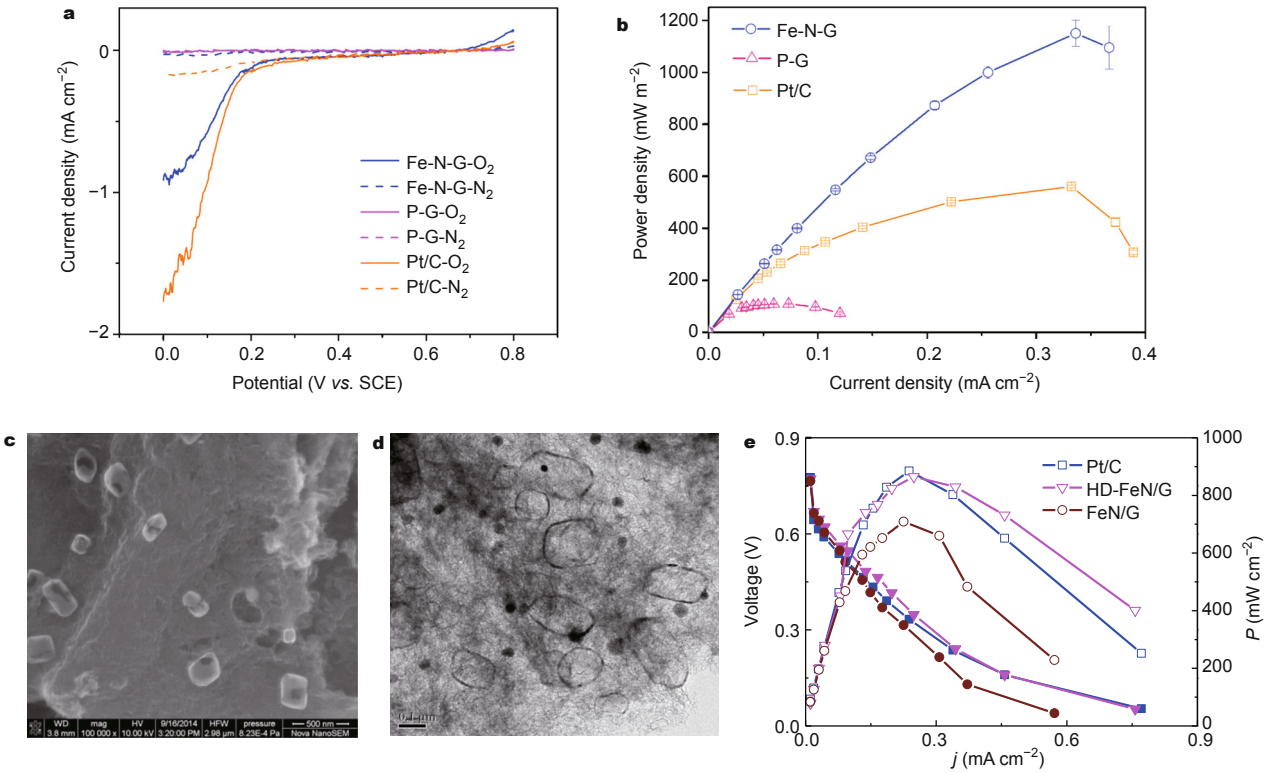

Figure 3 (a) LSV curves of FeNG, PG and Pt/C in O_2-saturated (solid line) or N_2-saturated (dashed line) PBS medium at a scan rate of 1 mV s^{-1}, and (b) power density curves of MFCs with different cathode catalysts (Reproduced with permission from Ref. [15], Copyright 2012, Elsevier). (c) SEM and (d) TEM images of HD-FeN/G, and (e) power density curves of MFCs equipped with different cathode electrocatalysts (Reproduced with permission from Ref. [47], Copyright 2012, Elsevier).

posites on graphene. The SEM and TEM images proved that cubic-like structure nanoparticles were clearly observed on the HD-FeN/G sample (Figs 3c and d). However, no obvious particle was observed in the FeN/G sample. HD-FeN/G outperformed FeN/G in terms of ORR electron transfer number, onset potential, and current density. Further studies showed that the HD-FeN/G-MFC achieved a maximum power density of 885 mW m^{-2}, much higher than that of FeN/G-MFC (708 mW m^{-2}, Fig. 3e) [47].

Metal free catalysts cathode catalysts

Regular reduced GO (rGO) is made by thermal exfoliation of GO at 200°C and the resulting material is typically flat sheet with wrinkles. Luo *et al.* [48] developed a new type of rGO particles by crumpling the flat sheets into crumpled paper ball-like structure by an aerosol-assisted capillary compression process. The maximum power densities with the crumpled graphene- and flat graphene-modified cathode electrodes were 3.3 and 2.5 W m^{-3}, respectively, significantly higher than 0.3 W m^{-3} with the unmodified carbon cloth, although still lower than a platinum cathode electrode [17]. Additionally, doping graphene with nitrogen atoms (NG) has been found to lead to a high electrocatalytic activity for ORR in the alkaline solution, with a great potential as a cathode catalyst in fuel cells [45,49]. When the NG was applied as the cathode catalyst of MFCs, the obtained maximum power density was comparable to that of conventional Pt/C catalysts. More importantly, MFCs with NG produced power more stable than those with Pt catalysts [50,51]. Nitrogen-doped graphene nanosheets (NGNSs) with a pore volume of as high as 3.42 m^3 g^{-1} were investigated as the cathode catalyst of MFCs, and they showed comparable catalytic performance for ORR with Pt/C catalysts in several electrochemical parameters, including the onset potential, the current density and the peak potential of ORR (Fig. 4a). The NGNSs also can efficiently catalyze the O_2 electrochemical reduction in the 4-electron pathway to produce H_2O (Figs 4b and c). Additionally, the maximal current density was 23.34 A m^{-3} for the NGNSs-based MFC (Fig. 4d), which was around 1.2 times higher than that achieved in Pt/C-MFC under identical conditions (19.3 A m^{-3}) [14,52]. However, the conductivity of regular NG was measured to be 35 S m^{-1}, which was still 10 S m^{-1} lower than Pt/C [4,50]. Therefore, it is of crucial importance to maximize the conductivity of graphene cathodes in practical applications. Graphene doped conducting polymers, such as polyaniline (PANI), exhibited an improved conductivity of 10 S cm^{-1} in comparison with 2 S cm^{-1} of pure PANI [53,54]. Electrochemical impedance spectroscopy (EIS) results revealed the diminished internal resistance for the PANI/GNS cathodes compared to the PANI cathode, with the PANI/GNS ratio of 9:1 being the most conductive electrode. Moreover, The $PANI/GNS_{0.1}$-MFC exhibited the maximal power density of 99 mW m^{-2} due to the outstanding electrical conductivity, 116 times that of the blank MFC (0.85 mW m^{-2}) [55]. PANI has been also used as an attractive precursor for synthesis of nitrogen-doped carbon material. For instance, Wu *et al.* [56] reported the nitrogen-doped graphene sheets as a new catalyst for ORR, which was prepared by the carbonization of polyaniline and Co precursors using MWNTs as a template. Wen *et al.* [57] provided a simple approach to prepare porous nitrogen-doped carbon nanosheet (PNCN) on graphene derived from GO–PANI hybrid through carbonization and activation treatment. As a result, the maximum power density of 1159.34 mW m^{-2} obtained with PNCN catalyst in a MFC was higher than that of Pt/C catalyst (858.49 mW m^{-2}). Additionally, carbon materials with multi-element doping, including nitrogen (N), boron (B), sulfur (S), or phosphorus (P) etc., have encouraged intensive research as promising metal-free ORR electrocatalysts in all kinds of fuel cells [19,58–62]. However, this has not yet been completely evaluated in MFCs.

GRAPHENE-BASED ANODE MATERIALS

Although a number of factors influence the performance of MFCs, the anode material, which is associated with bacterial adhesion and electron transfer from microbes to the electrode by different mechanisms (proteins on the cell membrane, soluble electron-shuttling molecules, and conductive pili [63]), strongly influences the power density. Therefore, an ideal anode electrode functions not only as a conductor, but also as a carrier of bacteria, and some special surface characteristics of the electrode materials, such as good biocompatibility, high surface area and roughness for accommodating a large quantity of microbes, and efficient electron transfer between bacteria and the electrode surface, are essential for high bio-catalytic activity. Commercially available carbon-based porous materials, such as carbon cloth, carbon paper, and carbon felt, have been widely used for MFCs because of their good chemical stability [64]. However, the relatively low power density and poor energy conversion efficiency of conventional carbon materials, resulting in sluggish electron transfer between bacteria and electrode, limiting the practical applications of MFCs. In this regard, graphene-based materials are promising candidates for highly efficient MFC anodes.

Graphene can be synthesized by the chemical oxidation-reduction treatment of graphite [65,66], during which toxic metal catalysts are not used, which is a desired prop-

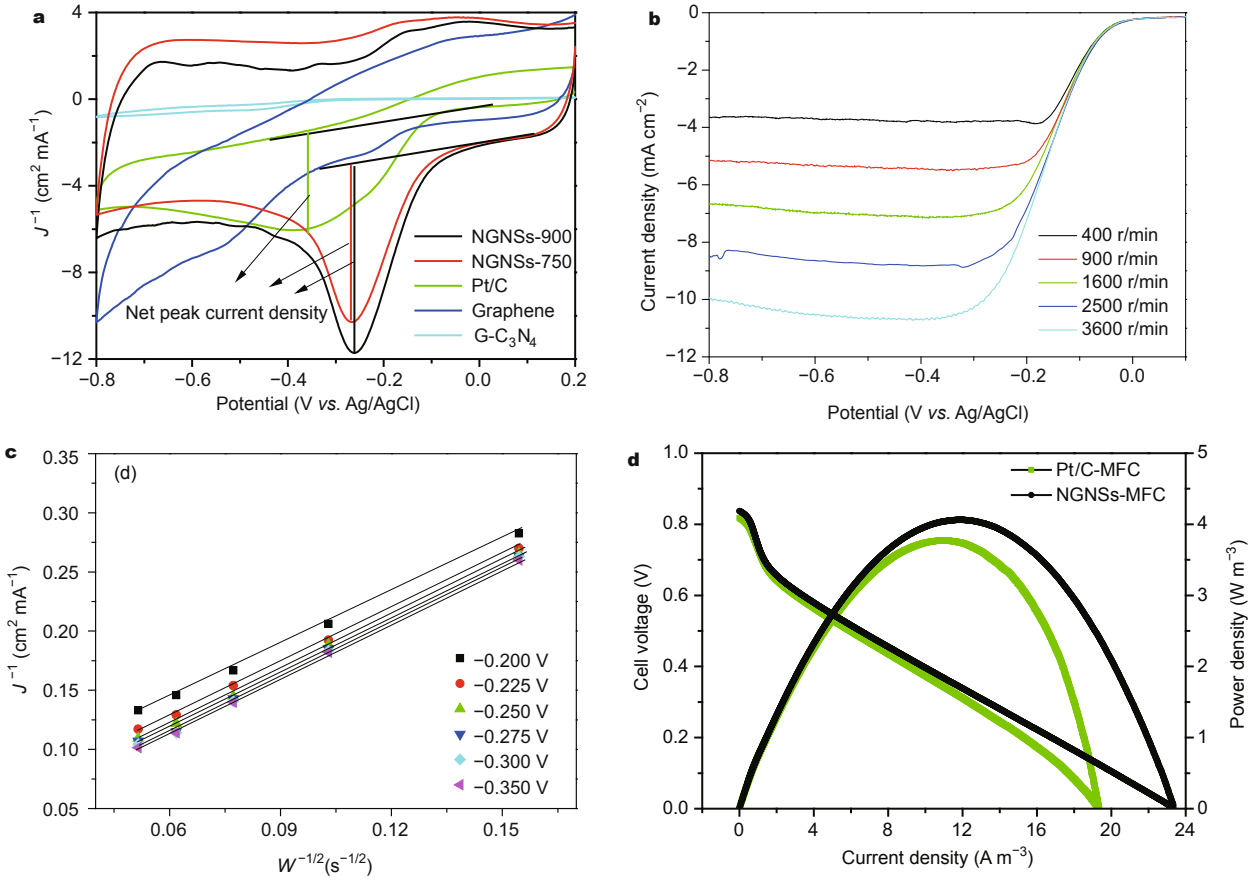

Figure 4 (a) CVs of the different electrodes in oxygen saturated 0.1 M KOH solution in the range of −0.8 to 0.2 V. Scan rate: 50 mV s^{-1}; (b) the linear-sweep voltammograms recorded with different rotation rates in an O_2 saturated 0.1 M KOH solution on NGNSs-900 electrode at a scan rate of 5 mV s^{-1}; (c) Koutecky-Levich plot of current density *vs.* $W^{-1/2}$ at different potentials on NGNSs-900 electrode; (d) MFC polarization and power density curves with Pt/C and NGNSs-900 cathode. Note: the power density was normalized based on the volume of anode solution (Reproduced with permission from Ref. [14], Copyright 2012, Springer).

erty for application in the MFCs. Zhang and coworkers reported the improved electrochemical performance of a dual-chamber MFC operated with graphene-modified stainless steel mesh (GMS) anode electrode [13]. Later on, a 3D macroporous anode with coating graphene on stainless steel fiber felts (SSFFs) was reported to deliver a maximum power density of 2142 mW m^{-2} at a current density of 6.1 A m^{-2} in MFC, greatly improving the performance of MFC compared with the unmodified SSFF-MFC. EIS measurements together with the polarization curves demonstrated that carbon nanoparticles modified anodes could greatly decrease MFCs' internal resistance [67]. Huang *et al.* [68] and Yuan *et al.* [69] found that graphene could enhance electron transfering in bioelectrochemical systems. Scanning electron microscopy (SEM) results indicate that the increase in power generation could be attributed to the high surface area of the anode and an increase in the number of bacteria attached to the anode. These studies revealed the great potential of using graphene to improve the electrode performance in MFCs. After that, some studies demonstrate that graphene-modified carbon cloth (CC) or graphite plate (GP) electrode exhibit higher power density than that of bare CC, activated carbon or the bare graphite modified electrode [17,70–72]. Some previous studies reported three-dimensional (3D) anodes were prepared by the graphene sponge (GS), which provided 3D open space with a large area for microbial colonization (Figs 5a and d). The surface of the GS surface was covered by microorganisms interconnected by microbial nanowires (Figs 5b and e), providing a probable direct path for the extracellular electron transfer, such highly porous graphene sponge guarantees their potential application in MFCs as flexible anode material. Compared with stainless-steel or commercial carbon felt as anode, graphene nanosheets modified

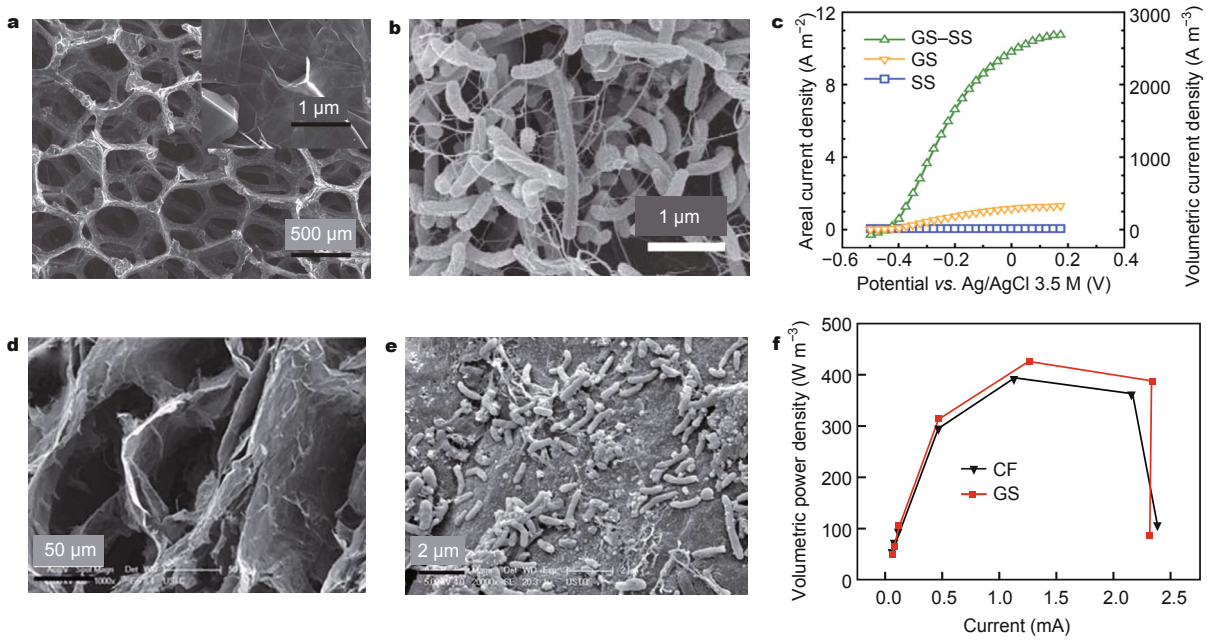

Figure 5 (a) SEM image of the graphene sponge (GS) showing the macroscale porous structure and the graphene surface (inset). (b) The GS anode surface is covered by microorganisms interconnected via microbial nanowires, and (c) the maximum current density achieved by the GS–SS electrode is eight times that of the GS electrode (Reproduced with permission from Ref. [18], Copyright 2012, the Royal Society of Chemistry). (d) Cross-sectional SEM images of graphene sponge, (e) micrographs of microorganism adhered on graphene sheet from cross-section of the GS, and (f) the maximum power densities achieved by using GS and CF as the anode (Reproduced with permission from Ref. [73], Copyright 2014, the Royal Society of Chemistry).

anode did improve the performance of MFC (Figs 5c and f) [18,73,74].

Conductive polymers, such as polypyrrole (PPy) and PANI, are utilized as anode catalysts in MFCs, owing to their prompt electron conduction properties [75,76]. Among the aforementioned conducting polymers, PANI has been considered as a unique polymer, owing to its low cost, easier synthesis protocols, high conductive properties, environmental stability, and biocompatibility. Recently, a macroporous and monolithic MFC anode based on PANI hybridized 3D-graphene demonstrated that the maximum power density obtained from the 3D graphene/PANI MFCs (~768 mW m^{-2}) was about four times higher than that from the carbon cloth MFCs (~158 mW m^{-2}) [77]. Hou and coworkers [78] also proved that the MFCs with the PANI-rGO/CC anode yielded a maximum power density of 1390 mW m^{-2}, which was three times larger than the MFC with the CC anode. Zhao *et al.* [79] modified the graphene nanoribbons with PANI by using the electropolymerization technique and the corresponding anode catalyst exhibited a maximum power density of 856 mW m^{-2}, which was about six times higher than that of bare electrode. The fact that the graphene associated with PANI modified MFC electrode outperforms the planar carbon electrode is due to its abilities to form a 3D interface with the bacterial biofilm, facilitating electron transfer and providing multiplexed and highly conductive pathways [77]. PPy has also been specifically preferred for anode modification among the studied conducting polymers. However, PPy exhibits some certain constraints due to its relative low conductivity, which limits its maximum MFC performances. If PPy is interfaced with GO or rGO, electrical conductivity and reinforcement stability of PPy could be improved, which may be beneficial for MFC performances. By the combined efforts of high electrical conductivity and number of catalytic active sites, the resulting PPy/GO composites are proved to have more advantages compared to the use of PPy alone that has been demonstrated to be efficient anode materials in MFCs, and GO alone that may have the problem of poor adhesion and low electronic conductivity [80,81]. Additionally, He *et al.* [82] successfully prepared a novel 3D chitosan/vacuum-stripped graphene (VSG) scaffold with hierarchically porous structure, which provided an open space in anode interior for bacteria colonization and enhanced the affinitive contact between multilayered bacteria and biocompatible VSG, thus contributing the remarkable 78 times maximum powder density improvement.

Titanium dioxide (TiO_2), as an important metal ox-

ide semiconductor, has been extensively studied in many fields because of its advantages of rich abundance, low cost, biocompatibility, and chemical stability. Although the intrinsically low electrical conductivity of TiO_2 significantly restricts its application in MFCs, it can be effectively overcome by integration TiO_2 with conducting polymers [83] or conductive carbon materials [84]. Recently, Zhao *et al.* [85] reported a graphene/amorphous TiO_2 hybrid synthesized by a microwave-assisted solvothermal process to improve the MFC performance. However, the amorphous TiO_2 was loosely deposited on the graphene surface resulting in poor catalytic utilization of TiO_2. Zou *et al.* [86] synthesized TiO_2/rGO hybrid with uniformly deposited small sized TiO_2 crystals on rGO nanosheets through a sol-gel process (Fig. 6a), which exhibited a typical type IV hysteresis loop [87], suggesting a typical mesoporous structure (inset in Fig. 6b). Moreover, nanocrystal TiO_2/rGO hybrid exhibited a large BET surface area (324.7 $m^2 g^{-1}$). The higher specific surface area of nanocrystal TiO_2/rGO hybrid with abundant mesopores was beneficial to achieve better electrocatalytic performance. As shown in Fig. 6c, the hybrid anode delivered a maximum power density of 540

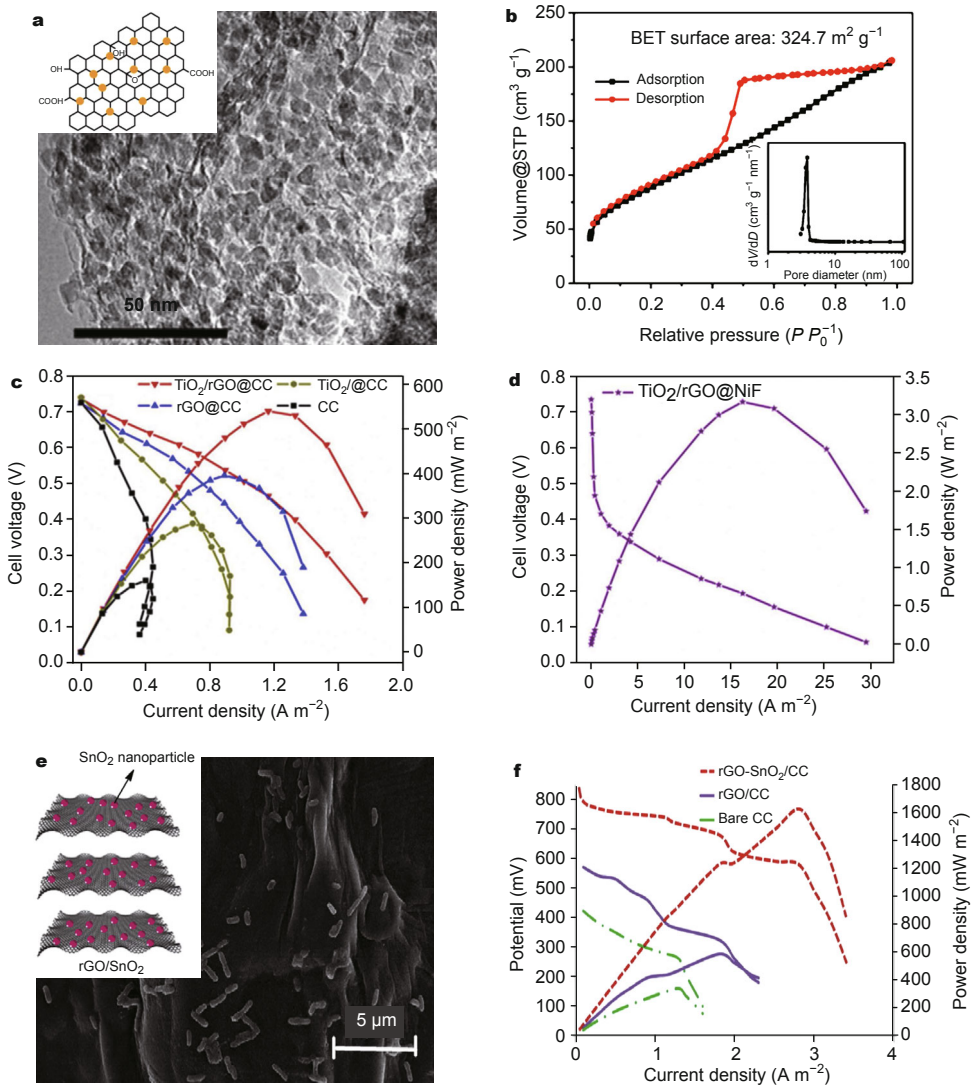

Figure 6 (a) TEM images of nanocrystal TiO_2/rGO hybrid. Inset: schematic illustration of the small sized nanocrystal TiO_2/rGO hybrid. (b) N_2 adsorptione-desorption isotherms and BJH pore size distribution plots (inset) of nanocrystal TiO_2/rGO hybrid. (c) Power density and cell polarization curves of MFCs equipped with different anodes coated on carbon cloth and (d) TiO_2-rGO anode coated on the nickle foam (Reproduced with permission from Ref. [86], Copyright 2015, Elsevier). (e) SEM images of bacteria formed on the rGO SnO_2/CC (inset: Schematic illustration of the rGO/SnO_2) and (f) polarization curves for rGO-SnO_2/CC, rGO/CC and bare CC. LSV was applied for polarization tests at a scan rate of 0.1 mV s^{-1} (Reproduced with permission from Ref. [90], Copyright 2014, Elsevier).

mW m^{-2} in *Shewanella putrefaciens* CN32 MFC, which was much larger than that of the conventional carbon cloth anode and reported TiO_2/carbon hybrid anode, thus offering great potential for practical applications of MFC. Nickel foam is also frequently used to load powder catalyst as an anode. Wang *et al.* [88] developed 3D rGO-nickel foam as the anode of MFCs through controlled deposition of rGO sheets onto the nickel foam substrate. Significantly, the rGO-nickel foam anode produced a remarkable volumetric power density of 661 W m^{-3}. This value was substantially higher than those of plain nickel foam and conventional carbon based electrodes measured in the same conditions. Fig. 6d shows that the nanocrystal TiO_2/rGO hybrid mentioned above coated on nickel foam (TiO_2/rGO@NiF) can deliver a maximum power density of 3169 mW m^{-2}, which is 19-fold higher than that of carbon cloth anode [86]. Additionally, high consideration has also been given to SnO_2 because of its unique properties such as electrical conductivity, chemical sensitivity and low cost. Although TiO_2 is one of the most used anode material in MFCs, it has been indicated that the nanoparticles of SnO_2 are more conductive than TiO_2 [89]. It was reported nanohybrids of rGO/SnO_2 can achieve a maximum power density of 1624 mW m^{-2} (Figs 6e and f), which was 2.8 and 4.8 times larger than that of rGO coated and bare anodes, respectively, demonstrating that the rGO/SnO_2 nanocomposite was advantageous material for the modification of anode and enhanced electricity generation of MFC [90]. Qiao *et al.* [91] found that most of the bacterial cells were adhered in graphene aerogel instead of the mental frame. A very interesting observation was that the cells not only grew on the outside surface of the graphene gel but also lived in the pores by adhering on the pore inside surface. This increases the loading of the biocatalyst (bacteria cells), and significantly facilitates the cell-to-cell electron communication for fast electron transferring at the anode side of MFCs.

CONCLUSIONS AND OUTLOOK

Great progress in MFCs technology has been made in the last decades to address the major challenges of low performance and high cost. At the current state of technology, the most efficient catalysts for MFCs are still expensive Pt-based catalysts supported on conventional carbon materials. To overcome these drawbacks, it is crucial to develop cost-effective, high-performance catalysts, particularly for the cathodic ORR. With the emergence of new carbon nanostructured materials, graphene-based materials have attracted a great deal of attention for many applications, including as MFCs cathode catalysts. Catalyst activity and stability are both strongly dependent on the catalyst itself and its supporting materials. It has been demonstrated that graphene-based materials can be used not only as supports to improve the performance of conventional catalysts, but also as metal-free catalysts with fascinating electrocatalytic activities for ORR. This review summarized the recent progress of graphene materials as both catalyst supports and metal-free catalysts, including the design of the catalyst, catalytic performance and the potential catalytic mechanisms. Generally, three approaches were reported to develop ORR electrocatalysts of MFCs: i) graphene as a support material for Pt and Pt-alloy catalysts; ii) graphene and doped graphene as support materials for non-precious metal catalysts; iii) graphene and doped graphene as metal-free catalysts.

The desired properties of an anode in an MFC should include excellent electric conductivity, large surface area, and high biocompatibility for bacteria colonization. The special properties of graphene provide excellent opportunity to improve the performance of bioelectrochemical systems, in which the blocked heterogeneous electron transfer was stimulated or the electron transfer was greatly facilitated with the formed graphene/biomolecules biocomposites [68]. It is worth noting that in most cases, the enhanced performance of anode electrodes, conferred by graphene materials, is a synergistic effect of the hybrid. For example, the hybrid of using the graphene as the substrate of conductive polymers or metal oxide semiconductors will benefit from not only the large specific areas of graphene but also the good biocompatibility and chemical stability of polymers or semiconductors, which enables the enhanced current and power density of the MFCs.

However, despite considerable progress, the following several challenges still remain and should be addressed in further work: i) graphene materials still suffer from relatively complicated synthesis procedures; ii) developing new methods for the mass production of graphene-based composites while achieving a considerable performance when used as electrode materials of MFCs; iii) insufficient fundamental understanding of the nature of electrocatalytically active ORR sites on graphene-based materials, particularly doped graphene materials. Thus, theoretical calculations using the modeling techniques or other characteristic are urgently needed. It can be expected that with the development in graphene research, there will be more research using graphene materials as electrode and catalyst for improving the performance of MFCs.

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Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 微生物燃料电池是一种采用微生物作为生物催化剂, 直接将储藏在废水中的化学能转化为电能的环境友好技术. 目前, 微生物燃料电池的商业发展仍受制于功率密度低、构成部件成本高这两个缺陷. 在制约微生物燃料电池商业化的因素中, 电极(包括阴极和阳极)材料具有举足轻重的地位. 相对于传统材料, 基于石墨烯的电极材料具有优异的导电性能、稳定的机械性能、较大的比表面积以及高的电催化活性, 它的使用大大提高了微生物燃料电池的性能. 本文主要综述了近期基于石墨烯基电极材料微生物燃料电池的研究进展, 基于石墨烯的电极材料有望用于可持续性的废水处理及生物能利用技术, 并在未来微生物燃料电池以及其他生物电化学系统中广泛应用.