Performance improvement of microbial fuel cells through assembling anodes modified with nanoscale materials

Huanhuan Liang¹,²,#, Jiali Han¹,²,#, Xingai Yang¹, Zhixing Qiao¹,² and Tao Yin¹,²

Abstract
In microbial fuel cell (MFC), the anode is the carrier of microbial attachment and growth, and its material and surface structure play a vital role in MFC electricity generation. Therefore, anode surface optimization is an effective way to improve MFC performance. Although the power generation of bacteria has been confirmed and studied as early as the beginning of the 20th century, up to now, MFC still has the extremely challenging problem of low current and low power output in practical application. To improve the performance of MFC, several strategies have been applied to enhance the bacterial extracellular electron transfer. One promising technology is the genetic engineering approach, and some outstanding research results have been obtained. Another effective strategy is to design and fabricate a high-performance electrode because anode material is the essential factor affecting MFC performance, which provides surface active sites for microbial adhesion, reproduction and interfacial electron transfer. At present, the MFC anodes mainly include carbon-based electrodes and a variety of metal electrodes, but untreated anodes have always been unable to overcome the obstacle of low power output. Anode modification, a common and effective method, is employed for improving the power output of MFC. For this reason, this review is primarily focused on the applications of various anode materials and its nanoscale modification in the field of MFC, including the influence of different anode materials on the power output of MFC, and analyzes the reasons why anode modification enhances output performance. Furthermore, the influence of anode research on the practical application of MFC in the future is prospected.

Keywords
microbial fuel cells, anode, nanoscale modification, extracellular electron transfer, electricity generation performance

Date received: 17 April 2022; accepted: 27 September 2022

1School of Medical Imaging, Shanxi Medical University, Taiyuan, People’s Republic of China
2Department of Radiology, First Clinical Medical College, Shanxi Medical University, Taiyuan, People’s Republic of China
#Equally contributed

Corresponding authors:
Zhixing Qiao, School of Medical Imaging, Shanxi Medical University, No. 56 Xinjian South Road, Taiyuan 030001, People’s Republic of China.
Email: qzx@sxmu.edu.cn
Tao Yin, School of Medical Imaging, Shanxi Medical University, No. 56 Xinjian South Road, Taiyuan 030001, People’s Republic of China.
Email: yintao1219@163.com

Creative Commons CC BY: This article is distributed under the terms of the Creative Commons Attribution 4.0 License (https://creativecommons.org/licenses/by/4.0/) which permits any use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (https://us.sagepub.com/en-us/nam/open-access-at-sage).
electricity-producing bacteria, select anode materials with excellent performance, analyze the effects of anode materials and surface characteristics on microbial growth and MFC output performance, and accelerate the interfacial electron transfer rate between bacterial outer membrane cytochrome c protein (OMCs) and the electrode. Due to its excellent conductivity, biocompatibility, chemical stability and low price, carbon electrode has become the most widely used anode material in the field of MFC, mainly including carbon paper (CP), carbon felt (CF), carbon cloth (CC), graphite rod, graphite fiber brush, reticulated vitreous carbon and so on. Microbial fuel cell anode equipped with CC was inoculated with anaerobic activated sludge to produce electricity. The maximum output power density of 610 mW/m² was obtained by starting the battery with sodium acetate as an electron donor. Desulfovibrio desulfuricans was inoculated into CC anode to generate electricity. The air cathode MFC was successfully started with sodium sulfate and magnesium sulfate as electron donors, respectively, and the power output was 0.51 mW/cm². Wang et al. fabricated an effective three-dimensional N-doped macroporous carbon foam (NMCF) bioanode, a power density of MFC has been dramatically improved. Such remarkable performances would be likely attributed to two major aspects. On the one hand, the unique 3D macroporous structure of NMCFs favored the bacterial proliferation and the enrichment of electroactive Geobacter genus on the electrode surface. On the other hand, the anodic N doping especially pyrrolic N promoted the extracellular electron transfer (EET) process of Geobacter. However, due to the high surface energy state of carbon element, it is easy to lose electrons to make the surface manifest reducibility. The electron transition generated by the metabolism of electrogenic microorganisms to the carbon electrode has to consume higher energy, resulting in a larger loss of anodic activation overpotential. Therefore, reducing the energy state of carbon-based anode surface and activation overpotential of anode reaction is the key to improve anode performance. Surface modification and nano-modification are the main technologies to significantly reduce the anode activation loss.

In order to obtain high performance anode and improve the power generation of MFC, noble metals such as Au, Pt and Pd are often used in MFC due to their excellent conductivity, wide potential range and high surface area. In addition, there are common metals such as Fe, Cu, Ni and other transition metals such as Mo, Ru, Mn, Ti and so on. Lovley research group used Au as anode and Geobacter sulfurreducens as electricity-producing bacteria to study the performance of MFC using acetate as substrate. The results indicated that the current output of MFC could be maintained at 0.4–0.7 mA after 6–10 days of operation, which was due to the effective electron transfer from bacteria to gold electrode. Generally speaking, the smooth surface of metal is not conducive to the attachment and growth of bacteria, and the high cost of precious metals limits its wide use, while copper dissolves in the anode solution during battery discharge, which has a great toxic effect on microorganisms and should be avoided. Therefore, the use of metal electrodes in MFC is not common, and the current reports mainly focus on stainless steel and titanium electrodes.

Microbial fuel cell power output depends on the substrate degradation rate of microorganisms, the transfer rate of metabolic electrons from intima to outer membrane, and then from outer membrane protein to anode, as well as the performance of the electrode itself. With substrate metabolism and EET, protons are also released into the anode solution and affect the power generation process. The anode affects the interaction and effective contact distance between microorganism and electrode, and then affects the adhesion, growth, EET pathway and electron transfer efficiency of microorganism. For example, the pretreatment of anode materials can shorten the start-up time of MFC and maintain the stability of biofilm, and good stability is helpful for the long-term operation of MFC. In addition, the anode material is also an important factor in determining the anode potential, which determines the final redox potential of intracellular electrons and thus determines the metabolic pathway of microorganisms. The physicochemical properties of different electrode materials are also quite different, and the electrode resistance is an important factor affecting the power output. Although reducing the electrode resistance does not always increase the power output in practical applications, high conductivity is still one of the important issues to be investigated when selecting electrode materials. In short, anode material and its surface structure affect microbial growth, electron transfer and Coulombic efficiency, so it is of great significance to select and optimize electrode materials to enhance MFC performance. Herein, this review mainly summarizes the effect of nano-scale modified anodes on MFC power output, analyzes the reasons for the enhancement of MFC performance, and discusses possible ways to further optimize anodes, as well as prospects for potential promising anode materials.

**Surface modification of anode**

To prepare high performance anodes, one is to select the appropriate materials and develop processing technology directly to obtain new anodes that are beneficial to microbial growth and electricity production, such as three-dimensional anodes with micron pores. Another effective and common method is to modify the electrode surface. Modification usually includes the change of morphology and structure, as well as using functional materials for surface modification. The property improvement for MFC
Modification of Conductive Nanomaterials

Conductive polymer modification. The conductive polymer modified electrode has good biocompatibility and is easy to be processed into a variety of complex shapes and sizes, light weight, good stability and adjustable resistivity. Therefore, it has been widely used to improve the performance of anode materials in the field of MFC, among which Polyaniline (PANI), polypyrrole (PPy) and poly neutral red film modified electrodes have been more studied. Ding et al. synthesized polypyrrole nanowire arrays (PPy-NA) on the surface of Au sheet by galvanostatic deposition method. The morphology was shown in Figure 2(a)–(d). PPy-NA exhibited excellent performance in mediating bacterial EET. The combined effect of the inherent electrochemical nature of PPy and the porous structured bacterial network that was generated on the PPy-NA enabled long-term stability. The high efficiency was attributed to the enhanced electron transfer rate between PPy-NA and microorganisms. Moreover, different nanostructure of conductive polymers can affect bacterial EET. The fiber PPy modified anode was more suitable for high power output of MFC. PPy and adhesive polydopamine (PDA) in situ modified electrogenic bacteria can improve the conductivity and adhesion of anode to improve the hydrophilicity of conductive polymer. PPy-PDA modified cells as anode not only greatly improve the direct EET, but also riboflavin secretion that is conducive to indirect EET is enhanced, thereby improving the power density output of MFC. The hybrid of TiO₂ and PANI can remarkably raise the output performance of MFC (Figure 2(e)). This is due to the synergistic effect between TiO₂ and PANI, which makes the charge transfer resistance at the anode interface significantly reduced, the transient charge storage capacity greatly improved, and the surface biomass also increased, thus promoting bacterial EET and maintaining high power density output during the long-term operation of MFC. In 2012, Ding et al. deposited PANI on the surface of gold electrode to form PANI nanowire (Polyaniline nanowire array), which proved that ordered PANI can act as a solid polymer mediator in microbial EET process, and can significantly enhance EET current in an adjustable manner at a specific potential. Additionally, the power output of CP anode modified by poly (3,4-ethylenedioxythiophene) (PEDOT) was increased compared with the unmodified anode. Cyclic voltammetry and electrochemical impedance spectroscopy analysis showed that PEDOT modification increased the effective redox active sites and reduced the interfacial electron transfer impedance of the anode. In brief, the conductive polymer modified electrode enhanced the conductivity, reduced the electron transfer resistance, and improved the electrode capacitance. The surface of the modified electrode became rougher and expanded the surface area of bacteria attachment. In order to further improve the output performance of MFC, conductive polymers are usually prepared into a three-dimensional porous structure to facilitate larger biofilm formation, or to improve the hydrophilicity of conductive polymers. The anode modified with conductive polymer is given in Table 1.

Carbon nanotube modification. Carbon nanotube (CNT) has good electrical conductivity, large specific surface area, high thermal stability and chemical inertness, and can form a mesoporous spatial structure. Therefore, CNT is a very ideal electrode material and is widely used in the anode research of MFC. Sun et al. used layer-by-layer self-assembly technology to modify multi-walled carbon nanotube (MWCNT) on CP electrode for the first time,
and studied the performance of composite electrode as MFC anode. The results showed that MFC equipped with the modified anode produced a higher power density by inoculating anaerobic granular sludge, which was 20% enhancement comparing to that of the bare CP anode. Impedance spectrum test proved that the charge transfer resistance of composite electrode decreased from 1163 Ω to 258 Ω. Especially, cytochrome C protein attached to MWCNTs modified electrode can significantly promote the direct electron transfer (DET) between cytochrome c and electrode. As shown in Figure 3(a), vertically grown MWCNTs were modified on the surface of nickel.
silicide for miniature (1.25 μL) MFC anode. The modified electrode has good biocompatibility and conductivity. Modify multi-walled carbon nanotubes increased the anode surface-to-volume ratio, which improved the ability of microbial coupling and electron transfer to the anode. These factors contributed to the power output of MFC.\textsuperscript{46} Liang\textsuperscript{47} proved that the combination of CNT and \textit{G. sulfurreducens} biofilm can shorten the start-up time of MFC and reduce the anode impedance. The results indicate that during the 40-days operation the anode impedance and voltage output of MFC with CNT powder are 180 Ω and 650 mV, respectively. The anode impedance without CNT powder increases from the initial 250 Ω–540 Ω, and the voltage decreases from 630 mV to 540 mV. Therefore, the addition of CNT powder is beneficial to stabilize the anode resistance and keep the internal resistance and power output of MFC running for a long time constant. From Figure 3(b)–(g), welding and assembling three-dimensional interconnected CNT on carbon electrodes to prepare high-performance anodes is a novel method. CNTs and polyelectrolytes form an integral network on CP surface by layer-by-layer assembly and welding (CP/CNT(W)). Due to the minimization of ohmic loss at the interface, MFCs assembled with CP/CNT(W) electrodes have excellent electrochemical performance to facilitate the formation of larger biofilm and electron transport.\textsuperscript{48} In addition, The composite modified anodes between several conductive polymers for MFC can greatly enhance power output, which is due to their synergistic effect and complementary advantages, jointly promoting the bacterial EET.\textsuperscript{49–51} Graphene modification. Graphene is a new member of the carbon family, which has a special two-dimensional crystal structure of single atomic layer, and the characteristics of large specific surface area, good mechanical strength, excellent electrical conductivity and high electrocatalytic performance, so it has become one of the research hotspots of anode modification in the field of MFC in recent years. Stainless steel mesh (SSM) modified with graphene (GMS) as MFC anode, the maximum output power density reached 2668 mW/m\textsuperscript{2}, which was 18 times and 17 times higher than that of SSM and polytetrafluoroethylene modified stainless steel mesh (PMS) anode, respectively. This result was attributed to the large specific surface area of GMS and the attachment of a large number of microorganisms to the anode surface, thus improving the power generation performance.\textsuperscript{52} Graphene was decorated onto CC anode by electrochemical deposition method, inoculated \textit{Pseudomonas aeruginosa}, and started dual-chamber MFC. The experimental results show that the power output and energy conversion rate of graphene modified MFC anode are 2.7 times and 3 times higher than those of unmodified CC, respectively. This is mainly due to the fact that graphene promotes the growth of bacteria on the electrode surface, leads to the increase of DET active sites and stimulates bacteria to secrete mediators with higher electron transfer efficiency.\textsuperscript{53} Huang et al.\textsuperscript{54} firstly modified graphene oxide nanoribbons (GONRs) network on CP surface by electrochemical deposition method as MFC anode. The results confirmed that the GONRs modified electrode had a larger electrochemical active surface area, which could promote the transfer of extracellular electrons to the electrode. The current density and power density were

Figure 3. (a) Scanning electron microscopy image of bacterial growth after operation. Image shows excellent compatibility and stability of modify multi-walled carbon nanotube. Scanning electron microscopy images of the biofilm adhered on carbon paper (b), carbon paper/carbon nanotube (d) and carbon paper/carbon nanotube(W) (f) anodes, and schematic electrons transfer on the surface of PV-4 and anodes after inoculation (c, e and g).
about 4 times higher than those of CP electrode. Graphene oxide nanoribbons played a role similar to nanowires in the EET process, which increased the distance of electron transfer. A three-dimensional reduced graphene (RGO) modified nickel foam anode was prepared by controllable deposition of reduced graphene sheets on nickel foam substrate. This electrode not only provides a higher specific surface area for bacterial growth and attachment of more electron mediators, but also uniform microporous scaffolds are conducive to the effective diffusion of culture medium. Based on the volume calculation of anode materials, the flexible reduced graphene composite foam nickel electrode inoculated with *Shewanella oneidensis* MR-1 has a power output of 661 W/m³, which is much higher than that of nickel foam electrode and traditional carbon electrode under the same experimental conditions.55 Xiao et al.56 researched two kinds of graphene materials with different morphologies, and modified MFC anodes with flake graphene and folded graphene respectively. The results showed that anode modified with folded graphene particles had higher current output, which was attributed to its higher conductivity, larger surface area, oxygen reduction catalytic activity and the open structure formed by stacking to promote mass transfer. Therefore, this kind of electrode has higher power output, up to 3.6 W/m³, which was twice as high as that of activated carbon modified electrode, while the power output of unmodified CC anode was only 0.3 W/m³.

**Nano-metal modification.** The internal resistance of MFC affects its power generation performance. Hence, reducing the internal resistance is beneficial to the output of high power density. Nano-metal materials used as catalysts have a variety of excellent properties, such as small size effect, high catalytic activity, good stability and biocompatibility. It can be dispersed and fixed on various carbon-based carriers such as activated carbon and graphite by physical or chemical methods. As an anode, it can effectively improve the electrical performance of MFC. The Pt is a common electrocatalyst in MFC, some studies have shown that Pt modified titanium electrode has good electrical properties, and pure titanium electrode is not suitable for MFC anode material.57 It can be seen from Figure 4 that a three-dimensional CF electrode decorated with Pt nanoarrays (CF@Pt) as bioanode for MFC. Pt nanoarrays act as excellent electron relays, reducing significantly the charge transfer resistance. CF@Pt anode equipped MFC can run stably for a long time. Having a large surface area and excellent electrical conductivity, this binder-free nanoscale electrode was found to effectively promote the growth of electrochemically active bacteria and facilitate EET from bacteria to their host.58 Sun et al.59 prepared gold-coated CP electrode for MFC, inoculated with *S. oneidensis* MR-1, the electricity production of MFC increased by 47% compared with naked CP electrode. Electrochemical cyclic voltammetry analysis and scanning electron microscopy observation revealed that the gold decorated CP electrode facilitated the formation of MR-1 biofilm. Consequently, gold composite carbon material anode can obviously reinforce the output performance of MFC. Nevertheless, the current output performance of MFC with pure gold anode is poor and cannot output continuously, which is due to the low compatibility between gold and bacteria.60 Transition metal Pt and tantalum (Ta) modified titanium electrodes have higher current output in long-term use. The biofilm formation by adding ferric iron and acetate indicates that there are many kinds of ferric reducing bacteria in the biofilm, which are in the dominant group on the electrode surface, while biofilm formation on the surface of the pure titanium electrode is poor and insufficient for further analyses.61 Ouitrakul et al.62 have studied the effects of silver, stainless steel, aluminum, nickel and other materials as anodes on the properties of MFC. It is found that nickel, aluminum and stainless steel electrodes can obtain higher open circuit voltage than carbon electrodes, but the power output is lower than that of carbon electrodes. In order to explain this phenomenon, impedance tests demonstrate that nickel and stainless steel electrodes have higher electrode/solution interface impedance, resulting in greater activation loss. Fan et al.63 modified graphite anode with Au and Pd nanoparticles and inoculated *S. oneidensis* MR-1 as electricity-producing bacteria. It was found that the electricity output of Au modified anode was 20 times higher than that of graphite anode, and Pd modified anode was 50–150% higher than that of the graphite anode, indicating that Au and Pd modified electrodes could facilitate bacterial EET and reinforce the electricity production performance of MFC. The anodes modified by nano-metal materials have a wide range of variety. In addition to precious metals such as Au, Pt, Pd, Rh, Ir, Ag, etc., other metals such as Ni and Cu64,65 are also used for anode decoration of MFC. Nevertheless, the cost of precious metals is too high to be widely used. The cost of stainless steel, titanium, aluminum and other electrodes is low, but the adhesion and growth ability of microorganisms on their surfaces is weak, which limits their widespread use in the field of MFC.

**Modification of nano-metal oxide materials**

**Iron oxide modification.** Metal oxides such as iron oxide, as electron acceptors of bacteria in natural environment, can also improve the performance of MFC. For Fe oxide, EET is mediated by OMCs and self-secretion flavin molecules. It has been reported that α-FeOOH nanowires with a diameter of 30–50 nm and a length of 500–800 nm form a porous structure on the surface of CP by hydrothermal method. This composite electrode is beneficial to microbial growth and mass transfer, and promotes EET.76 Nakamura et al.77 found that the addition of nano-Fe₂O₃ colloid into MFC
could facilitate the cross-linking of *Shewanella loihica* PV-4 cells to form a network structure conducive to long-distance electron transport. The results of CV test and analysis indicated that the current of MFC increased by more than 300 times compared with that without Fe$_2$O$_3$. The enhanced redox peak current proved the formation of long-distance EET channel in the colloid network. Nano-iron oxide modification increased the hydrophilicity and roughness of electrode surface that favored the attachment and growth of bacteria. The needle-like Fe$_3$O$_4$/Fe$_2$O$_3$ nanorods were formed on the surface of 304 stainless steel plates (SS) by 70 cycles of cyclic voltammetry treatment after oxidation for 8 min (CV-SS-8). The treated electrode drastically decreased the internal resistance and enhanced the current output. The needle-like Fe$_3$O$_4$ and larger Fe$_2$O$_3$ nanorods decreased the contact angle of the stainless steel surface (Figure 5), which increased the thickness of the attached electroactive bacteria biofilm. In 2012, Peng also studied the effect of nano-Fe$_3$O$_4$ and activated carbon (AC) powder mixed then pressing on SSM as an anode for electrical properties of MFC with air cathode. The results demonstrated that the anode with Fe$_3$O$_4$ composite had the maximum power output of 664 ± 17 mW/m$^2$, which was 22% higher than that of AC modified (AcM) and 56 times higher than that of SSM electrode. Tafel curve proved that the anode of composite Fe$_3$O$_4$ had the best dynamic activity. The charge-discharge test of MFC for the first time revealed that the addition of Fe$_3$O$_4$ reinforced the anode capacitance. The net charge reserve of the AcFeM electrode achieved 389 ± 18 C/m$^2$ after 10 min of open circuit, which was 32% higher than that of AcM (294 ± 30 C/m$^2$). Accordingly, the enhancement of anode capacitance contributes to the improvement of performance. According to the above literature reports, the anode modified by iron-containing compound nanoparticles improved the capacitance of the anode, increased the electron transfer distance, promoted the formation of biofilm, and effectively shortened the start-up time of MFC. Thus, the power output of MFC was reinforced.

**Titanium dioxide modification.** TiO$_2$ is an n-type semiconductor and one of the most attractive metal oxides, which has good chemical stability, biocompatibility and environmental friendliness. Therefore, TiO$_2$ has been widely used in capacitors, sensors, photocatalysis, solar cells and other fields. However, the relatively low conductivity limits the use of TiO$_2$ alone as anode modifier in MFC, which is mainly in the form of composite electrode in the literature. Zou et al. studied the CC electrode modified by small-size TiO$_2$ nanocrystals and reduced graphene composite (TiO$_2$/rGO), and inoculated *Shewanella putrefaciens* CN32 to produce electricity. The results showed that the TiO$_2$/rGO@CC anode produced a power output of 540 mW/m$^2$, which was 1.4, 1.9 and 3.4 times higher than that of rGO@CC (395 mW/m$^2$), TiO$_2$@CC (288 mW/m$^2$) and CC (160 mW/m$^2$) anodes, respectively. This is because the good biocompatibility and large specific surface area of TiO$_2$ nanocrystals are conducive to the large-scale growth of bacteria. The high conductivity of reduced graphene promotes the rapid transfer of electrons from extracellular membrane proteins to electrodes. The synergistic effect of the two greatly improves the power output of MFC. Maurer-Jones et al. revealed the effects of the type of TiO$_2$ nanoparticles on biofilm formation.
specific function and flavin secretion of *S. oneidensis*. The results showed that the formation of *S. oneidensis* biofilm slowed down in the presence of TiO$_2$ nanoparticles, but the flavin secretion and metal reduction ability were significantly enhanced. This change is not the result of bacterial oxidative stress, but the change in microbial gene expression caused by adjacent nanoparticles. As shown in Figure 6(a) and (b), TiO$_2$ nanoparticles combined with loofah sponge (LS), then carbonized them at 900°C in nitrogen atmosphere to successfully prepare carbon-covered TiO$_2$ nanoparticles (LSC-TiO$_2$) with three-dimensional core-shell structure. The maximum power output of MFC reached 2.59 ± 0.12 W/m$^2$ when inoculated with active anaerobic sludge for power generation, which was 63% and 201% higher than that of LSC and graphite anode, respectively. This was due to the interaction between TiO$_2$ and carbon enhanced the electrochemical capacitance of the three-dimensional electrode. Wen et al. synthesized anatase TiO$_2$ nanoparticles composite CNT modified CC anode. It is found that the anode potential of CNTs@TiO$_2$ is the most negative at the same current density, which is very beneficial to the generation of MFC bioelectricity. The maximum output power is 1.12 W/m$^2$, which is 1.5 and 1.7 times higher than that of CNT (0.73 W/m$^2$) and TiO$_2$ nanoparticles (0.67 W/m$^2$) modified anode, respectively. One of the reasons for the enhanced power output of the composite electrode is the synergy of CNT and TiO$_2$ nanoparticles, which makes the electrode have good biocompatibility and conductivity, and promotes the formation of larger biofilm and the transfer of interfacial electrons. In order to improve the electron transport of TiO$_2$, different nanostructures and morphologies are synthesized, in which ordered nanostructures are an effective method. Vertically oriented TiO$_2$ nanosheets modified CP electrodes (TiO$_2$-NSs/CP) were used for MFC anode without any composite conductive materials, and the biological electricity production was significantly better than that of CP electrodes (Figure 6(c)). Its unique surface structure played a key role in enhancing MFC power output. Vertically grown TiO$_2$-NSs on a CP surface formed vertically penetrating pores that offer a larger contact area to OMCs for DET, high biocompatibility and facilitating solution diffusion. The results demonstrated that the electrode surface modification with appropriate TiO$_2$ nanostructures was helpful for EET of exoelectrogens. In addition, in continuous and stable operation of MFCs, the electron transfer rate constant ($k_{et}$) of OMCs on TiO$_2$-NSs/CP anode is three times higher than that on CP anode due to the more favorable conformational change of OMCs on TiO$_2$-NSs and the synergistic energy level shift of electron donors and acceptors. These results revealed that TiO$_2$-NSs had intrinsic electrocatalytic activity in the microbial EET process. Nanoscale TiO$_2$ can be used as a suitable material to regulate the redox state of OMCs. Due to the inherent electrocatalytic activity, high biocompatibility and stability, and variable morphology and tunable surface properties of nano-TiO$_2$, it can be expected that the properly designed TiO$_2$ nanostructures can become excellent solid catalysts for microbial EET and redox protein DET, and more applications can be explored in the field of bioelectronic devices in the future. The performance of MFC equipped with the modification of anode via nano-metal oxide materials is listed in Table 2.

**Other metal oxides modification.** The anode modified by nano-metal oxide materials can increase the specific surface area, which affects the power generation efficiency of MFC. Therefore, the electrode composite nano-semiconductors applied in MFC should have low internal resistance, good electrocatalytic activity, low cost and non-toxic to cells. Mehdinia et al. used SnO$_2$ nanoparticles and RGO composite (RGO/SnO$_2$) modified CC for MFC anode by hydrothermal method combined with microwave assistance. The maximum output power density of 1624 mW/m$^2$ was obtained, which was 2.8 and 4.8 times higher than that of single RGO modification and CC electrode, respectively. This is because the high conductivity and large specific surface area of the nanocomposite electrode promote the formation of biofilm and accelerate the electron transfer. The results show that RGO/SnO$_2$ composite is a dominant anode material, which enhances the electricity output of MFC.
sized ruthenium oxide (RuO₂) particles exhibit fast and reversible redox behavior in a wide potential window, large surface area, high chemical stability and favorable metallic conductivity. Thus, it is also served as MFC anode. RuO₂ decorated CF as anode for dual-chamber MFC and inoculated with anaerobic activated sludge to generate electricity. The maximum output power was 17 times higher than that of the unmodified control electrode. Electrochemical tests showed that the electron transfer rate between bacteria and electrode was substantially improved, and it was also confirmed that the interaction between RuO₂ and cells could promote EET.\textsuperscript{94}

MnO₂ is a transition metal dioxide with high specific capacitance and environmentally benignity. It may be a potential pseudo-capacitive anode modifier. MnO₂ was modified on CF electrode by electrodeposition to enhance the performance of MFC. When the deposition time was 60 min, the anode capacitance increased by 46 times, and the maximum output power density reached 3580 ± 130 mW/m², which was 24.7% higher than that of pure CF anode (2870 mW/m²).\textsuperscript{95} Tungsten trioxide (WO₃) has favorable biocompatibility and its rough surface favors bacterial colonization. Consequently, WO₃ is considered as an excellent candidate for anode materials in MFC. Polyaniline was decorated onto mesoporous tungsten trioxide (m-WO₃) by chemical oxidation. The composite electrode was applied in MFC and inoculated with Escherichia coli. The m-WO₃ electrode loaded with PANI showed a unique electrocatalytic activity with a maximum output power density of 0.98 W/m², while only 0.76 W/m² and 0.48 W/m² for the MFC using individual m-WO₃ and PANI electrocatalyst, respectively. The improved electrocatalytic activity was attributed to the synergistic effect of good biocompatibility of m-WO₃ and excellent conductivity of PANI, which led to the high output performance of MFC. Most importantly, the

Table 2. Power density output of MFC equipped with the modification of anodes via nano-metal oxide materials.

| Anode materials       | Modification of anode | The maximum power density (mW/m²) | Bacteria            | MFC Configuration | Ref  |
|-----------------------|-----------------------|-----------------------------------|---------------------|-------------------|------|
| Carbon felt (CF) Bio-FeOx/CF | 797                   | Shewanella loihica PV-4           | Dual-chamber        | 97                |
| Carbon felt (CF) Fe₂O₃-PDHC/CF | 3184.4               | Electrogenic bacteria             | Dual-chamber        | 98                |
| Carbon felt (CF) graphene/Fe₂O₃ | 334                  | Anaerobically fermented biomass sludge | Dual-chamber        | 99                |
| Carbon foam (CF) NiO/CF | 928                   | Wastewater                        | Dual-chamber        | 100               |
| Carbon paper (CP) NTiO₂-NSs/CP | 747                  | Shewanella loihica PV-4           | Dual-chamber        | 101               |
| Stainless-steel mesh (SS) MgFe₂O₄/SS | 430.3     | Anaerobic sludge                  | Single-chamber      | 102               |
| Carbon felt (CF) MnCo₂O₄@CF | 945                   | Anaerobic sludge                  | Dual-chamber        | 103               |
| Carbon paper (CP) Fe₃O₄/CNT/CP | 865                  | Escherichia coli K12              | Dual-chamber        | 104               |
| Carbon paper (CP) α-FeOOH-NWs/CP | 122.6                | Shewanella loihica PV-4           | Dual-chamber        | 105               |
| Carbon felt (CF) MnFe₂O₄ | 3836                  | Anaerobic sludge                  | Dual-chamber        | 106               |
| Carbon felt (CF) NiFe₂O₄-MXene@CF | 1385                 | Anaerobic sludge                  | Dual-chamber        | 107               |

Note: Fe₂O₃-PDHC/CF (Fe₂O₃-polyaniline-dopamine composite modified carbon felt), MXene (Ti₃C₂Tx: titanium carbide), NTiO₂-NSs/CP (nitrogen doped TiO₂ nanosheets decorated carbon paper).

![Figure 6](image_url) (a) Current density of microbial fuel cells over three charge/discharge cycles with 10 min of charging and 30 min of discharging. (b) Relationship between the power densities of the microbial fuel cells and the areal capacitance values of the anodes. (c) TiO₂-NSs/carbon paper electrode, power output and polarization curves of the microbial fuel cells equipped using different anodes.
combination of m-WO$_3$ and PANI improved the electrochemical activity of proton gain and loss of PANI. Metal oxide decorated anodes, with good biocompatibility, stability and large specific surface area, will become one of the hotspots in the field of MFC anode modification.

**Conclusion and Outlook**

Anode is the carrier and electron acceptor of microbial growth, and its performance greatly affects the power density of MFC. Therefore, improving anode performance is of great research value for improving MFC output. In this review, we focus on the effect of anode and its modification on MFC power generation, and analyze the reason of anode modification to improve MFC power output. The modified anode mainly includes the following advantages: (1) enhanced biocompatibility and increased specific surface area are beneficial to the large-scale growth of electricity-producing bacteria and promote the formation of more active biofilm on the anode surface, (2) good environmental friendliness, light weight and easy operation, (3) good physical and chemical stability is helpful to the long-term operation of MFC, (4) reducing the internal resistance is conducive to high power density output, (5) increasing the active area and promoting mass transfer.

Although the anode modification has received extensive attention and achieved certain research results, the overall performance of MFC has also been improved, the low power density output is still the key to restrict its practical application and the most urgent problem to be solved. Therefore, there is still much room for improvement of anode. Due to the excellent characteristics of carbon-based electrodes, it is still the most attractive material in the future. Besides, nano-semiconductor electrode is also an alternative electrode for practical application of MFC in the future due to its good biocompatibility, stability and relatively low price. This is because the rich structure of nano-semiconductor is expected to design a surface morphology with fast electron transfer. In addition, its conductivity can be changed by doping, which can effectively reduce the charge transfer resistance between bacterial OMCs and the electrode, and increase the transient charge storage capacity of the electrode. The preparation process is simple, and the MFC power generation is significantly improved. With the rapid development of anodes, further exploration of the mechanism is expected to design new high-performance anodes, thereby improving the output performance of MFC and further facilitating the practical application of MFC.

**Declaration of Conflicting Interests**

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

**Funding**

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by Shanxi Natural Science Foundation of China (No. 201901111181).

**ORCID iD**

Tao Yin  [https://orcid.org/0000-0002-2745-3478](https://orcid.org/0000-0002-2745-3478)

**References**

1. Torres CI, Krajmalnik-Brown R, Parameswaran P, et al. Selecting anode-respiring bacteria based on anode potential: phylogenetic, electrochemical, and microscopic characterization. *Environ Sci Technol* 2009; 43: 9519–9524.
2. Manickam SS, Karra U, Huang LW, et al. Activated carbon nanofiber anodes for microbial fuel cells. *Carbon* 2012; 244: 19–28.
3. Guan YF, Zhang F, Huang BC, et al. Enhancing electricity generation of microbial fuel cell for wastewater treatment using nitrogen-doped carbon dots-supported carbon paper anode. *J Clean Prod* 2019; 229: 412–419.
4. Zhang YP, Sun J, Hou B, et al. Performance improvement of air-cathode single-chamber microbial fuel cell using a mesoporous carbon modified anode. *J Power Sour* 2011; 196: 7458–7464.
5. Zhao CE, Gai PP, Liu CH, et al. Polyaniline networks grown on graphene nanoribbons-coated carbon paper with a synergistic effect for high-performance microbial fuel cells. *J Mater Chem A* 2013; 1: 12587–12594.
6. Zhao CE, Gai PP, Song RB, et al. Graphene/Au composites as an anode modifier for improving electricity generation in Shewanella-inoculated microbial fuel cells. *Anal Methods* 2015; 7: 4640–4644.
7. He YR, Xiao X, Li WW, et al. Enhanced electricity production from microbial fuel cells with plasma-modified carbon paper anode. *Phys Chem Chem Phys* 2012; 14: 9966–9971.
8. Tommassi T, Sacco A, Armato C, et al. Dynamical analysis of microbial fuel cells based on planar and 3D-packed anodes. *Chem Eng J* 2016; 288: 38–49.
9. Planosroy N, Khawdas W, Watanabe K, et al. Microbial fuel cells equipped with an iron-plated carbon-felt anode and Shewanella oneidensis MR-1 with corn steep liquor as a fuel. *J Biosci Bioeng* 2012; 126: 514–521.
10. Duarte KDZ and Kwon Y. Enhanced extracellular electron transfer of yeast-based microbial fuel cells via one pot substrate-bound growth iron-manganese oxide nanoflowers. *J Power Sour* 2020; 474: 228496.
11. Hidalgo D, Tommassi T, Velayutham K, et al. Long term testing of microbial fuel cells: comparison of different anode materials. *Bioresour Technol* 2016; 219: 37–44.
12. Qiao Y, Wu XS, and Li CM. Interfacial electron transfer of Shewanella putrefaciens enhanced by nanoﬂaky nickel.
oxide array in microbial fuel cells. *J Power Sourc* 2014; 266: 226–231.

13. Narayanasamy S and Jayaprakash J. Carbon cloth/nickel cobaltite (NiCo2O4)/polyaniline (PANI) composite electrodes: preparation, characterization, and application in microbial fuel cells. *Fuel*. 2021; 301: 121016.

14. Liu D, Chang QH, Gao Y, et al. High performance of microbial fuel cell afforded by metallic tungsten carbide decorated carbon cloth anode. *Electrochim Acta* 2020; 330: 135243.

15. Huang LH, Li XF, Ren YP, et al. In-situ modified carbon cloth with polyaniline/graphene as anode to enhance performance of microbial fuel cell. *Int J Hydrogen Energy* 2016; 41: 11369–11379.

16. Wang ZJ and Lim B. Electric power generation from sediment microbial fuel cells with graphite rod array anode. *Environ Eng Res* 2020; 25: 238–242.

17. Iannaci A, Myles A, Philippot T, et al. Controlling the carbon-bio interface via glycan functional adlayers for applications in microbial fuel cell bioanodes. *Molecules* 2021; 26: 4755.

18. Ouis M, Kameche M, Innocent C, et al. Electro-polymerization of pyrrole on graphite electrode: enhancement of electron transfer in bioanode of microbial fuel cell. *Polym Bull* 2018; 75: 669–684.

19. Jia Y, Ma D, and Wang XY. Electrochemical preparation and application of PANI/MWNT and PPY/MWNT composite anodes for anaerobic fluidized bed microbial fuel cell. *J Biotech* 2020; 10: 3.

20. Gadkari S, Gu S, and Sadhukhan J. Two-dimensional mathematical model of an air-cathode microbial fuel cell with graphite fiber brush anode. *J Power Sourc* 2019; 441: 227145.

21. Wu SJ, He WH, Yang WL, et al. Combined carbon mesh and small graphite fiber brush anodes to enhance and stabilize power generation in microbial fuel cells treating domestic wastewater. *J Power Sourc* 2017; 356: 348–355.

22. Stager JL, Zhang XY, and Logan BE. Addition of acetate improves stability of power generation using microbial fuel cells treating domestic wastewater. *Bioelectrochem* 2017; 118: 154–160.

23. Rossi R, Evans PJ, and Logan BE. Impact of flow recirculation and anode dimensions on performance of a large scale microbial fuel cell. *J Power Sourc* 2019; 412: 294–300.

24. Blatter M, Delabays L, Furrer C, et al. Stretched 1000-L microbial fuel cell. *J Power Sourc* 2021; 483: 229130.

25. Lepage G, Perrier G, Merlin G, et al. Multifactorial evaluation of the electrochemical response of a microbial fuel cell. *RSC Adv* 2014; 4: 23815–23825.

26. Flexer V, Chen J, Donose BC, et al. The nanostructure of three-dimensional scaffolds enhances the current density of microbial bioelectrochemical systems. *Energy Environ Sci* 2013; 6: 1291–1298.

27. Roy JN, Luckarift HR, Sizemore SR, et al. Microbial-enzymatic-hybrid biological fuel cell with optimized growth conditions for Shewanella oneidensis DSP-10. *Enzyme Microb Technol* 2013; 53: 123–127.

28. Kim JR, Cheng S, Oh S-E, et al. Power generation using different cation, anion, and ultrafiltration membranes in microbial fuel cells. *Environ Sci Technol* 2007; 41: 1004–1009.

29. Zhao F, Rahunen N, Varcoe JR, et al. Activated carbon cloth as anode for sulfate removal in a microbial fuel cell. *Environ Sci Technol* 2008; 42: 4971–4976.

30. Wang YX, He CS, Li WQ, et al. High power generation in mixed-culture microbial fuel cells with corncob-derived three-dimensional N-doped bioanodes and the impact of N dopant states. *Chem Eng J* 2020; 399: 125848.

31. Richter H, McCarthy K, Nevin KP, et al. Electricity generation by Geobacter sulfurreducens attached to gold electrodes. *Langmuir* 2008; 24: 4376–4379.

32. Masoudi M, Rahimnejad M, and Mashkour M. Enhancing operating capacity of microbial fuel cells by using low-cost electrodes and multi-anode-cathode connections in a membrane-less configuration. *Int J Hydrogen Energy* 2021; 46: 8226–8238.

33. Tan SM, Ong SA, Ho LN, et al. Polypropylene biofilm carrier and fabricated stainless steel mesh supporting activated carbon: Integrated configuration for performances enhancement of microbial fuel cell. *Sustainable Energy Technol Assess* 2021; 46: 101268.

34. Ying X, Shen D, Wang M, et al. Titanium dioxide thin film-modified stainless steel mesh for enhanced current-generation in microbial fuel cells. *Chem Eng J* 2018; 333: 260–267.

35. Katuri K, Luisa Ferrer M, Gutierrez MC, et al. Three-dimensional microchannelled electrodes in flow-through configuration for bioanode formation and current generation. *Energy Environ Sci* 2011; 4: 4201–4210.

36. Kumar GG, Sarathi VGS, and Nahm KS. Recent advances and challenges in the anode architecture and their modifications for the applications of microbial fuel cells. *Biosens Bioelectron* 2013; 43: 461–475.

37. Ding C, Liu H, Lv M, et al. Hybrid bio-organic interfaces with matchable nanoscale topography for durable high extracellular electron transfer activity. *Nanoscale* 2014; 6: 7866–7871.

38. Zou Y, Pisciotta J, and Baskakov IV. Nanostructured polypyrrole-coated anode for sun-powered microbial fuel cells. *Bioelectrochem* 2010; 79: 50–56.

39. Wang DL, Pan JY, Xu M, et al. Surface modification of Shewanella oneidensis MR-1 with polypyrrole-dopamine coating for improvement of power generation in microbial fuel cells. *J Power Sourc* 2021; 483: 229220.

40. Yin T, Zhang H, Yang G, et al. Polyaniline composite TiO2 nanosheets modified carbon paper electrode as a high
performance bioanode for microbial fuel cells. *Synth Met* 2019; 252: 8–14.
41. Ding C, Liu H, Zhu Y, et al. Control of bacterial extracellular electron transfer by a solid-state mediator of polyaniline nanowire arrays. *Energy Environ Sci* 2012; 5: 8517–8522.
42. Liu X, Wu W, and Gu Z. Poly (3,4-ethylenedioxythiophene) promotes direct electron transfer at the interface between Shewanella loihica and the anode in a microbial fuel cell. *J Power Sour* 2015; 277: 110–115.
43. Kauffman DR and Star A. Carbon nanotube gas and vapor sensors. *Angew Chem Int Edit* 2008; 47: 6550–6570.
44. Sun JJ, Zhao HZ, Yang QZ, et al. A novel layer-by-layer self-assembled carbon nanotube-based anode: Preparation, characterization, and application in microbial fuel cell. *Electrochim Acta* 2010; 55: 3041–3047.
45. Zhao GC, Yin ZZ, Zhang L, et al. Direct electrochemistry of cytochrome c on a multi-walled carbon nanotubes modified electrode and its electrocatalytic activity for the reduction of H$_2$O$_2$. *Electrochem Commun* 2005; 7: 256–260.
46. Mink JE, Rojas JP, Logan BE, et al. Vertically grown multiwalled carbon nanotube anode and nickel silicide integrated high performance microsized (1.25 μm L) microbial fuel cell. *Nano Lett* 2012; 12: 791–795.
47. Liang P, Wang H, Xia X, et al. Carbon nanotube powders as electrode modifiers to enhance the activity of anodic biofilm in microbial fuel cells. *Biosens Bioelectron* 2011; 26: 3000–3004.
48. Yang Q, Zhao X, Yang J, et al. Welding assembly of 3D interconnected carbon nanotubes on carbon fiber as the high-performance anode of microbial fuel cells. *Int J Hydrogen Energy* 2019; 44: 20304–20311.
49. Zhao N, Ma Z, Song H, et al. Enhancement of bioelectricity generation by synergistic modification of vertical carbon nanotubes/poly pyrrole for the carbon fibers anode in microbial fuel cell. *Electrochim Acta* 2019; 296: 69–74.
50. Yellappa M, Sran JS, Sarkar O, et al. Modified conductive polyaniline-carbon nanotube composite electrodes for bioelectricity generation and waste remediation. *Bioreour Technol* 2019; 284: 148–154.
51. Zhao N, Ma ZK, Song HH, et al. Polyaniline/reduced graphene oxide-modified carbon fiber brush anode for high-performance microbial fuel cells. *Int J Hydrogen Energy* 2018; 43: 17867–17872.
52. Zhang YZ, Mo GQ, Li XW, et al. A graphene modified anode to improve the performance of microbial fuel cells. *J Power Sour* 2011; 196: 5402–5407.
53. Liu J, Qiao Y, Guo CX, et al. Graphene/carbon cloth anode for high-performance mediatorless microbial fuel cells. *Bioreour Technol* 2012; 114: 275–280.
54. Huang Y-X, Liu X-W, Xie J-F, et al. Graphene oxide nanoribbons greatly enhance extracellular electron transfer in bio-electrochemical systems. *Chem Commun* 2011; 47: 5795–5797.
55. Wang H, Wang G, Ling Y, et al. High power density microbial fuel cell with flexible 3D graphene-nickel foam as anode. *Nanoscale* 2013; 5: 10283–10290.
56. Xiao L, Damien J, Luo J, et al. Crumpled graphene particles for microbial fuel cell electrodes. *J Power Sour* 2012; 208: 187–192.
57. ter Heijne A, Hamelers HVM, Saakes M, et al. Performance of non-porous graphite and titanium-based anodes in microbial fuel cells. *Electrochim Acta* 2008; 53: 5697–5703.
58. Kosimanningrum WE, Ouïs M, Holade Y, et al. Platinum nanoarrays directly grown onto a 3D-carbon felt electrode as a bifunctional material for garden compost microbial fuel cell. *J Electrochem Soc* 2021; 168: 025501.
59. Sun M, Zhang F, Tong Z-H, et al. A gold-sputtered carbon paper as an anode for improved electricity generation from a microbial fuel cell inoculated with Shewanella oneidensis MR-1. *Biosens Bioelectron* 2010; 26: 338–343.
60. Crittenden SR, Sund CJ, and Sumner JJ. Mediating electron transfer from bacteria to a gold electrode via a self-assembled monolayer. *Langmuir* 2006; 22: 9473–9476.
61. Michaelidou U, ter Heijne A, Euverink GJW, et al. Microbial communities and electrochemical performance of titanium-based anodic electrodes in a microbial fuel cell. *Appl Environ Microbiol* 2011; 77: 1069–1075.
62. Ouitrakul S, Sriyudthsak M, Charojroochkul S, et al. Impedance analysis of bio-fuel cell electrodes. *Biosens Bioelectron* 2007; 23: 721–727.
63. Fan YZ, Xu ST, Schaller R, et al. Nanoparticle decorated anodes for enhanced current generation in microbial electrochemical cells. *Biosens Bioelectron* 2011; 26: 1908–1912.
64. Kargi F and Eker S. Electricity generation with simultaneous wastewater treatment by a microbial fuel cell (MFC) with Cu and Cu-Au electrodes. *J Chem Technol Biot* 2007; 82: 658–662.
65. Yang YC, Chen CC, Huang CS, et al. Developments of metallic anodes with various compositions and surfaces for the microbial fuel cells. *Int J Hydrogen Energy* 2017; 42: 22235–22242.
66. Zhai DD, Fang Z, Jin H, et al. Vertical alignment of polyaniline nanowire arrays. *Electrochim Acta* 2019; 296: 69–74.
67. Zhang YZ, Mo GQ, Li XW, et al. A graphene modified anode to improve the performance of microbial fuel cells. *J Power Sour* 2011; 196: 5402–5407.
68. Liu J, Qiao Y, Guo CX, et al. Graphene/carbon cloth anode for high-performance mediatorless microbial fuel cells. *Bioreour Technol* 2012; 114: 275–280.
69. Huang Y-X, Liu X-W, Xie J-F, et al. Graphene oxide nanoribbons greatly enhance extracellular electron transfer in bio-electrochemical systems. *Chem Commun* 2011; 47: 5795–5797.
70. Wang H, Wang G, Ling Y, et al. High power density microbial fuel cell with flexible 3D graphene-nickel foam as anode. *Nanoscale* 2013; 5: 10283–10290.
71. Xiao L, Damien J, Luo J, et al. Crumpled graphene particles for microbial fuel cell electrodes. *J Power Sour* 2012; 208: 187–192.
72. ter Heijne A, Hamelers HVM, Saakes M, et al. Performance of non-porous graphite and titanium-based anodes in microbial fuel cells. *Electrochim Acta* 2008; 53: 5697–5703.
73. Kosimanningrum WE, Ouïs M, Holade Y, et al. Platinum nanoarrays directly grown onto a 3D-carbon felt electrode as a bifunctional material for garden compost microbial fuel cell. *J Electrochem Soc* 2021; 168: 025501.
74. Sun M, Zhang F, Tong Z-H, et al. A gold-sputtered carbon paper as an anode for improved electricity generation from a microbial fuel cell inoculated with Shewanella oneidensis MR-1. *Biosens Bioelectron* 2010; 26: 338–343.
75. Crittenden SR, Sund CJ, and Sumner JJ. Mediating electron transfer from bacteria to a gold electrode via a self-assembled monolayer. *Langmuir* 2006; 22: 9473–9476.
76. Michaelidou U, ter Heijne A, Euverink GJW, et al. Microbial communities and electrochemical performance of titanium-based anodic electrodes in a microbial fuel cell. *Appl Environ Microbiol* 2011; 77: 1069–1075.
77. Ouitrakul S, Sriyudthsak M, Charojroochkul S, et al. Impedance analysis of bio-fuel cell electrodes. *Biosens Bioelectron* 2007; 23: 721–727.
78. Fan YZ, Xu ST, Schaller R, et al. Nanoparticle decorated anodes for enhanced current generation in microbial electrochemical cells. *Biosens Bioelectron* 2011; 26: 1908–1912.
79. Kargi F and Eker S. Electricity generation with simultaneous wastewater treatment by a microbial fuel cell (MFC) with Cu and Cu-Au electrodes. *J Chem Technol Biot* 2007; 82: 658–662.
80. Yang YC, Chen CC, Huang CS, et al. Developments of metallic anodes with various compositions and surfaces for the microbial fuel cells. *Int J Hydrogen Energy* 2017; 42: 22235–22242.
81. Zhai DD, Fang Z, Jin H, et al. Vertical alignment of polyaniline nanofibers on electrode surface for high-performance microbial fuel cells. *Bioreour Technol* 2019; 288: 121499.
82. Pu KB, Ma Q, Cai WF, et al. Polypyrrole modified stainless steel as high performance anode of microbial fuel cell. *Biochem Eng J* 2018; 132: 255–261.
83. Ma Q, Pu K-B, Cai W-F, et al. Characteristics of polypyrrole modified stainless steel as anode in microbial fuel cells. *Ind Eng Chem Res* 2018; 57: 6633–6638.
fuel cells applications. *Int J Energy Res* 2019; 43: 2795–2805.

70. Wu X, Shi Z, Zou L, et al. Pectin assisted one-pot synthesis of three dimensional porous NiO/graphene composite for enhanced bioelectrocatalysis in microbial fuel cells. *J Power Sourc* 2018; 378: 119–124.

71. Paul D, Noori MT, Rajesh PP, et al. Modification of carbon felt anode with graphene oxide-zelite composite for enhancing the performance of microbial fuel cell. *Sustain Energy Techn* 2018; 26: 77–82.

72. Li J, Yu Y, Chen D, et al. Hydrophilic graphene aerogel anodes enhance the performance of microbial electrochemical systems. *Bioresour Techn* 2020; 304: 122907.

73. Sumisha A and Haribabu K. Modification of graphite felt using nano polypyrrole and polystriol for microbial fuel cell applications-a comparative study. *Int J Hydrogen Energy* 2018; 43: 3308–3316.

74. Cai T, Huang MH, Huang YX, et al. Enhanced performance of microbial fuel cells by electrospinning carbon nanofibers hybrid carbon nanotubes composite anode. *Int J Hydrogen Energy* 2019; 44: 3088–3098.

75. Mohamed HO, Sayed ET, Obaid M, et al. Transition metal nanoparticles doped carbon paper as a cost-effective anode in a microbial fuel cell powered by pure and mixed bio-catalyst cultures. *Int J Hydrogen Energy* 2018; 43: 21560–21571.

76. Wang L, Su L, Chen H, et al. Carbon paper electrode modified by goethite nanowiskers promotes bacterial extracellular electron transfer. *Mater Lett* 2015; 141: 311–314.

77. Nakamura R, Kai F, Okamoto A, et al. Self-Constructed Electrically Conductive Bacterial Networks. *Angew Chem Int Edit* 2009; 48: 508–511.

78. Long X, Cao X, Wang C, et al. Preparation of needle-like FeOx/Fe3Ox nanorods on stainless steel plates to form inexpensive, high-performance bioanodes. *J Electroanal Chem* 2019; 855: 113497.

79. Peng X, Yu H, Wang X, et al. Enhanced performance and capacitance behavior of anode by rolling Fe3O4 into activated carbon in microbial fuel cells. *Bioresour Techn* 2012; 121: 450–453.

80. Liang JH, Tan HR, Liu M, et al. A thin-film silicon based photocathode with a hydrogen doped TiO2 protection layer for solar hydrogen evolution. *J Mater Chem A* 2016; 4: 16841–16848.

81. Wachesk CC, Seabra SH, Dos Santos TAT, et al. In vivo biocompatibility of diamond-like carbon films containing TiO2 nanoparticles for biomedical applications. *J Mater Sci Mater M* 2021; 32: 117.

82. Sarkar A and Khan GG. The formation and detection techniques of oxygen vacancies in titanium oxide-based nanostructures. *Nanoscale* 2019; 11: 3414–3444.

83. Usui H, Suzuki S, Domi Y, et al. TiO2/MnO2 composite electrode enabling photoelectric conversion and energy storage as photoelectrochemical capacitor. *Mater Today Energy* 2018; 9: 229–234.

84. Zhang ML, Ning T, Sun P, et al. Poisoning mechanisms of Mn-containing additives on the performance of TiO2 based lambda oxygen sensor. *Sensor Actuat B-Chem* 2018; 267: 565–569.

85. Guo Q, Ma ZB, Zhou CY, et al. Single Molecule Photocatalysis on TiO2 Surfaces. *Chem Rev* 2019; 119: 11020–11041.

86. Hashima Y, Ishikawa Y, Rairuku I, et al. Easy and green preparation of a graphene-TiO2 nanohybrid using a supramolecular biomaterial consisting of artificially bifunctionalized proteins and its application for a perovskite solar cell. *Nanoscale* 2018; 10: 19249–19253.

87. Zou L, Qiao Y, Wu X-S, et al. Synergistic effect of titanium dioxide nanocrystal/reduced graphene oxide hybrid on enhancement of microbial electrocatalysis. *J Power Sourc* 2015; 276: 208–214.

88. Maurer-Jones MA, Gunsolus IL, Meyer BM, et al. Impact of TiO2 nanoparticles on growth, biofiln formation, and flavin secretion in shewanella oneidensis. *Analog Chem* 2013; 85: 5810–5818.

89. Tang J, Yuan Y, Liu T, et al. High-capacity carbon-coated titanium dioxide core-shell nanoparticles modified three dimensional anodes for improved energy output in microbial fuel cells. *J Power Sourc* 2015; 274: 170–176.

90. Wen Z, Ci S, Mao S, et al. TiO2 nanoparticles-decorated carbon nanotubes for significantly improved bioelectricity generation in microbial fuel cells. *J Power Sourc* 2013; 234: 100–106.

91. Yin T, Lin Z, Su L, et al. Preparation of vertically oriented TiO2 nanosheets modified carbon paper electrode and its enhancement to the performance of MFCs. *ACS Appl Mater Inter* 2015; 7: 400–408.

92. Yin T, Li H, Su L, et al. The catalytic effect of TiO2 nanosheets on extracellular electron transfer of Shewanella loihica PV-4. *Phys Chem Chem Phys* 2016; 18: 29871–29878.

93. Mehdinia A, Ziaei E, and Jabbari A. Facile microwave-assisted synthesized reduced graphene oxide/tin oxide nanocomposite and using as anode material of microbial fuel cell to improve power generation. *Int J Hydrogen Energy* 2014; 39: 10724–10730.

94. Ly Z, Xie D, Yue X, et al. Ruthenium oxide-coated carbon felt electrode: A highly active anode for microbial fuel cell applications. *J Power Sourc* 2012; 210: 26–31.

95. Zhang C, Liang P, Jiang Y, et al. Enhanced power generation of microbial fuel cell using manganese dioxide-coated anode in flow-through mode. *J Power Sourc* 2015; 273: 580–583.

96. Wang Y, Li B, Zeng L, et al. Polyaniiline/mesoporous tungsten trioxide composite as anode electrocatalyst for high-performance microbial fuel cells. *Biosens Bioelectron* 2013; 41: 582–588.
97. Yang QZ, Yang SQ, Liu GL, et al. Boosting the anode performance of microbial fuel cells with a bacteria-derived biological iron oxide carbon nanocomposite catalyst. *Chemosphere* 2021; 268: 128800.
98. Jian M, Xue P, Shi K, et al. Efficient degradation of indole by microbial fuel cell based Fe₂O₃-polyaniline-dopamine hybrid composite modified carbon felt anode. *J Hazard Mater* 2020; 388: 122123.
99. Fu L, Wang HQ, Huang Q, et al. Modification of carbon felt anode with graphene/Fe₂O₃ composite for enhancing the performance of microbial fuel cell. *Bioproc Biosyst Eng* 2020; 43: 373–381.
100. Singh S, Pophali A, Omar RA, et al. A nickel oxide-decorated in situ grown 3-D graphitic forest engrained carbon foam electrode for microbial fuel cells. *Chem Commun* 2021; 57: 879–882.
101. Yin T, Su L, Li H, et al. Nitrogen doping of TiO₂ nanosheets greatly enhances bioelectricity generation of S-loihica PV-4. *Electrochim Acta* 2017; 258: 1072–1080.
102. Khan N, Anwer AH, Khan MD, et al. Magnesium ferrite spinels as anode modifier for the treatment of Congo red and energy recovery in a single chambered microbial fuel cell. *J Hazard Mater* 2021; 410: 124561.
103. Tahir K, Miran W, Jang J, et al. MnCo₂O₄ coated carbon felt anode for enhanced microbial fuel cell performance. *Chemosphere*. 2021; 265: 129098.
104. Park IH, Kim P, Kumar GG, et al. The influence of active carbon supports toward the electrocatalytic behavior of Fe₃O₄ nanoparticles for the extended energy generation of mediatorless microbial fuel cells. *Appl Biochem Biotechnol* 2016; 179: 1170–1183.
105. Xian JL, Ma H, Li Z, et al. Alpha-FeOOH nanowires loaded on carbon paper anodes improve the performance of microbial fuel cells. *Chemosphere* 2021; 273: 129669.
106. Xue P, Jiang S, Li W, et al. Bimetallic oxide MnFe₂O₄ modified carbon felt anode by drip coating: an effective approach enhancing power generation performance of microbial fuel cell. *Bioproc Biosyst Eng* 2021; 44: 1119–1130.
107. Tahir K, Miran W, Jang J, et al. Nickel ferrite/MXene-coated carbon felt anodes for enhanced microbial fuel cell performance. *Chemosphere* 2021; 268: 128784.