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Review Paper

A review on the application of nanomaterials in improving microbial fuel cells

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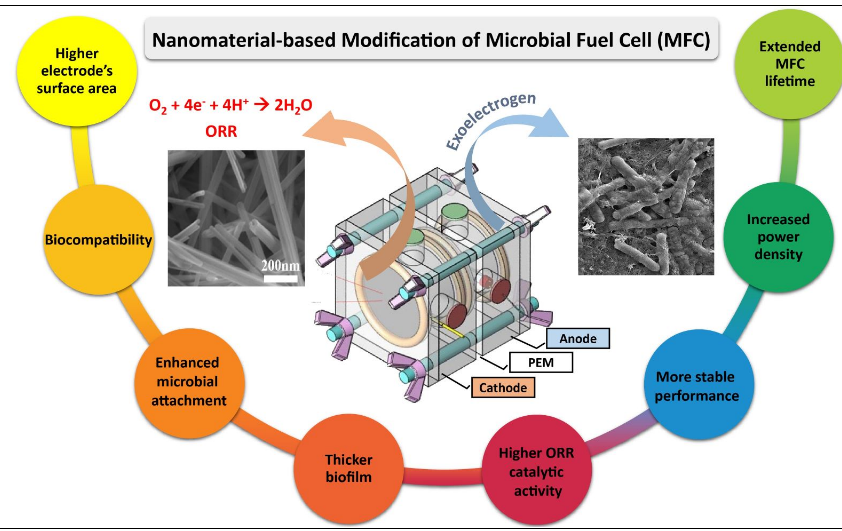
HIGHLIGHTS

- ➢Nanomaterials and their roles in improving microbial fuel cells (MFCs) are reviewed.
- ➢Significant effects of nanomaterials on growing active biofilm and electron transfer are discussed.
- ➢Nanomaterials lead to higher catalytic activity for electrodes, and higher proton conductivity, and less biofouling for membranes.
- ➢Inexpensive and high-performance nanocomposites for more practical MFC applications are presented and discussed.
- ➢Future perspectives of using nanomaterials in MFCs are explained.

GRAPHICAL ABSTRACT



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ABSTRACT

Materials at the nanoscale show exciting and different properties. In this review, the applications of nanomaterials for modifying the main components of microbial fuel cell (MFC) systems (i.e., electrodes and membranes) and their effect on cell performance are reviewed and critically discussed. Carbon and metal-based nanoparticles and conductive polymers could contribute to the growth of thick anodic and cathodic microbial biofilms, leading to enhanced electron transfer between the electrodes and the biofilm. Extending active surface area, increasing conductivity, and biocompatibility are among the significant attributes of promising nanomaterials used in MFC modifications. The application of nanomaterials in fabricating cathode catalysts (catalyzing oxygen reduction reaction) is also reviewed herein. Among the various nanocatalysts used on the cathode side, metal-based nanocatalysts such as metal oxides and metal-organic frameworks (MOFs) are regarded as inexpensive and high-performance alternatives to the conventionally used high-cost Pt. In addition, polymeric membranes modified with hydrophilic and antibacterial nanoparticles could lead to higher proton conductivity and mitigated biofouling compared to the conventionally used and expensive Nafion. These improvements could lead to more promising cell performance in power generation, wastewater treatment, and nanobiosensing. Future research efforts should also take into account decreasing the production cost of the nanomaterials and the environmental safety aspects of these compounds.

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Abbreviations

3D	Three-dimensional
AgNPs	Silver nanoparticles
AuNPs	Gold nanoparticles
BC	Bacterial cellulose
BOD	Biological oxygen demand
brGO	Biologically reduced graphene oxide
CNT	Carbon nanotubes
COD	Chemical oxygen demand
CoNPs	Cobalt nanoparticles
DCMFC	Dual-chamber microbial fuel cell
EET	Extracellular electron transfer
EIS	Electrochemical impedance spectroscopy
FeCNPs	Iron carbide nanoparticles
GDE	Gas diffusion electrode
GO	Graphene oxide
IR	Internal resistance
MEA	Membrane electrode assembly
MES	Microbial electrosynthesis
MFC	Microbial fuel cell
MOFs	Metal-organic frameworks
MWCNTs	Multi-walled carbon nanotubes
NiNPs	Nickel nanoparticles
NPs	Nanoparticles
NZ	Nano-zycosil
ORR	Oxygen reduction reaction
PANI	Polyaniline
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT: PSS	Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate
PEMs	Proton exchange membranes
PES	Polyethersulfone
PHF	Porous hollow fibers
rGO	Reduced graphene oxide
SCMFC	Single chamber microbial fuel cell
SPEEK	Sulfonated poly(ether ether ketone)
SPSEBS	Sulfonated polystyrene ethylene butylene polystyrene
SS	Stainless steel
$sTiO_2$	Sulfonated TiO_2
WO_3	Tungsten oxide
ZnONPs	Zinc oxide nanoparticles

Nomenclatures

R_{ct}	Charge transfer resistance

1. Introduction

Microbial fuel cell (MFC) is one of the potential sources to supply renewable energy. In MFCs, microorganisms serve as biocatalysts in the oxidation reaction of substrates, i.e., organic materials (Izadi et al., 2015; Ivars-Barceló et al., 2018; Masoudi et al., 2020). In better words, MFCs transform the chemical bond energy of organic compounds directly into electricity without passing through additional intermediate stages and the consequent losses (Kiran and Gaur, 2013; Xu et al., 2016; Berchmans, 2018). Therefore, similar to thermoelectric, photoelectric, thermionic devices, MFCs are also considered direct energy converters. Mechanistically, there is a bio-electrochemical cycle in MFCs by which microbial and chemical processes occur (Zhang et al., 2018a). Bacteria consume the substrate anaerobically, resulting in the production of electrons and protons. Then, the generated electrons through the anode and the external circuit reach the cathode's surface, on which a chemical reaction takes place in the presence of protons and oxygen (Lu et al., 2015; Masoudi et al., 2021). Accordingly, in an MFC system, the main components include microorganisms, membranes, and electrodes, i.e., anode and cathode (Logan et al., 2015).

MFC is a multidisciplinary area of research that needs developments in biotechnology, electrochemistry, and material sciences. One of the most critical challenges in MFCs is the low electricity generation caused by the low efficiency of MFC components like electrodes, membrane, catalyst, and weak biofilm formation. Advanced materials fabricated through the recent developments in nanotechnology have played a considerable role in improving MFCs (Ghasemi et al., 2013). Materials in the nanoscale represent novel properties. For instance, they can accelerate microorganisms' biocatalytic activity by providing a high surface area for biofilm formation. Moreover, the oxygen reduction reaction (ORR) rate can be improved by nanoscale carbon or metal catalysts (Santoro et al., 2014). While on the other hand, the antibacterial properties of nanomaterials like metal oxides increase air-cathode lifetime (Yang et al., 2016). Nanomaterials have also been widely used in producing MFC electrodes to achieve a more significant number of active reaction sites. These improvements have led to higher performance MFCs for electricity generation applications, wastewater treatment, and bio-sensing.

Table 1 tabulates the various aspects of nanotechnology applications in MFCs covered by the present review compared to the review articles published over the last several years (2015-2021). To the best of the authors' knowledge, this is the first paper comprehensively and simultaneously discussing the impacts of nanotechnology on the performance of the MFC's main compartments and most of its known applications. The benefits and drawbacks of different nanomaterials are thoroughly explained. Also, improvements in MFCs for electricity generation, self-powered nanobiosensing, and wastewater treatment by considering the effect of nanomaterial modifiers are discussed.

2. Nanomaterials in MFC's compartments

Improving MFC's performance is proportional to enhancing the features of its constituents, i.e., microorganisms, electrodes (anode and cathode), and membrane. Nanomaterials can serve this purpose; **Table 2** tabulates the potential effects of nanotechnology on improving the attributes of different

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Table 1.
Comparing the present review paper with previously published reviews (2015-2021) on the application of nanotechnology in MFCs.

Nanotechnology in MFC compartments				Nanotechnology in MFC applications					Reference
Biofilm-nanomaterial interaction	Anode	Cathode	Membrane	Electricity generation	Microbial electrosynthesis	Biohydrogen production	Wastewater treatment	Self-powered Nanobiosensing	
×	√	√	×	√	×	×	×	×	Ci et al. (2015)
×	×	√	×	√	×	×	×	×	Kannan et al. (2016)*
×	√	×	×	√	×	×	×	×	Hindatu et al. (2017)
√	×	×	×	×	×	×	×	×	Zhang, et al. (2018b)
√	√	×	×	×	×	×	×	×	Mouhib et al. (2019)
×	×	×	√	√	×	×	√	×	Shabani et al. (2020)
√	√	√	√	√	×	√	×	×	Olabi et al. (2020)*
×	√	×	×	√	×	×	×	×	Liu et al. (2020)
×	√	√	×	√	×	×	×	×	Kaur et al. (2020)
×	√	×	×	√	×	×	×	×	Cai et al. (2020a)
×	√	√	×	√	×	×	×	×	Narayanasamy et al. (2020)
√	×	×	×	×	×	×	×	×	Wang et al. (2021)
×	×	√	×	√	×	×	×	×	Peera et al. (2021)
√	√	√	√	√	√	×	√	√	**This review**

√: Included
×: Not included
* For the case of graphene

Table 2.
Potential effects of nanotechnology on enhancing the attributes of different constituents of MFC systems.

MFC constituent	Potential effects of nanotechnology
Microorganisms	Growth rate, bacteria attachment, extracellular electron transfer, the activity of biofilm in a redox reaction, biofilm resistance
Anode	Conductivity, high surface area, porosity, charge transfer, capacitance, biocompatibility
Cathode	Conductivity, high surface area, porosity, charge transfer, capacitance, oxygen reduction reaction (ORR) rate, gas diffusion, anti-fouling
Membrane	Proton conductivity, oxygen cross-over, water uptake, separation, anti-fouling

MFC parts. Nevertheless, the cost of nanomaterials might still be a limiting factor, and hence, efforts should be put into developing low-cost nanomaterials of outstanding features.

2.1. Microorganisms and electrodes

Microorganisms utilized in MFCs are classified into two main groups: exoelectrogens on the anode and electrotrophs on the cathode (biocathode) (**Fig. 1a**) (Logan et al., 2006 and 2019). Exoelectrogens are vital and form a biofilm on the anode surface to decompose organic substrates like glucose, acetate, and waste materials to generate electrons and protons. Thus, this group is necessary for electricity generation. These microorganisms can transport electrons from electron donors (substrate) to electrode surfaces by various mechanisms, including direct contact, nano-wires, and mediators produced by them (Logan, 2009). **Figure 1b** demonstrates the mentioned electron transport mechanisms. Electrotrophs (electrotrophic microorganisms) need electrons as feed to grow and use various electron acceptors like carbon dioxide. These microorganisms (**Fig. 1c**) are instrumental in the reactions taking place on the cathode. Electrotrophs play a vital role as a biocathode in microbial electrosynthesis (MES) systems.

2.1.1. Effects of nanomaterials on exoelectrogens and anode performance

As mentioned earlier, exoelectrogens in anodic biofilms form active sites for the oxidation of organic molecules fed to MFCs. The properties of the anode surface are of great importance for the colonization of exoelctrogenic bacteria by influencing the transfer of electrons and bacterial attachment (Lv et al., 2019; Palanisamy et al., 2019). An ideal MFC anode material has to expedite the flow of electrons and accelerate the attachment of microbes using conduction. Graphite (plate, rod, and brush), carbon paper, carbon felt, and carbon cloth are the conventional carbon-based materials utilized as anodes in MFC systems (Ghasemi et al., 2013) and are commercially available. In general, carbon as an anti-corrosion material with good conductivity is considered suitable for electrode fabrication in MFC. However, using conventional anodes, electron movement from microbial biofilm to the electrode surface is restricted due to bacteria's weak attachment. This issue impacts the MFC function by decreasing the power output and consequently hinders the practical utilization of the MFC technology. The other significant shortcoming is high internal resistance (IR), resulting in a low rate of charge transfer and high-cost materials.

Inexpensive nanomaterials can provide an extended surface area for bacteria growth on the anode and enhance microbial attachment. This improvement (i.e., enhanced exoelectrogens colonization) through increased extracellular electron transfer (EET) and substrate metabolism lead to augmented function and effectiveness of the MFC (Patel et al., 2019; Salar-García and Ortiz-Martínez, 2019). The increase in the number of exoelectrogenic colonies boosts the redox activity of anodic biofilm, and hence, more electrons and protons are generated. **Table 3** tabulates the effects of different nanomaterials used for modifying anodes and the consequent improvements in the power density of the investigated MFC systems, including various exoelectrogens.

Multi-walled carbon nanotubes (MWCNTs) are among the most widely used nanomaterials for anode modification. They can provide an excellent active surface for microbial attachment. As presented in **Table 3**, Nambiar et al. (2009) utilized MWCNTs for improving the growth of *Enterobacter cloacae* on a commercial carbon sheet anode in a dual-chamber MFC (DCMFC) with a platinum-coated carbon sheet cathode. In this work, a maximum power density increase of 256% was achieved using the MWCNTs modified anode rather than the bare carbon sheet. The authors

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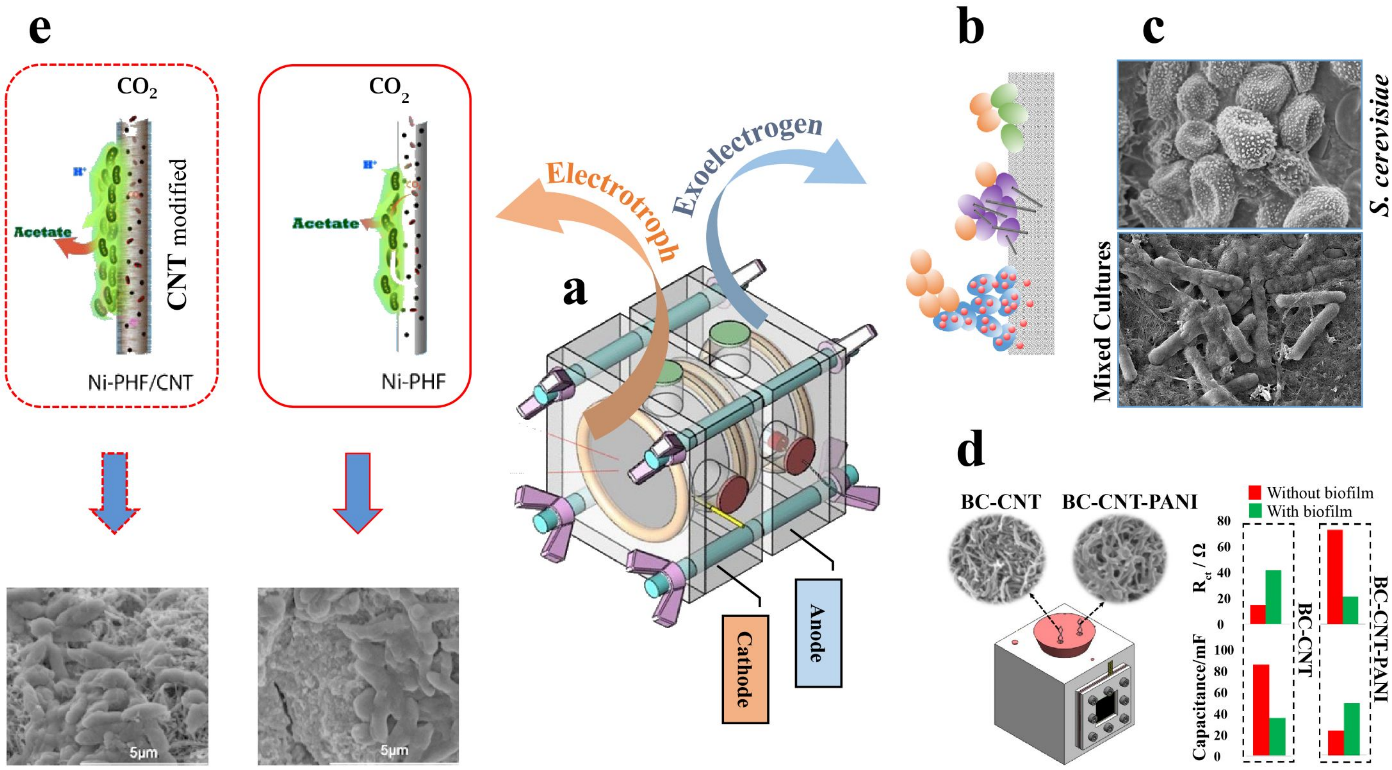

Fig. 1. Cubic dual-chambered MFC with anodic and cathodic microorganisms **(a)**, Different mechanism of electron transfer from exoelectrogens of the anode to electrode surface: direct contact (green), nanowire (violet), and mediators (blue and brown) **(b)**, two morphologies of exoelectrogens **(c),** the effect of polyaniline (PANI)-coated bacterial cellulose carbon nanotubes (BC-CNT) on charge transfer resistance (R_{ct}) of mixed culture anodic biofilm **(d)** (Mashkour et al., 2020) (Reproduced with permission from Elsevier. Copyright©2020. License No. 5053250047165), and the effect of CNT on *Sporomusa ovate* cathodic biofilm formation **(e)** (Bian et al., 2018) (Reproduced with permission from Royal Society of Chemistry. Copyright©2018. License No. 1112686-1).

attributed the improvement made to the extended highly conductive surface area on the carbon sheet obtained using a high concentration of MWCNTs ink (10 mg/mL) and chitosan as a green binder (Nambiar et al., 2009). Despite the increased surface area for bacterial colonization, these nanomaterials have been reported as toxic at specific concentrations against bacteria. A recent work investigating the MWCNT's toxicity effect on microbial growth of *Geobacter sulfurreducens* biofilm revealed that the maximum MWCNTs concentration for improving anodic biofilm performance (i.e., highest power and current density compared to bare carbon sheet) was found to be 0.1 mg/mL (Jiang et al., 2018). However, further increments in MWCNTs concentration resulted in anodic biofilm's weak performance, suggesting that the MWCNTs concentration must have exceeded its toxic threshold (Jiang et al., 2018).

The following reasons could explain the significantly different optimal concentrations reported by these two studies; 1) the differences in the biofilms developed and 2) the differences in the time of measurements. As for the latter, it is imperative to allow the microbial colonization process (biofilm formation) to complete before performance outputs are measured. In better words, high power density values might be obtained on the onset of MFC operation due to the high conductivity and surface area of the nanomaterials-based anode; however, performance deterioration would likely occur in response to low biocompatibility of the nanomaterials or their higher-than-threshold-concentration. Under toxic conditions, nanomaterials could deactivate microbial populations colonized on the anode leading to increased anode resistance and deteriorated performance parameters. So, the findings reported by Nambiar et al. (2009) could have been more conclusive if the authors had considered a longer colonization process.

To better understand the toxicity effect of MWCNTs (0.4 mg/mL) on anodic biofilm, a more recent comprehensive research was performed by Mashkour et al. (2020) using electrochemical impedance spectroscopy (EIS). They utilized two MWCNTs-coated bacterial cellulose (BC) based anodes (BC-CNT) in two similar single-chamber MFCs (SCMFCs) with the same mixed-cultures as anodic bacteria. They studied charge transfer resistance (R_{ct}) of the anode before the colonization process, after three weeks of colonization when biofilm was formed on the anode, and after 50 d. The BC-CNT without biofilm showed the lowest resistance, while in response to microbial colonization, the R_{ct} showed an increasing trend (Mashkour et al., 2020). These findings were indicative of the toxicity effect of MWCNTs (at the tested concentration of 0.4 mg/mL) on the mixed-culture biofilm and were approximately in agreement with the data reported by Jiang et al. (2018). To mitigate the toxicity effects of MWCNTs on the developed anode biofilm and to enhance its activity, Mashkour et al. (2020) tried to modify MWCNTs using biocompatible nanomaterials like polyaniline (PANI) (**Fig. 1d**). The authors claimed that the modification could successfully mitigate the toxicity of the nanocomposite and consequently decrease the R_{ct}.

Other carbon-based nanomaterials have also been used for anode modification. For instance, reduced graphene oxide (rGO) nanosheets have been recently utilized for improving the exoelectrogenic biofilm activity of *Shewanella putrefaciens* in an MFC system (Zhu et al., 2019). Graphene oxide (GO) was dispersed in an anolyte solution of bacteria and was then reduced on carbon felt *in situ* biologically (br-GO). The power density generated by the modified anode stood at 240 mW/m^2, which was substantially higher than the value recorded for the unmodified carbon (0.015 mW/m^2) (Zhu et al., 2019). Mechanistically, br-GO must have formed a high-surface-area conductive bridge between the microbial biofilm and the carbon felt fibers, facilitating the extracellular transfer of electrons between them. Moreover, br-GO was found highly biocompatible, which must have also contributed to the high affinity of the bacterial populations to grow at higher rates, more effectively colonize, and form a thicker layer of active biofilm on the anode (Zhu et al., 2019).

Various other biocompatible nanomaterials have also been studied for anode modification to boost biofilm formation and activity. For instance, a mixture of nickel nanoparticles (NPs), Poly(3,4-ethylenedioxythiophene) (PEDOT), and graphene was employed by Hernandez et al. (2019) to

Table 3.
Effects of anode modifications using nanomaterials on the performance (power density) of different MFC systems with different exoelectrogens.

Exoelectrogenic microorganisms	Device configuration	Anode (Control)	Anode (modified by nanomaterials)	Cathode	Power density (mW/m^2)*		Reference
					Control	Modified	
Enterobacter cloacae	DCMFC	Carbon paper	Multi-walled carbon nanotube (MWCNTs) modified carbon paper	Carbon sheet	256% improvement*		Nambiar et al. (2009)
Mixed culture	Single-chamber microbial fuel cell (SCMFC)	Carbon cloth	PANI-graphene modified carbon cloth	Pt/carbon cloth	454	884	Huang et al. (2016)
Mixed culture	DCMFC	Graphite plate	Wet BC-PANI	Graphite plate	1	117	Mashkour et al. (2016)
Mixed culture	DCMFC	Graphite plate	Wet BC-Polypyrrole	Graphite plate	1	136	Mashkour et al. (2017a)
Geobacter sulfurreducens	DCMFC	Carbon sheet	Carbon nanotubes (CNTs) modified carbon sheet	-	200% improvement		Jiang et al. (2018)
Mixed culture	SCMFC	Graphite	Iron carbide nanoparticles-porous graphite	Pt/carbon cloth	997	1856	Hu et al. (2019)
Shewanella loihica PV-4	DCMFC	TiO_2 nano sheet/ carbon cloth	PANI modified TiO_2 nano sheet/ carbon cloth	-	63% improvement		Yin et al. (2019)
Shewanella putrefaciens	Dual-chamber microbial fuel cell (DCMFC)	Carbon felt	Bio-reduced graphene oxide modified carbon felt	Pt sheet	0.015	240	Zhu et al. (2019)
Escherichia coli	DCMFC	Stainless steel (SS)	Poly(3,4-ethylenedioxythiophene) (PEDOT)/graphene/nickel-nanoparticles SS	Graphite	1800	3200	Hernández et al. (2019)
Saccharomyces cerevisiae	SCMFC	Carbon felt	Gold nanoparticle-carbon felt	-	381	2271	Duarte et al. (2019)
Mixed culture	SCMFC	Bacterial cellulose-CNTs (BC-CNT)	Polyaniline (PANI) modified BC-CNT	Activated carbon-SS	20% improvement		Mashkour et al. (2020)
Shewanella xiamenensis	DCMFC	BC-PANI	Titanium dioxide modified BC-PANI	Graphite	137	179	Truong et al. (2021)
S. loihica PV-4	DCMFC	Carbon felt	Iron oxide modified carbon felt	Pt/carbon paper	220	797	Yang et al. (2021)

* Only variations in power density (%) were reported in some studies.

modify a stainless steel (SS) anode with *E.Coli* as anodic bacteria in a DCMFC. The high surface area of graphene and its good conductivity on the one hand and the high redox activity of PEDOT, on the other hand, provided the SS anode with suitable sites for exoelectrogenic activity. Also, NiNPs accelerated the anodic biofilm formation because of their biocompatibility. The generated power density was improved by around twice compared with bare SS anode (Hernández et al., 2019).

Gold NPs (AuNPs) were also used to modify anode electrode in an SCMFC by Duarte et al. (2019). Anodic biofilm activity of *Saccharomyces cerevisiae* on polyethyleneimine-functionalized carbon felt increased after the anode was coated by AuNPs. The modified anode led to an enhanced power density of 2271 mW/m^2 vs. 381 mW/m^2 recorded for the control. The authors performed an in-depth analysis using high-resolution scanning electron microscopy to shed light on the exact role of AuNPs. Anode surface analysis showed a strong interaction between the yeasts` external cellular membranes and the AuNPs but a weak one with the carbon fibers confirming the excellent biocompatibility of the former (Duarte et al., 2019). Moreover, the AuNPs attachment onto *S. cerevisiae* membrane could result in direct electron transfer. In other words, the high conductivity of AuNPs mimicks nanowires' behavior for the yeast biofilm, leading to enhanced activity. Despite the promising results obtained using AuNPs, it should be noted that they are costly materials and that this would limit their real-world application in MFC technology.

Inexpensive nanometals have been used to address the cost challenges associated with applying precious nanometals such as AuNPs. Iron carbide NPs (FeCNPs) were synthesized on carbon felt as an anode in an MFC with mixed-culture bacteria (Hu et al., 2019). Compared with the bare carbon felt, the power density of the modified anode increased by about 200% (Hu et al., 2019). FeCNPs could enrich the exoelectrogenic biofilm of mixed cultures and speed up the redox reaction. Moreover, the FeCNPs provided a much lower R_{ct} than carbon felt. High activity of FeCNPs might also be attributed to the similar nature of microbial heme to Fe, resulting in higher biocompatibility of the FeCNPs to anodic biofilms.

Nanocellulose is a low-cost group of useful materials for bacteria colonization. They can be coated and modified with a vast range of carbon, metal, and polymer-based materials to make this compound conductive for use in MFCs (**Fig. 2**). Mashkour et al. (2016 and 2017a) introduced a new generation of anode electrodes called hydrogel bio-anode. They fabricated porous hydrogel BC-based anodes coated by conductive polymers, i.e., PANI (Mashkour et al., 2016) and polypyrrole (Mashkour et al., 2017a). The capillary effect between the BC nanofibers resulted in permanent access of bacteria to nutrients and prevented bacteria spoilage and clogging of pores (Mashkour et al., 2013). The bio-anode improved the power density of the investigated MFCs significantly compared to the graphite plate (Mashkour et al., 2016 and 2017a). The biocompatibility of both BC and the conductive polymers contributed to a more effective adhesion of the bacteria onto the anode, facilitating electron transfer. Moreover, the bio-anode led to higher redox activity, whose mechanism should be further investigated by future studies. It should be noted that the wet hydrogel electrode (bio-anode) used by Mashkour et al. (2016 and 2017a) possessed low pH values, which could have contributed to the excellent conductivity of the modified BC. However, the authors did not consider the effects of pH variations on the performance of the fabricated electrodes. Given the pH-dependent nature of conductive polymers (Hong and Park, 2005), different results could have been obtained if different pH values had been taken into consideration. This should also be a topic of future investigation.

Overall, for anode modification using nanomaterials, various properties of these compounds, including redox properties, conductivity, surface area, biocompatibility, and cost, should be considered. From an economic perspective, carbon-based nanomaterials, conductive polymers, and inexpensive nanometals could be regarded as excellent choices. It should

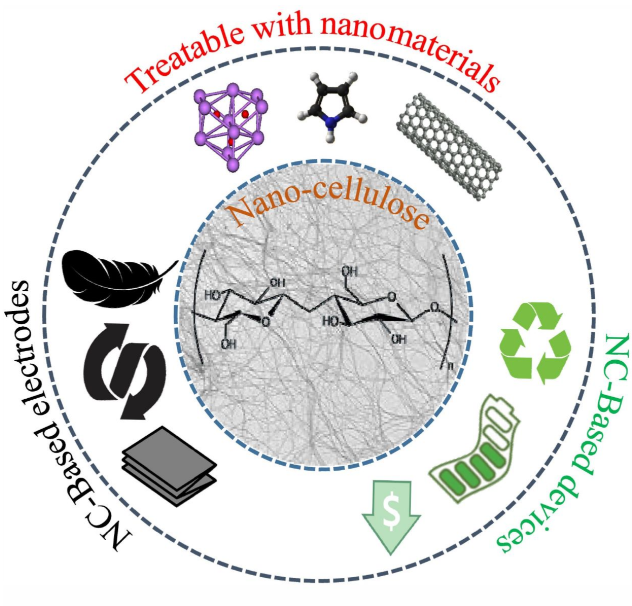

Fig. 2. A brief overview of nanocellulose and its features.

also be noted that the effect of nanomaterials might differ for each species of exoelectrogens as shown by Chen et al. (2020), and should be taken into consideration during experimental designs.

2.1.2. Effect of nanomaterials on electrotrophs and cathode performance

The effect of nanomaterials on electrotrophs' performance is generally similar to what is explained for exoelectrogens. In addition to those, nanomaterials can increase gas adsorption on the cathode side, leading to enhanced electrotrophic performance. This is essential in the electrosynthesis of chemicals in bioelectrochemical systems. Moreover, nanomaterials with photocatalytic properties might also benefit the electrotrophic activity by boosting the reaction taking place over the cathode. **Table 4** presents the results of several case studies investigating the application of nanomaterials in MES systems for producing acetate by different kinds of electrotrophs.

For acetate production from CO_2 in an MES system, Bian et al. (2018) modified the cathode surface with porous hollow fibers of nickel (Ni-PHF) and CNT in the presence of *Sporomusa ovate* (**Fig. 1e**). The porous structure of Ni-PHF could provide *S. ovata* with direct access to CO_2 on the cathode surface. At the same time, the high specific area of CNT could increase CO_2 adsorption by more than eleven times and improved charge transfer by boosting cathodic current density from 214 to 332 mA/m^2 (Bian et al., 2018). In a different study but using the same electrotroph, a reduced graphene oxide sheet was used as a cathode for microbial colonization (Aryal et al., 2017). The authors claimed that acetate production rate and current density were increased by 7 and 8 times, respectively, compared to the carbon paper electrode.

Compared to carbon cloth, the surface area of the cathodic biofilm of *Clostridium ljungdahlii* was expanded by 3.2 folds through incorporating graphene and CNT in a three-dimensional (3D) cathode structure (Han et al., 2019). The modified structure elevated the NADH/NAD$^+$ ratio, and the excess NADH could be used in CO_2 fixation. Consequently, acetate production and cathodic current density increased by 5 and 4.4 times, respectively, compared to the values recorded for carbon cloth (Han et al., 2019). In a more recent study, carbon cloth was modified by GO and electro-polymerized conductive PEDOT to improve the interaction between *Methanobacterium* and CO_2 for a higher acetate production rate (Li et al., 2020). The authors compared three types of modified carbon cloth, i.e., GO, PEDOT, and GO-PEDOT modified carbon cloth, as shown in **Figure 3**. They reported that the biofilm density increased due to the GO's high surface area, and a higher electron transfer rate from cathode to bacteria was obtained through the function of the conductive PEDOT (Li et al., 2020).

Recently, a cathode modified by tungsten oxide (WO_3) and molybdenum oxide (MoO_3) NPs was reported used for a photo-assisted MES system. *Serratia marcescens* was utilized as an electrotroph to produce acetate from HCO_3 (**Fig. 4**). The photocurrent generated by the nanoparticle oxides-modified cathode was about five times higher than that of the bare carbon felt-based cathode. Photo-induced electrons placed on the conduction bands of the modified biocathode improved the hydrogen evolution reaction. The produced hydrogen promoted acetate production by the electrotroph *S. marcescens* (Cai et al., 2020b).

Overall, it could be concluded that the modification of cathode surface in MES systems using nanomaterials, by increasing surface area, could provide electrotrophs (responsible for producing chemicals) with more electrons and more gas molecules such as CO_2. The latter is ascribed to the higher gas adsorbtion rates of the nanomaterial-based modified cathodes. It should be noted that for these advantages to work, the nanomaterials used in cathode modification are bound to be biocompatible so that electrotrophs can grow densely, forming a thick biofilm. Also, the adsorption capacity of

Table 4.
Effects of cathode modifications using nanomaterials on the performance (cathodic current density) of different MES systems with different electrotrphs.

Electrotrophic microorganisms	Device configuration	Anode	Cathode (Control)	Cathode (modified by nanomaterials)	Cathodic current density (mA/m^2)		Reference
					Control	Modified	
Methanol-adapted *Sporomusa ovata*	Dual-chamber microbial electrosynthesis (DCMES)	Graphite stick	Carbon cloth	Reduced graphene oxide-tetraethylenepentamine modified carbon cloth	420	2358	Chen et al. (2016)
S. ovata	DCMES	Graphite stick	Carbon paper	Reduced graphene oxide paper	700% improvement*		Aryal et al. (2017)
S. ovata	DCMES	IrO_2-carbon cloth	Nickel fibers	CNT modified porous nickel hollow fiber	214	332	Bian et al. (2018)
Clostridium ljungdahlii	DCMES	-	Carbon cloth	Graphene–CNTs modified carbon cloth	135	595	Han et al. (2019)
S. ovata	DCMES	Graphite stick	Cooper foam	Reduced graphene oxide modified cooper foam	300% improvement*		Aryal et al. (2019)
Autotrophic microbe	DCMES	Carbon felt	Carbon felt	MnO_2-modified carbon felt	200% improvement*		Anwer et al. (2019)
Serratia marcescens	DCMES	Carbon rod	Carbon felt	WO_3/MoO_3 nanoparticles modified g-C_3N_4 carbon felt	1500	2500	Cai et al. (2020b)
Methanobacterium	DCMES	Carbon felt	Carbon cloth	Graphene oxide-PEDOT modified carbon cloth	840	2540	Li et al. (2020)

* Only variations in cathodic current density (%) were reported in some studies.

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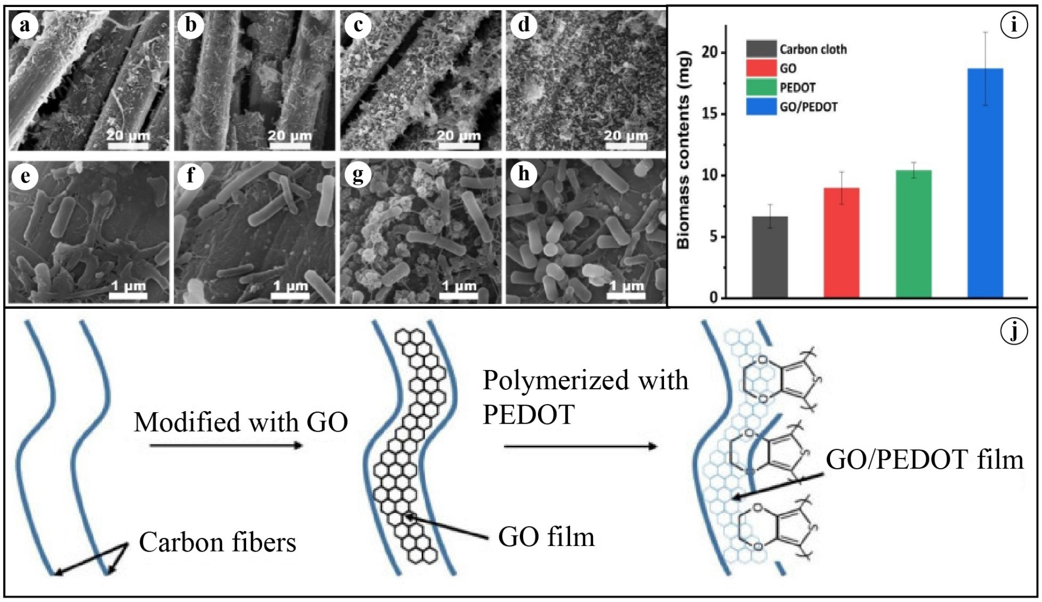

Fig. 3. Comparison of *Methanobacterium* biofilm on **(a and e)** carbon cloth, **(b and f)** GO, **(c and g)** PEDOT, and **(d and h)** GO-PEDOT modified carbon cloth as cathodes. Comparison of biomass contents for the investigated cathodes is presented **(i)**. The synthesis procedure of the GO-PEDOT file is also shown **(J)** (Li et al., 2020). All figures were reproduced with permission from the Royal Society of Chemistry Copyright©2020. License No.: 1112703-1.

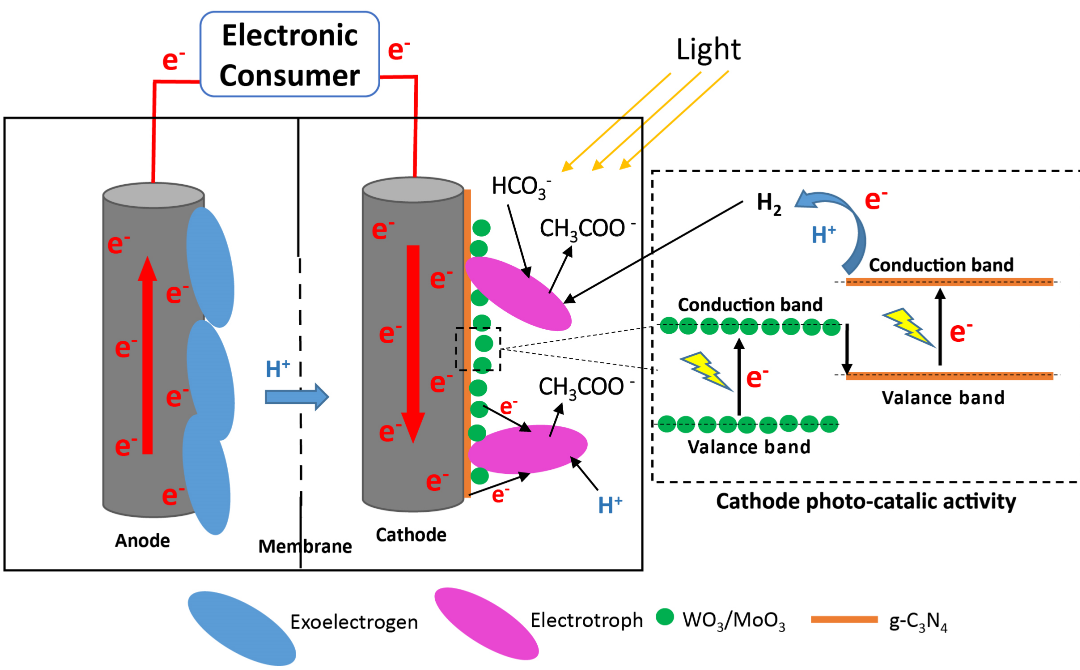

Fig. 4. Effect of cathode modification with WO_3 and MoO_3 nanoparticles (possessing photocatalytic activity) on the system performance, i.e., promoting hydrogen evolution and the consequent increased acetate production by the electrotroph *Serratia marcescens*. Adapted from Cai et al. (2020b).

the utilized nanomaterials is vital in providing electrotrophs with additional gas molecules in reaction sites existing over the biocathode.

In MFC systems, ORR is desired to occur at the highest rates possible, signifying the critical role of catalysts (i.e., catalytic activity). On the other hand, the cost of the catalyst used for catalyzing ORR on the cathode is significantly important to achieve an economically viable system. Pt is a known high-performance catalyst used in various types of fuel cells. However, its use in MFC is limited because of its high cost and bacteria's poisonous effect on the Pt-based catalysts (Mashkour and Rahimnejad, 2015; Xue et al., 2020). Inexpensive nanomaterials are considered excellent choices to achieve the mentioned objective by extending the surface of the cathode (Fig. 5).

Metal oxides nanomaterials are among the promising alternatives to Pt for use as cathode catalysts. Tofighi et al. (2019) coated carbon cloth with a mixture of α-MnO_2-GO and activated carbon and used it as the cathode in a DCMFC. The authors argued that the modified cathode possessed a substantially higher catalytic activity resulting in an increased power

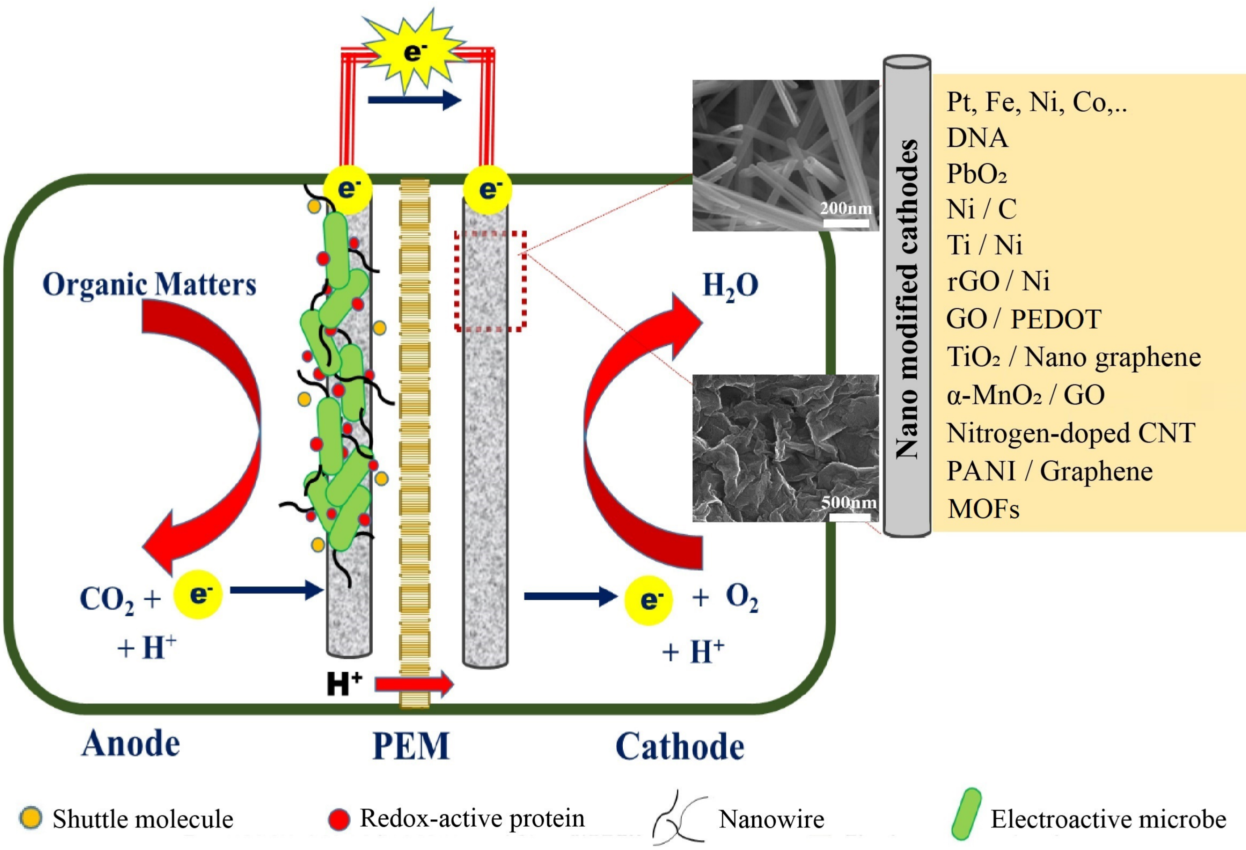

Fig. 5. Application of nanomaterials for modifying MFC cathode surface.

density of 140 μW/cm^2 *vs.* 0.6 μW/m^2 recorded for bare carbon cloth. A PANI/MnO_2 nanocomposite was introduced by Ansari et al. (2016). Both metal oxide nanomaterials and conductive polymers are categorized as pseudo-capacitors. Hence, the nanocomposite showed significant capacitance (525 F/g) and 76.9% cycling stability for 1000 cycles. The maximum power density of 37.6 mW/m^2 was reported, which was considerably higher than the value recorded for carbon paper (approx. 0.003 mW/m^2). TiO_2 NPs were also utilized by Mashkour et al. (2017b) to modify a graphite-based cathode. The higher slope of the linear sweep voltammogram was indicative of the higher catalytic response of the modified cathode. This was reportedly also translated into a higher power density (85 mW/m^2)$_2$ compared to 32 mW/m^2 recorded for the bare graphite (Mashkour et al., 2017b).

In addition to metal oxides nanomaterials, nitrogen-doped carbonous nanostructures have also been used to synthesize high-performance catalysts for cathode modification. The higher ratio of nitrogen to oxygen, obtained by the nitrogen doping process, is an effective ORR rate parameter. He et al. (2016) used nitrogen-doped CNT to modify carbon cloth cathode. The catalytic activity of the new composite electrode in ORR was higher than the Pt-coated carbon cloth. A maximum power density of 542 mW/m^3 was generated by the cathode, which was higher than that of the Pt coated one (approx. 500 mW/m^3) (He et al., 2016). In addition to nitrogen doping, phosphorus doping has also been reported by Liu et al. (2015) who performed a dual-doping procedure by *in-situ* pyrolysis of cellulose in the presence of ammonium phosphate as nitrogen and phosphorus source. They claimed remarkable enhancement in power density compared to the Pt coated cathode (2293 mW/m^2 *vs.* 1680 mW/m^2, respectively) (Liu et al., 2015) Cobalt is another choice for doping. Liu et al. (2016) and Zhong et al. (2021) synthesized cobalt-doped carbon mixtures showing comparable performance in terms of power density with their nitrogen-doped counterparts. Moreover, to develop nitrogen- and cobalt-doped carbonous nanostructures, metal organic frameworks (MOFs) have been used recently. For instance, Zhao et al. (2020) synthesized an ORR nanocatalyst by pyrolyzing a core-shell Co-MOF and adding rGO to the residue. The power density of the MFC equipped with the cathode modified by the MOF-based nanocatalyst increased to 2350 mW/m^2 *vs.* 2002 mW/m^2 measured for Pt (Zhao et al., 2020). In a different study, Zhong et al. (2019) introduced a Zr-based MOF as an excellent template for a nitrogen- and cobalt co-doped naocomposite ORR catalyst. They showed that the MOF-based catalyst could enhance MFC output (power density) to near the value reached by Pt-coated cathode (300 mW/m^2 *vs.* 313 mW/m^2, respectively) (Zhong et al., 2019). **Table 5** tabulates the results of several case studies investigating the application of nanomaterials in cathode modification on the performance (power density) of various MFC systems.

- Application of nanomaterials for mitigating cathode biofouling

Biofilm formation on the air-breathing cathode surface is a challenge in SCMFCs (**Fig. 6a**). The cathodic biofilm formed by anaerobic bacteria decreases the active sites of ORR on the cathode surface. So, hindering bacterial growth on air-cathode might be considered a solution in the long-term operation of MFCs. There are numerous efforts to mitigate the biofouling of air-cathode, including physical method, chemical cleaning, electrokinetic control, and surface modification (Al Lawati et al., 2019; Yang et al., 2019). Surface modification of air-cathodes using nanomaterials can also assist with mitigating this unfavorable phenomenon. Ma et al. (2015) used silver (Ag) and iron oxide (Fe_3O_4) NPs in the carbon composite of the cathode and managed to control biofouling. They argued that the recovered power density after 17 cycles was about 96% of the initial value compared to 60% for the bare cathode. Similarly, Noori et al. (2018) also reported that the incorporation of silver in the catalyst layer of the composite helped recover 95% of the initial power density after 90 cycles. Both studies attributed the achievements made to the antibacterial properties of the silver NPs (AgNPs) (Yang et al., 2016; An et al., 2017).

Table 5.
Effects of cathode modifications using nanomaterials on the performance (power density) of different MFC systems.

Microorganism	Device configuration	Anode	Cathode (Control)	Cathode (modified by nanomaterials)	Power density (mA/m^2)		Reference
					Control	Modified	
Mixed culture	Double chamber microbial fuel cell (DCMFC)	Graphite	Carbon paper	Pt/carbon nanotubes coated carbon paper	2.8	16.3	Mashkour and Rahimnejad (2015)
Escherichia coli	Single chamber microbial fuel cell (SCMFC)	Carbon cloth	Pt-coated carbon paper	Carbon paper coated with Co/Ni and nitrogen co-doped carbonous nanoparticles	2520	4336	Tang et al. (2016)
Mixed culture	SCMFC	Carbon brush	Pt-coated carbon cloth	Reduced graphene oxide (rGO) coated carbon cloth	2021	1683	Valipour et al. (2016)
Mixed culture	DCMFC	Graphite	Graphite paste	Hybrid graphene-modified graphite paste	30	220	Mashkour et al. (2017b)
Mixed culture	SCMFC	Carbon brush	Activated carbon-Carbon black (AC-CB) based	Iron aminoantipyrine-graphene nanosheet modified AC-CB	1030	2030	Kodali et al. (2018)
Mixed culture	SCMFC	Graphite felt	Carbon paper coated with Cu-based metal organic framework (MOF)	Carbon paper coated with pyrolyzed Cu-based MOF	126	326	Zhang et al. (2018c)
Mixed culture	SCMFC	Carbon cloth	Pt-coated carbon cloth	Nickel-nickel oxide-polypyrrol-rGO coated carbon cloth	481	678	Pattanayak et al. (2019)
Mixed culture	SCMFC	Carbon felt	Activated carbon	Pyrolised ZnCo zeolitic imidazolate framework	2252	888	Zhang et al. (2019)
Mixed culture	SCMFC	Carbon cloth	Pt-coated carbon cloth	GO-Zn/CoO coated carbon cloth	744	773	Yang et al. (2019)
Mixed culture	SCMFC	Graphite felt	Stainless steel (SS) based	NiFe layered double hydroxide-Co_3O_4 modified SS	6.25	467	Jiang et al. (2020)
Mixed culture	SCMFC	Carbon felt	Pt-coated carbon felt	Ni-sheathed NiO_x nanoparticle coated carbon felt	489	1630	Choi et al. (2020)
Mixed culture	SCMFC	-	Carbon felt	SnO_2-polyaniline modified carbon felt	200% improvement*		Tiwari et al. (2020)
-	SCMFC	Carbon felt	Pt-coated carbon cloth	Pyrolyzed gC_3N_4-MOF	126	136	Wang et al. (2020)
Mixed culture	SCMFC	Carbon felt	Activated carbon based	Co/Nitrogen-doped carbon-carbon nanotubes modified AC	714	2479	Zhong et al. (2021)

* Only variations in power density (%) were reported in some studies.

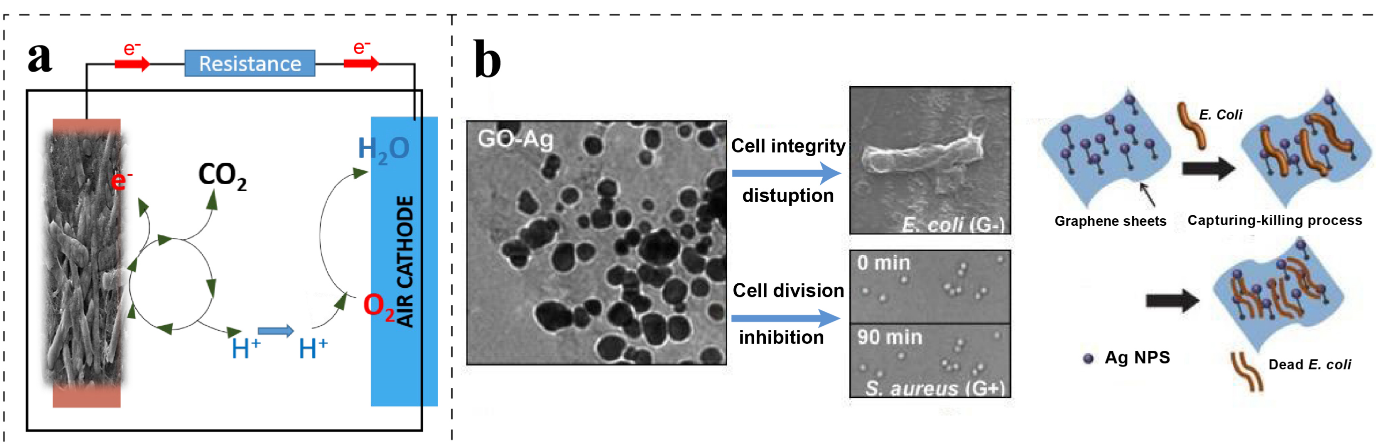

Fig. 6. (**a**) Air-breathing MFC configuration and biofilm formation on the cathode surface and (**b**) antibacterial behavior of AgNPs (Panel **b**: Zhu et al. (2017); reproduced with permission from Royal Society of Chemistry. Copyright©2017. License No. 1113216-1.).

Figure 6b depicts the effect of AgNPs-coated GO on gram-negative and gram-positive bacteria (Zhu et al., 2017). ZnONPs and CoNPs with antimicrobial properties were also applied to fabricate the catalyst layer of air-cathodes (Yang et al., 2019). By decreasing cathode biofouling, less power density drop was recorded after 30 cycles than for Pt catalyst as control.

2.2. Application of nanomaterials in MFC membranes

Membranes are among the main factors affecting the performance of MFCs. Proton exchange membranes (PEMs) transfer protons from the anode to the cathode, prevent substrate leakage from the anode to the cathode, and stops oxygen cross-over between the cathode and the anode (Shabani et al., 2020). In MFCs, typical commercial membranes, including Ultrex and Nafion, are generally used (San-Martín et al., 2019). However, these membranes suffer from several disadvantages, including high prices (e.g., 1500 USD/m^2 for Nafion 115), biofouling, and oxygen and substrate cross-over (Dizge et al., 2019; Palanisamy et al., 2019). The disadvantages of the commercial membranes have motivated the synthesis of diverse materials, particularly in their nano-sized forms, and their incorporation into membrane structures to address the mentioned challenges. **Figure 7** shows the MFC membranes, which could be modified using nanomaterials. **Table 6** tabulates the results of several case studies investigating the application of nanomaterials in membrane modification on the performance (power density) of various MFC systems.

Bazrgar Bajestani and Mousavi (2016) modified a conventional Nafion using TiO_2 NPs. The formation of Ti-OH groups in the TiO_2-based nanocomposite membrane increased the exchange sites over the membrane, leading to higher ion conductivity than Nafion. The nanocomposite could also provide a higher water uptake comparatively (Bazrgar Bajestani and Mousavi, 2016). Sulfonated TiO_2 ($sTiO_2$) NPs were also reported as a modifier for sulfonated polystyrene ethylene butylene polystyrene (SPSEBS). The nanocomposite membrane showed higher proton conductivity, much lower oxygen cross-over, and much lower cost (200 USD/m^2) than commercial Nafion 117 (Ayyaru and Dharmalingam, 2015). Due to the mentioned improved features, power density and coulombic efficiency of the MFC with the $sTiO_2$-SPSEBS membrane increased.

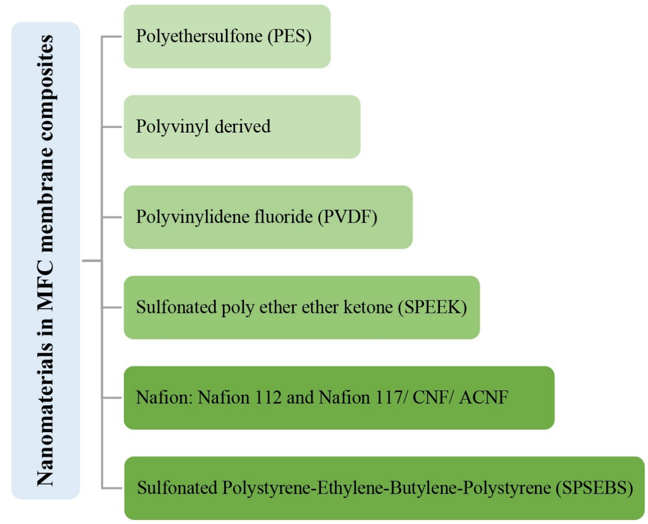

Fig. 7. Various microbial fuel cell (MFC) membranes which could be modified using nanomaterials.

Table 6.
Effects of membrane modifications using nanomaterials on the performance (power density) of different MFC systems.

Device configuration	Anode	Cathode	Microorganism	Membrane (Control)	Membrane (modified by nanomaterials)	Power density (mW/m^2)		Reference
						Control	Modified	
Double chamber microbial fuel cell (DCMFC)	Carbon paper	Pt-coated carbon paper	Mixed culture	Sulfonated polyether ether ketone (SPEEK)	Graphene oxide (GO) modified SPEEK	812	902	Leong et al. (2015)
Single chamber microbial fuel cell (SCMFC)	Carbon cloth	Pt-coated carbon cloth	Mixed culture	SPEEK	SPEEK-SiO_2	680.0	802.0	Sivasankaran and Sangeetha (2015)
SCMFC	Carbon cloth/Carbon vulcan	Pt-coated Carbon cloth/Carbon vulcan	Mixed culture	Quaternized polysulphone (QPSU)	GO modified QPSU	800	1050	Elangovan and Dharmalingam (2016)
DCMFC	Carbon rod	Carbon rod	Mixed culture	Phosphoric acid-treated chitosan	Phosphoric acid-treated chitosan-GO	0.25	3.87	Holder et al. (2017)
DCMFC	Carbon paper	Carbon paper	Mixed culture	Polyethersulfone (PES)	Fe_3O_4 nanoparticles modified PES	0.1	9.6	Di Palma et al. (2018)
DCMFC	Carbon felt	Carbon felt	Mixed culture	poly(-vinylidene fluoride) grafted sodium styrene sulfonate (PVDF-g-PSSA)	Sulphonated GO-SiO_2 modified PVDF-g-PSSA	147	185	Xu et al. (2019)
DCMFC	Carbon paper	Pt-coated carbon paper	Mixed culture	Nafion 117	Ag-GO modified GO-SPEEK	1013	1049	Liew et al. (2020)
SCMFC	Graphite rod	Carbon cloth	Mixed culture	SPEEK	Sulphonated titanium nanotubes modified SPEEK	59	121	Kugarajah and Dharmalingam (2020)
SCMFC	Graphite rod	Carbon cloth	Mixed culture	SPEEK	SPEEK-Ag nanoparticles	60	160	Kugarajah and Dharmalingam (2021)
SCMFC	Carbon brush	-	Mixed culture	No membrane (Carbon cloth-PTFE air-cathode)	Nano-zycosil treated bacterial cellulose-carbon nanotubes	920	1790	Mashkour et al. (2021)

* Polyvinylidene fluoride

Sulfonated poly(ether ether ketone) (SPEEK) is also a typical polymer used to synthesize nanocomposite membranes for MFCs and is a low-cost polymer compared to Nafion. A nanocomposite made by SPEEK and sulfonated SiO_2 has been reported as a PEM for an SCMFC (Sivasankaran and Sangeetha, 2015). The SiO_2-modified membrane had an increased water uptake and proton conductivity compared to the bare SPEEK. Also, as a low-cost membrane, it showed much higher power density than Nafion 115. Moreover, the nanocomposite membrane showed a lower oxygen mass transfer coefficient and reduced substrate leakage. The high performance of the SPEEK nanocomposite was obtained using 7.5% SiO_2 in the polymer matrix (Sivasankaran and Sangeetha, 2015). For improving SPEEK, Shabani et al. (2019) suggested adding GO nanosheets to the SPEEK mixture during synthesis. They claimed that oxygen cross-over of the nanocomposite membrane was about 50% lower than that of Nafion 117 while its conductivity was 25% higher.

Contrary to the favorable results obtained using TiO_2 and SiO_2 NPs in nanocomposite membranes, using Fe_3O_4 NPs in a polyethersulfone (PES) matrix led to lower performance than Nafion, i.e., lower conductivity and higher oxygen cross-over (Di Palma et al., 2018). Moreover, increasing the NPs content in the nanocomposite resulted in reduced water uptake and increased oxygen transfer coefficient owing to the lack of sulfonated NPs and increased void space in the matrix, respectively. Therefore, the adverse effects associated with using nanocomposite membranes in MFCs should also be considered by future studies.

Ceramic membranes are also used in MFCs owing to their low cost. Ahilan et al. (2019) synthesized a polysiloxane-derived ceramic nanocomposite membrane with MWCNTs and GO and compared them with Nafion as control. The maximum power density obtained using the investigated membranes was in the following order: GO-modified membrane > Nafion > MWCNTs-modified membrane. However, the fresh nanomaterial-modified ceramic membranes showed less ion conductivity and higher oxygen cross-over than the Nafion (Ahilan et al., 2019). Nevertheless, it should be emphasized that the ion conductivity of the modified membrane might be sustained throughout time, whereas that of Nafion's is likely to diminish due to biofouling.

In addition to membrane composition, membrane electrode assembly (MEA) is also of great importance for the performance of SCMFCs. Nanocellulosic materials, by providing 3D nanoporous structures (Mashkour et al., 2018), are among the most exciting substrates for fabricating MEAs. In a recent investigation, a BC-based MEA was reported to outperform a carbon cloth-based gas diffusion electrode (GDE) (Mashkour et al., 2021). In this study, one side of the BC was coated with MWCNTs for ORR. In contrast, the other side was coated by the hydrophobic nano-zycosil (NZ) to moderate the highly hydrophilic nature of the BC. This strategy would assist with achieving a favorable proton transfer driven by the hydrophilic nature of the BC and mitigating substrate leakage caused by the hydrophobic nature of NZ (Fig. 8). Interestingly, despite the existing BC membrane resistance, the cell's internal resistance with BC MEA was lower than that of the cell harboring the carbon cloth-based GDE (Mashkour et al., 2021).

This phenomenon could be attributed to the high conductivity of MWCNTs, homogeneous coating, and excellent behavior of NZ as a low-cost hydrophobic agent. Also, oxygen cross-over was lower in the BC MEA than the carbon cloth-based GDE, which could be explained by the barrier properties of nano cellulosic fibers (Aulin et al., 2010).

3. Improved MFC applications through nanomaterial-based modification

The improvements achieved in MFC applications through modifying its different compartments by nanomaterials are presented and discussed in this section. Electricity generation is excluded, as was discussed previously.

3.1. Wastewater treatment

MFC, as a biological wastewater treatment system, has a high theoretical energy conversion rate and produces less sludge than other treatment technologies. The elimination of various types of compounds, including heavy metals (Cr (VI), Cu (II), Zn (II)), azo dyes, and nutrients, has been reported by MFC technology (Feng et al., 2017). MFCs can also eliminate nitrogen and phosphorous-based compounds in their biocathode chambers. **Figure 9** depicts the application of MFCs for the elimination of various sources of pollution. Despite the beneficial characteristics of MFCs, they need to be enhanced (in terms of power output and wastewater treatment capacity) to outcompete the traditional wastewater treatment procedures (Ci et al., 2017; Salar-García and Ortiz-Martínez, 2019). Applying efficient advanced materials such as nanomaterials is widely regarded as a strategy to achieve this objective (Kim et al., 2016; Feng et al., 2017; Salar-García and Ortiz-Martínez, 2019).

Nanomaterials have multiple functions, including enhancing the separator's selectivity, improving catalyst activity, decreasing oxygen cross-over, improving the growth of anodic biofilm (Munoz-Cupa et al., 2020). It should be highlighted that anodic biofilm activity in MFCs is critical for chemical oxygen demand (COD) removal. Using a high-

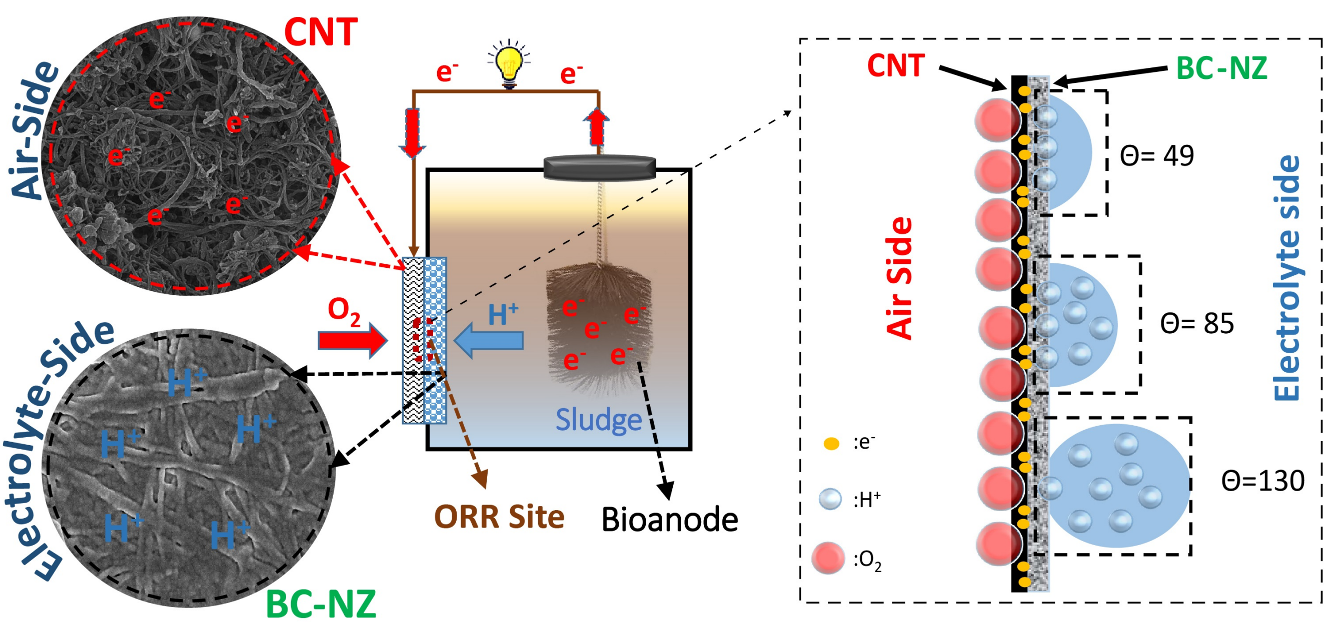

Fig. 8. (a) Membrane electrode assembly (MEA) fabricated by bacterial nanocellulose, nano-zycosil, and MWCNTs and (b) the effect of water contact angle of the MEA on oxygen reduction reaction (ORR) (Mashkour et al., 2021). With permission from Elsevier. Copyright©2021. License No.: 5052280823847.

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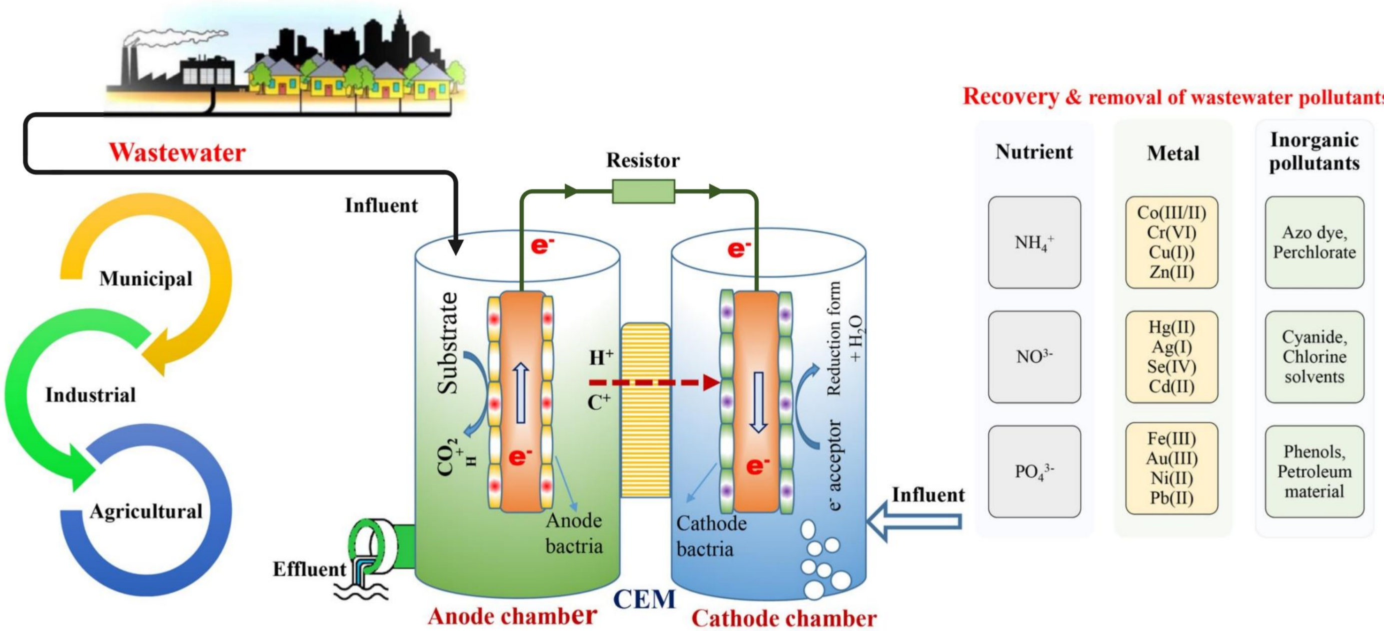

Fig. 9. Potential applications of microbial fuel cells (MFCs) for eliminating various sources of pollution and power generation.

performance membrane modified by nanomaterials could offer a low oxygen cross-over, providing a stable anaerobic condition for microbial activity. High surface area and high prosity of nanomaterial-based electrodes can accelerate the adsorption process of toxic compounds and increase bacterial colonization, resulting in higher treatment rates. Cathode modifications using nanomaterials could lead to higher surface areas and redox activities. Such an enhanced cathode could assist with controlling neutral conditions in the anode chamber by reducing proton accumulation in the analyte.

3.2. Self-powered nanobiosensing

One of the essential applications of MFCs is detecting the quality of wastewater as self-powered biosensors. The high sensitivity of microbes to a different spectrum of analytes makes MFCs capable of being used as high-performance biosensors. MFCs can be utilized as biological oxygen demand (BOD), dissolved oxygen, volatile fatty acid, organic carbon, toxicity, and microbial activity measurement device (Ivars-Barceló et al., 2018; Cui et al., 2019). A noticeable feature of MFC-based biosensors is that no transducers are required for reading and converting the signal. However, their applications have been limited by low sensitivity, low stability, long response time, and irreproducibility (Chen et al., 2019; Do et al., 2020). Electrode improvements might be a valuable and essential solution for enhancing the performance of MFC-based biosensors. In recent years, the detection resolution of MFC biosensors has increased using nanomaterials in electrode surface modifications. A considerable range of nanomaterials, including carbon NPs, AuNPs, PEDOT:PSS conductive polymer, and $CoMn_2O_4$ NPs, have been utilized in enhancing MFC-based biosensors, as tabulated in **Table 7**.

To better understand nanomaterials' effect on the performance of MFC-based nanobiosensors, it is vital to know the sensing mechanism. For example, for toxicity determination, the anode is the active point of the MFC sensor, while for detecting H_2O_2, the cathode is the active point. Also, having a higher voltage and current range in MFCs may lead to the system's higher sensitivity. Therefore , nanomaterials , through boosting the

Table 7.
Use of nanomaterials for fabricating MFC-based nanobiosensors.

Analyte	Device configuration	Anode	Nanomaterial-modified Cathode	Reported features	Reference
DNA	DCMFC	Graphite plate	AuNPs/graphite	Range of detection: 0.0–0.1 mM Limit of detection: 3.1 nM LOD	Asghary et al. (2016)
BOD	SCMFC	Carbon cloth	Carbon cloth with MnO_2 NPs and CNTs	Range of detection: 50–100 mg/L Stability: 1.5 yr	Kharkwal et al. (2017)
Levofloxacin	SCMFC	Microbial	$FePO_4$ nanoparticles	Range of detection: 0.1–100 µg/L Limit of detection: 0.1 µg/L	Zeng et al. (2017)
H_2O_2	DCMFC	Microorganism	$CoMn_2O_4$/graphite	Range of detection: 1–1000 mM Limit of detection: 40.2 µM	Liu et al. (2018)
Formaldehyde	Screen printed MFC	Carbon nanofiber modified α-cellulose paper	Carbon nanofiber modified α-cellulose paper	Detecting the analyte at 0.1% concentration only	Chouler et al. (2018)
Formaldehyde	Dry DCMFC	Cellulose-PEDOT:PSS	Cellulose-Ag_2O PEDOT:PSS	Range of detection: 0.001%–0.2%	Cho et al. (2019)
BOD	SCMFC	Graphite rode	Carbon paper with carbon nanoparticles	Range of detection: 32–1280 mg/L	Do et al. (2020)
BOD	micro-DCMFC	CNT-treated carbon cloth	-	Range of detection: 0.1-0.7 g/L	Xiao et al. (2020)

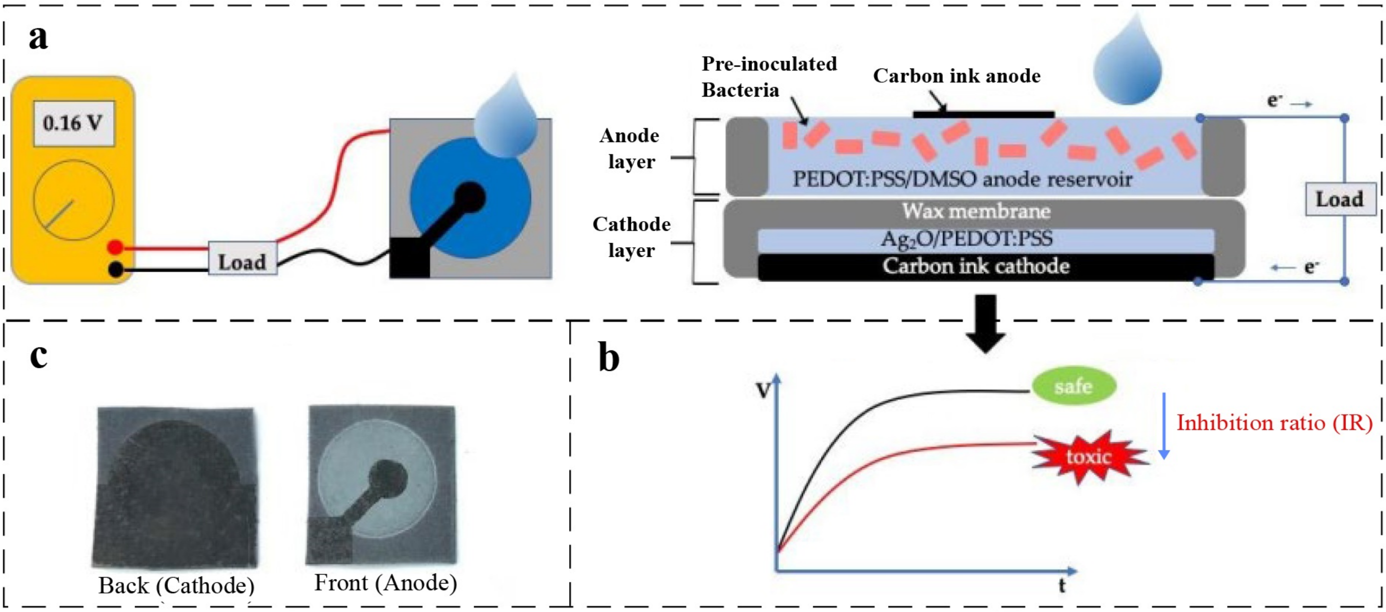

Fig. 10. Nanocomposite electrodes developed and used in a cellulose-based MFC nanobiosensor, **(a)** the cellulose-based MFC nanobiosensor, **(b)** cross-section and working principle, and **(c)** image of the front and back sides of the MFC nanobionsensor (Cho et al., 2019). Reproduced with permission from MDPI.

performance of different MFC compartments could result in increased biosensing performance.

Among various nanomaterials used in MFC modifications, cellulosic nanomaterials and their application in fabricating cellulose-based electrodes have attracted a great deal of attention. This is ascribed to the fact that these modified electrodes can decrease the costs of MFC-based nanobiosensors. A paper-based water quality biosensor based on MFC's anodic activity was recently introduced for detecting formaldehyde in water (Cho et al., 2019). As shown in **Figure 10**, in the developed system, two layers of PEDOT:PSS modified paper were used as anode and cathode. PEDOT:PSS nano-coating made the surface of the cellulose-based anode more biocompatible, facilitating bacterial colonization. Moreover, the modified anode could absorb water more quickly, further enhancing microbial growth. Nano-coated electrodes were also more conductive, decreasing the time needed for the MFC to reach a stable voltage for starting the detection process (Cho et al., 2019).

4. Concluding remarks and future research directions

Nanotechnology offers extensive possibilities for MFC improvements. In this review, the applications of nanomaterials in different MFC compartments were reviewed and discussed in detail. The following main conclusions could be drawn from the reviewed literature:

- High-surface-area/biocompatible nanomaterials are instrumentals in developing thick biofilms on electrodes' surface.
- Conductive NPs act as bridges between the biofilm and electrode surface and decrease electron transfer resistance. However, more investigation on the effect of nanoparticle morphology on electron transfer is still needed.
- Toxicity of CNTs to microbial biofilms would depend on CNTs' concentration. Also, the adverse effects associated with electrode modifications using CNTs could be moderated by adding biocompatible nanomaterials such as PANI.
- Nanoporous materials increase cathodic gas adsorption, leading to increased microbial electrosynthesis of chemicals.
- Metal oxide- and MOF-based nanocomposites can efficiently catalyze the ORR and are considered inexpensive alternatives to Pt. They are also higher more stable in microbial environments.
- Nitrogen- and metal-doping can extend ORR active sites of carbonous nanomaterials.
- Inexpensive and high-performance alternatives to conventional PEMs could be obtained by modifying polymeric membranes with hydrophilic and antimicrobial NPs. The modified membranes are also less prone to biofouling.
- High-performance electrodes and membranes can be achieved by modifyng BC with nanomaterials.

Nanomaterials have vastly improved MFC applications in wastewater treatment and biosensing. However, for a stable and reproducible response, MFCs should still be further improved. The unknown environmental impacts of nanomaterials used in MFC modification, caused by their release into soil and water, are considered a significant challenge to the overall sustainability of the whole technology. Hence, future research efforts should also take into account the human and environmental safety features of nanomaterial-modified MFCs.

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