Current Natural Sciences & Engineering
Volume 2, Issue 2, 2025, 591-627

Role of Carbonaceous Nanomaterials in Deciding Efficiency of Bio-Electrochemical Systems (BES)

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Received date:05/04/2025, Acceptance date: 24/04/2025

***DOI:* http://doi.org/10.63015/1re-2458.2.2**

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Abstract

Bioelectrochemical systems (BES) utilize microbes for energy generation, which means microbes that are known to be harmful can still be non-harmful for their capability to produce alternate energy sources, thus giving dual benefits: waste reduction with simultaneous energy generation. However, the performance of these systems depends on the electrode material, which controls the electrode's extracellular electron transfer and electron retrieval mechanism. Different materials have been tested as electrode materials to maximize energy efficiency. Recently, carbon-based nanomaterials like graphene sheets, carbon nano-tubes/wires, and quantum dots have been employed successfully as cathode and anode electrodes. These nanomaterials are environment-friendly, non-toxic, and have high physical/chemical stability. This review is an attempt to provide a comprehensive summary of different carbon-based nanomaterials used as electrode modifier materials for BES systems covering the dimensionality of the functional materials (0-D, 1-D, and 2-D), synthesis of materials, carbon composite materials, and (iv) their application in microbial/bio photovoltaic fuel cells (electro/photocatalysis). This review article will also discuss various electrode materials generally used in BESs. There is a surge in the use of carbon-based materials and the opting for low-cost optimised electrodes over expensive, efficient ones. After that, a discussion will be made on the researched nanomaterial approach, their use as advanced working electrode material, with respect to their dimensionality, and the reported power generated by incorporating these materials as electrodes. Then, a detailed discussion will be made on the composite structures that have been reported as more efficient electrode materials than conventional and metal-based electrodes. The coming section briefly explains the design and working principle of MFCs.

Keywords: *Bioelectrochemical systems, Microbial fuel cell, Bio photovoltaics, Nanomaterials, Waste reduction.*

1. **Introduction:** In the past few decades, the human population has increased at an exponential rate. According to the Population Census 2023, the human population has nearly tripled since the 1950s and is expected to increase to around 9.8 billion by 2050 [1]. This population burst is mainly due to the breakthrough advancements in healthcare and industrial sectors that have led to the significant development of the world economy. This exponential growth in the human population and world economy has also resulted in a proportional increase in the demand for energy. Therefore, the energy demand is expected to increase to almost double by 2050 to compensate for the increase in human population and economy development [2, 3] . Hence explosive growth in human population necessitates a greater demand for food, water and energy.

Currently, the majority of the energy demand is fulfilled using conventional energy sources like coal-based electric power plants. However, the power generated by conventional sources is not green and is associated with the production of large amounts of pollution([4]. For example, the burning of coal and natural gas to generate electricity has resulted in major negative impacts on Earth's ecosystems like global warming [5]. So, the use of conventional energy sources cannot be sustained for in the long term. Accordingly, the need to replace conventional sources with more sustainable and green energy alternatives is of prime importance. Various technologies have been studied in depth for sustainable energy production and waste remediation, like the use of activated sludge process [6], biogas cultivation [7], biofuel production [8], chemical reforming of waste [9], and bioelectrochemical systems [10].

Out of these sustainable technologies, the bioelectrochemical system (BES) is one of the most popular and most researched technology. It is an interesting and self-powered water energy nexus technology because it involves microbial decomposition of organic matter to simultaneously generate electricity [11]. M.C. Potter was the first researcher to report electricity generation using bacteria and laid the foundation of BES [12]. His pioneering work started a research trend, and other researchers also adapted the basic schematic, i.e. microbial respiration for energy production and subsequent scale-up operations [13].

Currently, the BES technology has been implemented at various waste treatment plants on a pilot scale and transforming such plants to attain a self-sufficient state [14]. Owing to such success, several other countries are also implementing BES technologies to produce self-sufficient waste treatment plants, a major step towards sustainable living [15].

BES technology can be categorised into various types depending on their function and the type of microorganism utilized. BES includes Microbial Fuel cells (MFCs) [16-18], Bio photovoltaic cells (BPVs) [19-21], Microbial Electrolysis cells (MECs) [22-24], Microbial Desalination cells (MDCs) [25-27] and many more. Microbial Fuel Cell (MFC) and Bio photovoltaic cells (BPV) are the significant forms of BES and have a variety of practical applications, such as decomposable waste reduction [28], electricity generation [29], wastewater treatment [30], biosensor applications [31], etc. The characteristic feature of MFCs is the presence of special electrogenic microbial species that oxidize the decomposable organic matter and also release electrons as a byproduct [32]. On the other hand, BPVs utilize solar energy and photosynthetic microorganisms for electrical energy production [15]. The basic working principle of BPCs is that the oxygenic photosynthetic microorganism can harvest the incoming solar energy for electricity generation. Both work on the principle of redox reaction [33] and is similar to that of conventional Fuel cells. However, the significant difference between these energy conversion devices is the use of microorganisms for energy generation in MFC in place of chemical reagents, as in the case of fuel cells [34].

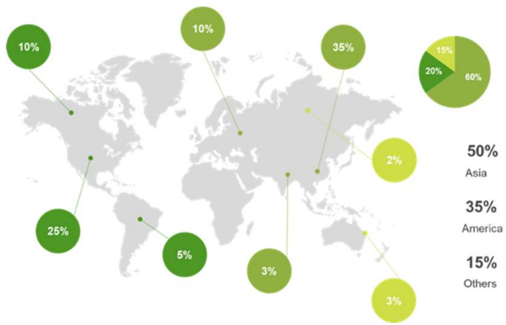

Figure 1: Contribution of different countries in the research progress for BES technology.

Recently, different types of BES have seen tremendous research growth, especially since the discovery of special electrogenic microorganisms that are discussed in later sections [32]. Fig. 1 & 2 summarise the bibliographic trends worldwide from 2004 to 2024 (data retrieved from Web of Science algorithm). The bibliometric trend was evaluated based on the search results for "Bioelectrochemical systems," "carbon nanomaterials in BES," "carbon nanomaterials in MFCs," and lastly, "Carbon nanomaterials in Biophotovoltaic systems." The results in the bar graph suggest the rising trend in this water-nexus technology for renewable energy production (BPVs) or, bioremediation (MESs) or both (MFCs). The figures depict the rise of research in the BES domain, with around 1500+ research papers published in the past four years alone. This analysis was crucial in providing insight into the growth of the technology in terms of research advancements [35]. Figure 2b shows the development of research in various countries, including China, the United States of America (USA), and India, which are leading the research in BES. Bibliometric assessment benefits the readers and researchers by providing them with the current and developing research issues [36, 37]. The databases will surely proliferate with passing time and trends will differ from their past counterparts, but the domain of BES will foster the change.

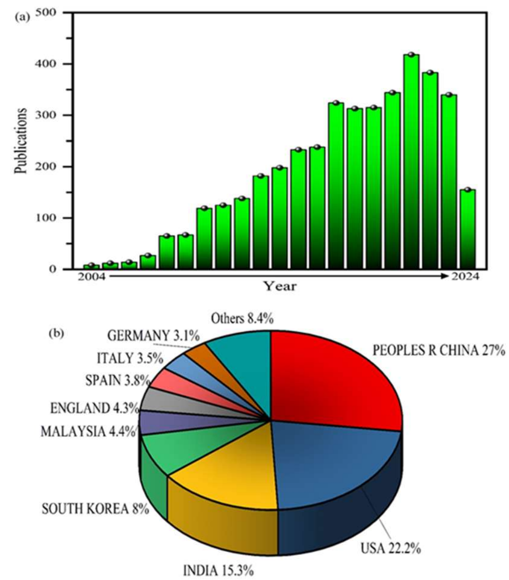

Figure 2: Publication trends among different attributes, (a)year-wise number of publications in the research area of BESs, and (b) publication trends among countries and their output for the same.

2. Microbial fuel cell: Design and working principle

Microbial Fuel Cell (MFC) is the most popular type of BES, mainly due to its simple setup and mild operating condition. For MFCs functioning, the electroactive microorganisms oxidize the organic matter in the analyte solution and produce protons, electrons, and carbon dioxide as by-products [38]. The protons produced in the anodic chamber migrate towards the negatively charged cathode through a selectively permeable membrane and undergo reduction, while the electrons flow through an external circuit to the cathode, producing electricity [39]. Electrons and protons combine to produce water molecules by reducing oxygen in the cathodic chamber [40]. This functioning takes place in MFC setup consisting of the following elements: (i) Anode and Cathode chamber where reactions take place, (ii) Proton exchange membrane for movement of ions across the chambers, (iii) Microbial culture and electron transfer mediator for easy transfer of electrons from microbes to electrodes, (iv) Energy source for microbial growth, (v) Electrodes (made of conductive material for easy electron capturing and circuit formation), (vi) External reader circuit for reading output values from MFC [41].

Based on the chamber configurations, MFCs can be of two types: (1) Single-chambered MFCs (SCMFCs) or (2) Dual-chambered MFCs (DCMFCs) [42]. The main difference between DCMFC and SCMFC is the presence of a separate chamber for the cathode compartment [43]. SCMFC uses O_2 in the air as a reducing agent and, thus, doesn't require a separate chamber for the oxidation process [44]. This grants SCMFC the ability to scale quickly, use in batch and continuous mode, and utilise less material for fabrication, thus providing a low-cost option for technology implementation [45]. The DC–MFC comprises two chambers, i.e. anode chamber and a cathode chamber, which are separated by an ion exchange membrane. The oxidation and reduction process occurs separately in the anode and cathode chambers, respectively [44], and a short incubation time is required for energy generation [43]. It has been found that the performance of the MFC is highly dependent on the anodic oxidation by microbes and the efficient transfer of protons from the anodic to the cathodic chamber [46]. This grants DCMFC the ability to have a short reaction time for energy generation, increased sensitivity towards electrolytes, and temperature/pH change [47-50]. Fig. 3 showcases both single-chambered and double-chambered MFC fed with wastewater as a substrate source [51].

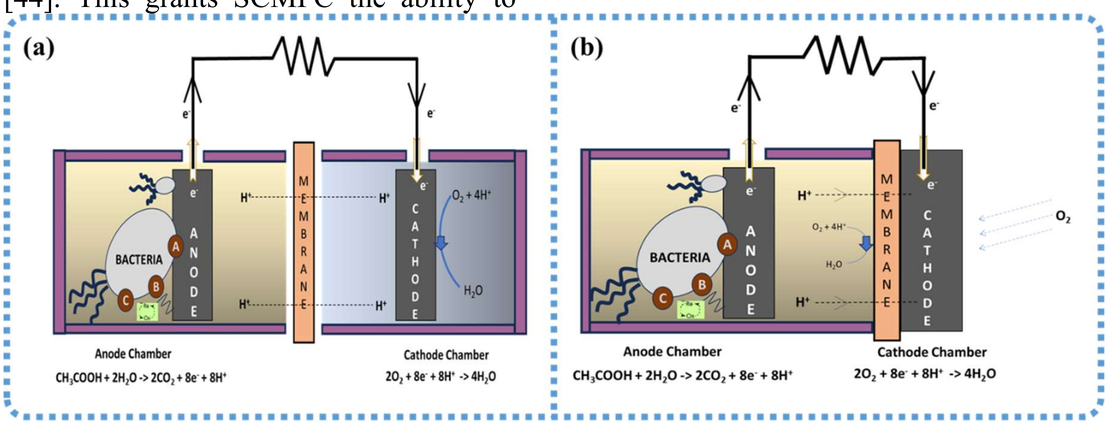

Figure 3: Schematic diagram of (a) Dual-chambered MFC and (b) Single-chambered MFC (A, B, and C refer to the electron transfer: direct (A) and indirect (B & C))

The proton exchange membrane (PEM) (or a salt bridge) aids in the transfer of ions by incorporating electro-osmotic drag between the two chambers [52, 53]. The primary purpose of using a selective proton exchange membrane is to allow the flow of only protons from the anodic to the cathodic chamber to maintain electrical neutrality and a barrier between both chambers [54]. It only enables the transfer of H+ and prevents the movement of anions and crossover of any gaseous molecules, especially O_2, from the cathodic to the anodic chambers [55]. Oxygen diffusion from cathode to anode leads to lower efficiency as the electrons reduce the O_2 molecule more readily than the anode material [56]. Hence, the membrane should not allow oxygen diffusion and flow of ionic species, which hinders cell growth or proliferation rate [57]. The membrane that allows for the highly selective and efficient transfer of the selected molecules while preventing the transfer of unwanted molecules is highly preferred as it reduces resistive losses, thereby increasing the overall efficiency of MFCs [58]. The thickness of the membranes also has a significant effect on the performance of MFCs [59].

Usually, MFCs with thinner membranes possess less internal resistance as they offer higher permeability to electroactive species compared to thicker membranes[58]. Electroactive microorganisms can also form a thin layer on the anode side of the membrane due to biofouling that restricts the movement of protons and ultimately chokes them [53, 59]. The most commonly used membrane is Nafion from DuPont [60] due to its excellent proton conductivity and antifouling capacity [61]. It comprises a conductive sulfonated Polytetrafluoroethylene backbone with strong C-F bonds [62]. This backbone confers excellent chemical and mechanical stability [62]. The terminal sulphonation of the backbone imparts a negative charge and allows for selective preconcentration of positively charged particles via electrostatic interactions [63]. The backbone also has an amphiphilic nature with hydrophilic –SO3H and hydrophobic perfluoroalkyl backbone [57].

Along with all these positive roles of PEMs, a major disadvantage is also associated with incorporating PEM in MFC. The expensive nature of PEMs like Nafion has restricted their application, and as a result, cheaper but less efficient alternatives like salt bridges are preferred over PEMS to limit the cost of the device [53, 59, 64]. Other than that, the researchers are also trying to develop a more efficient membrane with enhanced proton conductivity and ion exchange capacity [65]. Modifying membranes using nanoparticles is one of the simplest and most effective ways to enhance the desired properties of the membrane [39]. Use of non-fluorinated polymeric membrane materials such as sulfonated silicon dioxide (S-SiO2) in sulfonated polystyrene ethylene butylene polystyrene (SSEBS), sulfonated polyether ether ketone (SPEEK) and graphene oxide sulfonated polyether ether ketone (GO/SPEEK) membranes showed promising results and proved to be an alternative material to Nafion 117 [66-70].

Microbes reside in the anodic chamber, breaking down the organic compounds to produce energy [71]. Though a wide variety of microorganisms can be employed for energy generation in MFCs, the energy yield can further be enhanced using mixed microbial cultures (co-cultures) or special recombinant microbial strains [72]. As MFC finds its use as a bioremediatory, sludge and wastewater can be used in the anodic chamber as substrate and microbial sources [73].

The power output and efficiency of the MFCs are heavily impacted by the organic substrates available for microorganisms. Spent waste materials, including dye wastewater, activated sludge, landfill leachates, brewery wastewater, and industrial effluents, have been successfully used as substrates for MFCs. This thereby shows the potential of MFCs as a versatile bioremediation energy conversion device [41, 71, 74]. The organic waste has all the dietary components a microbe would need to respire and produce energy [74]. It also contains a consortium of species with different growth requirements, resulting in various energy production rates.

While MFCs are widely used and have been the subject of much research in the field of green energy conversion devices, other similar devices, such as bio-photovoltaic (BPV) cells, Bioelectrolysis cells, etc., are also being thoroughly studied and investigated for potential commercial use. The next section dives into the introduction of BPVs.

2.1 Bio-photovoltaic systems: another form of BES

BPVs are a type of energy-harvesting BES and are also known as photo-microbial cells or microbial solar cells [75]. Due to their simple nature, they are gaining a lot of research interest. The general structure and mechanism of processes in BPV can be illustrated in Fig 4. BPVs involve the use of oxygenic photosynthetic microorganisms (mainly cyanobacteria and algae) to convert solar energy to electrical energy. Although both MFCs and BPVs utilize microorganisms as biocatalysts to produce electrical energy, however, the major difference between them is the nature of microorganisms and the requirement of organic matter as substrate. BPVs use oxygenic photosynthetic microorganisms to generate electricity using solar energy and do not require any additional substrate like organic matter and use water as an electron source, whereas MFCs use anoxic heterotrophic microorganisms to generate electricity and use organic matter as an electron source.

Similar to MFCs, BPVs can be categorized into single-chamber and dual-chamber based on the device configuration and similarly have an anode chamber where electrodes are generated by the photosynthetic microorganisms under sunlight and a cathode chamber where the selectively transferred H^+ are oxidized to form water. Microbes in this system are usually made to grow on the electrode surface in layers, and the microbe's exoelectrogenic property may depend on the growth conditions provided [76]. The larger surface area of the electrode supports microbial growth and biofilm formation. Many microbial species have been employed for BPV systems. For instance, Bombelli et al. employed *Pseudanabaena limenetica* biofilms for energy generation and compared various electrode substrate materials (Indium Tin Oxide(ITO), Stainless Steel(ss), carbon paper, etc.) [77].

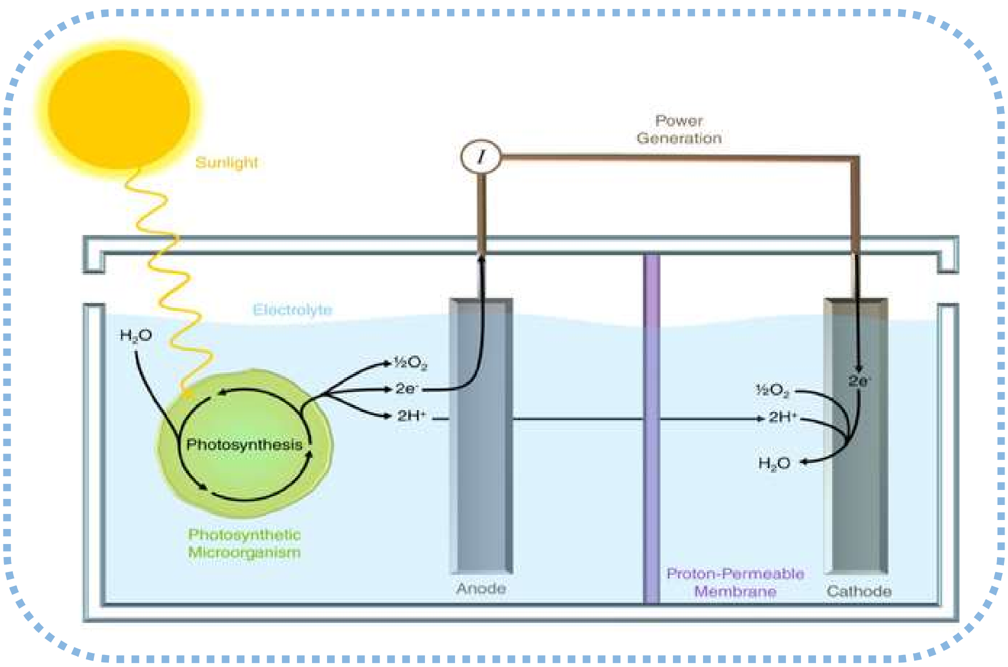

Figure 4: Basic diagram of BioPhotovoltaic (BPV) fuel cell depicting the flow of ions and basic mechanisms that govern microbial respiration and electron generation. (Adapted from [78]

Energy production in BPV systems again depends on the photosynthetic microbe's electron transfer and extracellular electron transfer (EET) rate, which can be affected by the electrode material [79]. Indium tin oxide (ITO) is one of the most commonly used base materials for the electrode, due to its excellent biocompatibility [80]. The properties of these electrodes can be further enhanced by further functionalisations or modifications like nanomaterial coatings, etc. Graphene oxides and graphene quantum dots have been extensively studied and utilized as a coating for bare ITO surfaces due to their excellent photo-catalytic ability and highly conductive nature [81]. The following section discusses the native EET mechanisms of microbes and the harnessing of this mechanism for energy production.

3. Native EET mechanisms of microbial species

As mentioned above, the efficiency and performance of BES systems are highly dependent on the electrode materials and microbial species. Optimal growth conditions are highly dependent on the microorganism and vary from species to species [56]. The microbial species that have the ability to release electrons in the surrounding environment while oxidizing the organic substrate are termed electricigens and are highly sought after for their application in microbial fuel cells [82]. Electricigens are classified as alpha, beta, gamma, and delta proteobacteria in this phylum [38]. Various electricigens and their combinations have been used in MFCs, resulting in higher outputs than non-electricigenic microorganisms [54]. Proteobacteria is a vast class of electricigens (the largest in bacterial species) with strains that are dominantly used in MFC production [83]. Two halophiles were tested at the anode of MFC. The maximum power and current densities reached 11.87/4.57 μW/cm^2 and 49.67/22.03 μA/cm^2, respectively. In the case of *H.volacni*, the power density and current density were further enhanced using electron mediator–neutral red [84]. Several members of this phylum showed electrochemical activity. *Geothrixfermentans*, when used in MFC, reached a peak current of 0.6 mA and achieved 97 % electron recovery [85]. The microbial fuel cell systems based on the phylum cyanobacteria were called photosynthetic MFCs (PMFCs). A double-chambered Photosynthetic-MFC was built using model cyanobacteria *Synechocystis* PCC-6803 in an anode chamber. The energy production rate of the mentioned PMFC reached stability, with the maximum power density reaching 72.3 mW/m^2 [86]. Researchers have also tested *Saccharomyces cerevisiae* for electricity generation [12]. The maximum current density and power density were achieved using yeast extract as an electron mediator in double-chambered MFC, which attained 300 mA/cm^2 and 70 mW/cm^2 of current and power densities, respectively [87].

The exoelectrogenic species have also evolved to facilitate EET to the anode. The extracellular electron transfer mechanism to the anode can be categorized into three different classes: (i) direct electron transfer, (ii) electron transfer through mediators, and (iii) electron transfer through nanowires [67]. Most of the EET mechanisms found in microbes can be categorized as direct electron transfer or mediated electron transfer [83]. This mechanism can be performed either via surface-exposed c-type cytochromes (direct EET) or nanowires/mediators (mediated EET) [38]. A well-characterized system for direct extracellular electron transfer (EET) by a multi-heme, c-type cytochrome is the metal-reducing (Mtr) pathway that occurs in *Shewanella oneidensis [88]*. This pathway requires specific proteins like CymA, FccA, STC, MtrCAB complex, and OmcA to extract free electrons from the electron pool in the cytoplasmic membrane [89]. The MtrCAB complex is the protein responsible for connecting the periplasm with the outer surface of *Shewanella oneidensis* for easy transfer of electrons [90]. It comprises the outer β-barrel membrane protein, MtrB, and the decaheme cytochromes, MtrA and MtrC. MtrA and MtrC proteins are believed to be connected from the inside pores formed by MtrB from the extracellular and periplasmic sides, respectively [91].

Certain microorganisms like *Geobacter sulfurreducens* develop thread-like structures with lengths up to 20 µm extending from the plasma membrane. These fine threads are termed as "nanowires" and are highly conductive and facilitate the transfer of electrons from the microbe to the electrode [92]. Nanowires are also capable of inter/intra-cellular electron transfer; for instance, nanowires were shown to penetrate aggregates of *Geobacter sulfurreducens* and *Geobacter metallireducens* to facilitate electron transfer [93]. The nanowire composition and mechanism of electrical conductivity have been extensively studied for the model organism of *Geobacter sulfurreducens*. Observations suggested that nanowires were mostly type IV pili with PilA protein as a major component [94]. To back up this suggestion, studies showed that the strains that lack PilA or contain mutant PilA will show poor conductivity, which led to the postulation that electron transfer occurred due to the presence of a chain of aromatic residues in PilA [94, 95].

In the above sections, we have briefly discussed the design and working of BES, the significance of proton exchange membrane and salt bridge, biophotovoltaic cells and most importantly, the driving force of BES, i.e. microorganisms. However, the efficiency and performance of BES is also heavily affected by the electrode material and their design. Hence, in the coming section, we will elaborate on the various materials used as electrodes in BES and their properties. We will also focus on the conventionally used electrode materials and the development of the advanced carbon-based electrode materials including carbon nanodots, carbon nanotubes. A brief theoretical discussion is also provided for the preparation and synthesis of said materials, highlighting the advantages and disadvantages of the processes concerning the material obtained for application. The next section provides a brief introduction to electrode materials and their properties and converges to the application of carbon-based materials in electrode preparation and functionalisation.

4. Electrode materials for BES application

The electrodes are the most significant component of the BES and play a major role in determining the overall efficiency and output of the cell. Hence, it becomes of utmost importance to choose the appropriate electrode material. Electrode materials are selected based on specific features that promote EET and microbial growth [79]. Some of these features include (i) biocompatibility [96], (ii) large surface area [97] and porosity [98], (iii) high electrical conductivity [99], (iv) stability and durability [100], and (v) electrode cost and availability [101]. Excellent biocompatible electrode material enhances the adherence of the electro-active microorganisms and biofilm formation, thereby enhancing the system's energy output [66]. The surface area and porosity of electrode materials significantly determine the biofilm formation [75]. The increased porosity allows for better microbial adhesion by providing a large, accessible active area, decreasing the ohmic losses [102]. Theoretically, the maximum open circuit voltage (OCV) of MFC cannot increase beyond 1.1V, mainly due to the thermodynamic limit generated by the difference in the redox potential associated with the oxidation of organic matter and redox potential associated with the reduction of oxygen [103-105]. An alternative solution to increase the OCV involves using multiple MFC arrangements (cascading MFCs). Excellent electrical conductivity of electrodes ensures sufficient and continuous operation of the MFC system [80]. As oxidation reactions occur inside the anode chamber, hence, the functioning electrode materials should be able to show extraordinary physiochemical stability to avoid unwanted corrosion/decomposition [106]. Furthermore, the electrode material should be highly resistant and possess hydrophilic elements to avoid unfavourable decomposition or corrosion because of long-term contact with a watery environment [67].

Above all, the cost and availability of electrode materials are significant limiting steps in the commercialization process of BESs [39]. Expensive materials may come with excellent conductivity and stability, but the increased energy output cannot balance the increased production cost [65]. Materials like platinum, silver and their alloys, metal nanomaterials, etc., show exceptional conductivity and are employed as electrode materials for research purposes. These materials are very costly due to their chemical synthesis and cannot be used commercially. Such expensive materials can be replaced with cheaper carbon-based materials generated through green synthesis routes, e.g., graphene, carbon nanotubes, activated carbon, etc [68].

The coming section dives into conventional materials and carbon-based materials as their substitute. Traditional electrode materials involve the use of conductive metal electrodes as anode materials, but the introduction of nanomaterials and composite materials has received positive feedback from the researchers. The benefits were to such an extent that traditional materials have vanished from play, and the composite materials have been extensively studied for their use. In the coming sections, we will discuss the use of nanomaterials and composite materials and their application in BES technology.

4.1 Conventional materials for electrodes

Conventionally, metal and metal-oxide-based electrodes are popularly used as anode and cathode materials in MFCs mainly due to their excellent electrical conductivity [107]. In 1910, when M.C. Potter demonstrated his pioneering work of BES technology, his apparatus used the platinum electrode as both anode and cathode [12]. Since then, the platinum electrode has been extensively used as a cathode electrode due to its resistance towards oxidation and ability to absorb hydrogen [69]. Figure 5 broadly classifies conventional materials as carbon-based, metal/metal oxide-based and composite electrode materials. Among these materials, carbon-based materials are predominantly because of their advantages over metal-based electrodes.

Figure 5: Digital Photo of commonly used conventional electrode materials for BES applications. (a) carbon cloth, (b) Carbon brush, (c) Carbon rod, (d) Carbon Mesh, (e) Carbon Veil, (f) Carbon Paper, (g) Carbon Felt, (h) Granular activated carbon, (i) Granular Graphite, (j) Carbonized Cardboard, (k) Graphite Plate, (i) Reticulated Vitreous Carbon, (m) Stainless Steel Plate, (n) Stainless Steel Mesh, (o) Stainless Steel Scrubber, (p) Silver Sheet, (q) Nickel Sheet, ® Copper Sheet, (s) Gold Sheet, (t) Titanium Plate (Figure 5 is adapted from [43], published by Elsevier)

4.2 Carbon-based electrodes: Traditional and Nanomaterials Based

Other than metal and metal oxide-based materials, Carbon materials like carbon rods, carbon brushes, carbon foam, carbon cloth, carbon felt, etc, have been extensively used as electrode materials in BESs mainly due to the following advantages: (i) High chemical and mechanical stability [108], (ii) Cost-effectiveness [109], (iii) High conductivity [110], (iv) Good biocompatibility [111], and (v) good electron transfer kinetics with large surface area [112]. However, the low EET rate shown by such materials has highly limited their practical use and further scaling up [113]. To overcome these problems, various other materials and nanomaterials have been explored in the recent past [114-117].

Nanomaterials are materials with dimensions in nanometre scale (10^{-9} meters) and have an extremely large surface area, available for microbial adhesion. Nanomaterials can also be modified to act as a platform for electrons to travel from the cellular surface of microorganisms towards the anode [118]. Due to the extremely large surface area, nanomaterials can adhere and connect to multiple microorganisms at a time. Their porous nature further increases the surface area while consuming little to no volume [119]. Due to these advantages and their characteristic properties, certain nanomaterials have cemented a place in energy production and storage technologies.

5. Carbon nanomaterials for energy production enhancement

As mentioned above, the electrode material should have a large surface area so that the microbial species can have more area to adhere to and transport the released electrons directly to the anode [120]. To achieve this, nanomaterials come into play as they consume low volume to offer large surface areas [121]. Nano-materials have widespread applications due to their extraordinarily large surface area, current withstanding capacity, charge storage capacities and tensile strength [122]. Based on their size and structures, these materials can be subdivided into Zero Dimensional (0D), One Dimensional (1D), Two Dimensional (2D) and Three Dimensional (3D). In the coming section, these materials, especially carbon-based materials, will be discussed, starting with point materials.

5.1 Zero dimensional or Point Materials

Zero-dimensional or 0D materials are a class of nanomaterials where the dimensions of the structure in all three dimensions are on a nanometre scale. These 0D materials are commonly represented by spherical nanomaterials, hence giving the name point materials to this class of nanomaterials. Common examples of point materials are carbon nanodots, graphene quantum dots, fullerenes, and metallic nanoparticles. Out of these materials, carbon-based quantum dots have been extensively used as an electrode modifier due to their conductive nature, large surface area and easy modification [123]. The precursors required for quantum dot synthesis usually include a precursor molecule that can be larger or smaller than the nanoparticles, depending on the synthesis approach used. The top-down approach generally works with larger precursor molecules for the breakdown and formation of nanoparticles. The bottom-up approach, on the other hand, works with smaller precursor molecules for aggregation and formation of nanoparticles. Recently, considerable work has been done in this class due to their promising features [124]. These materials have been widely used in bioimaging, drug delivery, photocatalysis, sensing etc and have gained the scientific community's recognition for their performance and efficiency in next-gen electronic systems [125]. Graphene has extraordinary electrical properties, but the zero-band gap limits its widespread application in MFCs. To overcome this limitation, graphene-based quantum dots are synthesized with excellent electrical properties and biocompatibility [126]. Keeping this in mind, Graphene quantum dots (GQDs) are another alternative that can be used for many applications, such as photovoltaic systems, organic LED systems, and energy-storage devices. Owing to their excellent photoluminescence, quantum yield (QY), low toxicity, and resistance to photodegradation, GQDs have been used for other purposes also viz, bioimaging [127], biosensing [128], and possible cancer treatments [129-131].

a. One Dimensional or Tube/Fibre materials

One-dimensional nanomaterials are materials where the structure can expand only in one dimension, while the remaining two dimensions are restricted to the nanometre scale (1-100nm). Their structure closely resembles tubes and fibres. Common examples of 1D material include Carbon Nanotubes, nanowires, conducting polymers, nanorods and more. Carbon nanotubes (CNTs) are the most commonly used (1D) carbon nanomaterial having a tube-like structure. CNTs have high tensile strength, excellent thermal and electrical conductivities, high flexibility and greater surface area [132]. Depending on the number of concentric tubes that make up the CNT, they can be single-walled (SWCNTs) or multi-walled MWCNTs [133]. Owing to its high conductive nature and high aspect ratio, carbon nanotubes imitate the working of nanowires in facilitating native EET. When used in MFC as anode modification, the maximum power density achieved was 3660.25 mW/m^2, using activated sludge as fuel and microbial consortium [134]. Recently, CNTs have been investigated to build good-quality electron transfer networks by having hierarchical porous structures that are able to entrap bacterial species. Due to the presence of macropores that promote microbial growth and mesopores that result in a higher concentration of electron shuttles (i.e., flavin for *Shewanella oneidensis* as inoculum), the maximum power output observed is significantly higher than the power output obtained by the conventional carbon cloth electrodes [134]. The modified anodes possess smaller resistance for charge transfer which in return provides higher power efficiency. This method adheres and embeds bacteria in 3-D CNT networks of porous structure, thereby bypassing the biofilm formation step, which is generally the most time-consuming step in MFC fabrication [135]. Table 1 showcases the applied nanomaterials, their role in MFC and their performance. Most of the entries present on the table rely on the use of composite materials as these materials have the advantage of enhancing the electrochemical properties, which can be seen by the report presented by Habibi et al., in which they stated an increase of 87% when using Fe/Fe_2O_3 with N doped CQDs as compared to solo N-CQDs [34]. Reports by Lan et al. and Yan et al., suggest the use of carbon nanoparticles and metallic nanostructures to enhance electrode conductivity and provide efficient charge transfer [136, 137]. The composition of different dimensionality of materials (nanowires with nanoparticles, nanotubes with nanosheets etc.) encourages the researchers to find a facile and sustainable synthesis method that can be scaled up for commercialization. Carbon nanomaterials have been the centre of discussion due to their extravagant availability, biocompatibility and facile synthesis procedures. Feng et al. reported the use of nitrogen-doped carbon nanotubes as a metal-free electrode catalyst and deployed it at the cathode of the MFC [138]. They reported a higher power density of 1600 mWm^{-2} than the conventionally used platinum counter electrode (1393 mWm^{-2}). The table below (Table 1) holds some notable examples of reports where nanomaterials and carbon-composite materials are used for MFC application.

Table 1: Nanomaterials as electrode material and mediator in MFCs.

Material(s)	Synthesis method	Role in MFC fabrication	Power density	Microbial species	References
Zero-dimensional or Point Materials					
Fe/Fe2O3 with N-doped CQDs	Hydrothermal + Electrochemical oxidation method	Anode	836 mW/m^2	Activated sludge	[34]
N, S co-doped CQDs on Cu2O-Cu NWs	-	Cathode	924.5 mW/m^2	Microbial consortium	[136]
B doped GQDs on Bi-MOFs	Solvothermal	Cathode catalyst	703.55 mW/m^2	Domestic wastewater	[137]

CdS QDs with PANI nanocomposites	In-situ synthesis	Photo cathode	166.93 mW/m^2	Anaerobic sludge	[139]
One Dimensional or Tube/Fibre materials					
CF modified with CNT/PPy	-	Anode	3660.25 mW/m^2	Activated sludge	[134]
N-doped CNTs	Chemical vapour deposition	Cathode catalyst	1600 mW/m^2	Domestic wastewater	[138]
Pt nanoparticles anchored with MWCNT	Chemical vapour deposition	Cathode catalyst	2470 mW/m^2	*E.coli* (DH5α)	[46]
Textile anode modified with MWCNTs	-	Anode	1098 mW/m^2	Domestic wastewater	[140]
Pt/CNTs modification	-	Cathode	1118 mW/m^2	Wastewater species	[141]
2 Dimensional or Sheet materials					
FeS_2 nanoparticles decorated graphene	Modified Hummer's method + hydrothermal method	Anode	3220 mW/m^2	Microbial consortium	[142]
3-D graphene aerogel with Pt NPs	Hummer's method	Anode	1460 mW/m^2	*S.oneidensis* MR-1	[143]
3-D graphene/PANI	Chemical vapour deposition	Anode	768 mW/m^2	*S.oneidensis* MR-1	[144]
Graphene modified SSM	Chemical oxidation-reduction	Anode	2668 mW/m^2	*E. coli*	[145]

The main disadvantage of CNTs is their limited solubility [146] in aqueous media and limited long-term stability [147-149]. To overcome these limitations and improve long term stability, researchers have tried to modify the exposed surface of CNT through functionalization with hydrophilic moieties [150]. CNTs-modified graphite felt electrodes demonstrated stable performance throughout the course of the experiment (13 months). Carbon nanofibers are rarely used as electrode modifiers because the exoelectrogenic species have the tendency to form nano fibres from pili (as discussed in section 1.3: native EET mechanism of microbial species) [151].

The use of nanofibers/wires in BES can prove beneficial for their mimicking of pili for strains that cannot form natural fibres, thus making most microbes electricigens.

b. 2-Dimensional materials

The 2D materials were investigated after the discovery of graphene (Andre Geim and Konstantin Novoselov, 2004), a 2-D carbon-based material with excellent electrical conductivity [152, 153] and is the most prominent example of 2-D materials. Graphene is a single carbon atom-wide layer organised in a 2-D structure with a trigonal planar lattice. It has ultra-high active surface area, excellent biocompatibility and extraordinary mechanical properties [154]. Due to these features, graphene has made a league for itself, revealing great potential for use as an effective anode modifier. A graphene-modified stainless–steel mesh anode showed enhanced energy output and power generation mainly due to increased active surface area, resulting in greater adherence of microorganisms [154].

The use of nanomaterials can enhance EET, and the coming section covers discusses the interactions and mechanisms that undergo during the EET in the presence of nanomaterials.

6. Nanomaterials for enhancing EET efficiency

Nanomaterials (NMs) can be utilised alongside native extracellular electron transfer (EET) pathways in order to assist the electronic bridging between the periplasm/membranes of microorganisms to the anode and are being widely used for various applications due to their extraordinarily large surface area, current withstanding capacity, charge storage capacities and tensile strength [122]. Further, unlike proteins, they do not degrade easily and offer extended lifetime [155]. Highly conductive nanoparticles can bind to the cell surface and enhance the conductivity of the exoelectrogen, thereby improving the electron transfer to solid electron acceptor [156]. Furthermore, covering the cell surface with conductive NPs that are capable of interacting with each other opens doors for the creation of conductive cell aggregates that form an immobilised film on the electrode surface [157]. Entities, including neutral red and lignin, were used previously to enhance the bio-catalytic effectiveness in the anode of MFCs, but nanoparticles have proven to be better modifications for anode electrodes [158]. Several anode characteristics, like the surface area available for microbial adhesion and transmittance, are crucial, and such characteristics can be enhanced using nano-dimensioned materials, [159]. The EET can also be enhanced using electron shuttles/mediators that act as a bridge between the microorganism and the electrode. Upon comparison, carbon quantum dots performed a much better role as an electron shuttle as compared to conventionally used Methylene blue [160]. Quantum dots show excellent conductivity and are photocatalytic, which means that they can be used in photosynthetic microbial fuel cells (or BPV fuel cells) [161]. These particles interact with the cell in 3 possible ways: (i) NMs-cell surface interactions, (ii) NMs-cell membrane interactions and (iii) NMs-cytoplasm/periplasm interactions. These interactions are mentioned below in details:

6.1 NMs-cell surface interactions:

The electrode surface is usually crowded by bacteria adhered to the surface. The limited surface area of the electrode renders the majority of the bacteria in the medium for poor electron transfer rate due to overcrowding at the electrode surface. A solution to this problem will be to use electron mediators that can transfer electrons in an invisible shuttle. The mediators are used to collect electrons at the bacteria surface and travel to the electrode under the influence of the negative bias produced by the anode. Some bacterial species produce their own mediator compounds in order to facilitate the electron transfer like the S.oneidensis that produces riboflavin and flavin mononucleotide as electron mediators [162]. But not all bacterial species can produce mediators and thus, require external mediators for electron transfer. Nanomaterials can act as shuttles for electron transport and can also act as redox mediators for contaminants' degradation. Carbon nanomaterials have the advantage of outstanding electrical conductivity, good biocompatibility, high surface area, reduced production cost and low waste generation rate as compared to other nanomaterials. Zou et el. Presented a report on the use of porous MWCNTs and GO composite for anode modification [163]. The prepared composite was found to incorporate more bacteria at the electrode surface and assisted in the formation of denser biofilms as compared to the individual use of MWCNTs or GO. A report by Wu et al. presented the idea of using porous N-doped CNTs with rGO as a composite material for anode preparation [157]. Besides enhancing EET rates, the material also provided an increased surface area that facilitated the formation of denser biofilms.

6.2 NMs-membrane interactions:

Microbial membranes can be easily influenced by the use of nanomaterials. The shape and biological functions can be altered or enhanced based on the nanomaterial-membrane interaction [164]. The interaction happens in three possible and crucial phases, attachment, encapsulation and intercalation. Similar to their application in drug delivery, nanomaterials are used in BES as electron shuttles or electrode modifiers [165-167]. Nanoparticles, rods, ribbons, tubes, fibres etc are normally used as nanomaterials but recent research trends have preferred conjugated oligoelectrolytes over nanomaterials for enhancing the electrogenicity of the microbes [168, 169]. Conjugated oligoelectrolytes (COs) contain a hydrophobic core region and hydrophilic head groups, which have a structure similar to the phospholipid bilayers that constitute biological membranes [170]. These are synthetic molecules that are able to successfully impart exoelectrogenicity [171]. Their central core region consists of π-conjugated polymers responsible for their conductivity. Furthermore, COs have the ability to self-insert into already-formed lipid bilayers [172]. Various COs have been used in miniaturised E.coli-based MFCs that show up to a 25-fold increase in power density. Besides differences in power output, the various COs showed distinct influences on anodic biofilm morphology [173].

6.3 NMs-cytochrome interactions:

Microbial species contain cytochromes as electron carriers for intracellular electron transfer. These proteins contain a heme group that is essential for the IET in cellular respirations and play a vital role in cell signalling/ energy production. The latter application of cytochromes can be enhanced by the use of nanomaterials. The c-type cytochromes perform the direct electron transfer in the IET process and conjugation of nanomaterials with the cytochrome increases the availability of active sites for the released electrons. The nanomaterials can be synthesised biologically inside the cell. The biosynthesis of nanoparticles is not entirely extracellular, which means these particles can be synthesised in the cytoplasm or periplasm also [174]. Pd NP synthesis has been reported in the periplasm of Desulfovibriode sulfuricans. Once synthesised, these nanoparticles were used as the electron mediators, transporting electrons between membrane-associated cytochromes to fill the electronic gaps that occur within the periplasm [175]. In a similar fashion, QDs can also be biosynthesised. Biosynthesised CdS QDs have been reported to localise intracellularly in Saccharomyces cerevisiae cells and boost photocurrent production when grown on ITO electrodes under light-dark-cycling [176]. These interactions suggest that nanomaterials have positive impact on the EET pathways.

7 Photocatalytic electrodes and their applications in BPV cells

Just like MFCs, most research on BPVs focuses on improving interactions between cells and modified bio-anodes. In a BPV system, light absorption determines the electron flux that a single cell can produce. The incident light consists of both UV region and visible region but the photosystem I and II absorbs light only in the visible region [177]. This results in a loss of incident light energy for the UV region that constitutes half of the incident light energy and therefore, it is crucial to improve the light-harvesting capacity of the photosystem. Nanomaterials can work as auxiliary light absorbers for photosynthetic microbes as these materials are able to absorb light with different wavelengths [178]. The absorbed light energy can be transferred into the light-harvesting complex of the photosystem via the Förster resonance energy transfer (FRET) pathway [179].

Surface modification of anodes using CNPs, CNTs, or porous electrodes (MOF-modified or ITO-based electrodes) has been reported to promote electron transfer [180]. Conductive metal/metal oxide-modified electrodes show better power densities when compared to both ITO-coated polyethylene terephthalate (ITO-PET) and conventional carbon-based electrodes. However, recent studies show that both *Nostoc sp*. and *Synechocystis sp.* PCC 6803, when immobilized on CNT-based electrodes, are capable of generating electrical energy in response to light. The CNTs coated on carbon paper electrodes facilitates an intimate cell–electrode interaction by forming multiple sites for attachment, which, in turn, contributes to higher power output, compared to those generated by using conventional electrodes [181]. In addition to providing a support structure for improved immobilization, nanotubes (CNTs) also act as electron collectors in the electron transfer pathways. Cyanobacteria, in this case, *Synechocystis sp.* PCC 6803 were printed onto the paper to ensure a homogenously thin, solid layer of cells on the ink-printed electrode. The current output achieved in this configuration was much better than that obtained by the use of the same Synechocystis strain deposited by cell adhesion on the ITO-PET electrode. Furthermore, this procedure obviates any need for a liquid reservoir that is generally used in standard BPV systems, thus making miniaturization of solid-state BPVs possible [182].

Quantum dots (QDs), on the other hand, are photocatalytic nanoparticles and photocatalysis mechanism of QD composites follows three major steps, i.e., photoexcitation, recombination and oxidation-reduction reactions [183]. The photocatalysis is achieved due to a few reasons:

(i) QDs have a narrow bandgap than most transition metal oxides (e.g., TiO_2, RuO_2, MnO_2, etc.). So, when QDs are coupled with metal oxide nanoparticles, improved photocatalytic performance is observed [184].

(ii) At further lower levels, say angstrom levels, GQDs exhibit a 2D mat structure, which is comprised of carbon atoms in a planar hexagonal lattice. The atoms are connected through both σ-bonds and π-bonds by sp^2-electrons and p_z electrons, respectively. These chemical features grant GQDs with many unique properties like high electron and hole mobilities and greater surface area per unit mass (approximately 2600m^2/g) [185].

(iii) GQDs can become a sink for photogenerated electrons due to discrete electronic levels and substantial electronic conductivity. Furthermore, GQDs can be coupled with transition metal oxide nanoparticles to facilitate donor-acceptor contact [186].

(iv) Most of the pollutants we see in the environment have aromatic structures. As GQDs also have a similar nature, they can act as an active site for the adsorption of these aromatic pollutants, thus accelerating the photodegradation process [187].

Recently, QDs have been used as electrode material for photocathodes. In BPV fuel cells, GQD/MOF hybrid electrodes can be used for photocatalysis. Li et al. used silicon quantum dots to amplify the light-harvesting capacity of the Italian lettuce plant [188]. The concept was to utilise the UV region of incident light and enhance the photosynthesis process in the plant. The study provided new perspectives for using quantum dots to amplify the use of UV light in photosynthesis. Luo et al. reported the use of CuInS2/ZnS quantum dots as a unique periplasmic photosensitised biohybrid system [189]. The QDs were translocated into *Shewanella oneidensis* MR-1 cells for the photoexcitation and electron transfer processes to occur simultaneously. The biosystem had an increased photocatalytic hydrogen generation rate with the rate being 8.6 times higher than that of bare QDs. Carbon quantum dots have also been used in these photosynthetic systems for their advantageous nature. CQDs can be prepared by various precursor materials (including waste), they are easily synthesisable and have comparative ability when semiconductor QDs are considered. Liu et al. presented a study wherein CQDs are used to enhance the extracellular electron transfer in the dark and light modes of photosynthesis [190]. They suggested enhanced conductivity and boost in EET in dark mode and CQDs were able to absorb light in light mode.

In the next section, we will discuss the use of carbonaceous waste as precursor materials for electrode modification and biomass use.

8 Carbonaceous waste as a precursor material for the synthesis

Substrates, also referred to as analytes, serve as nutrient and energy sources. They are one of the most important parts of MFC as the adequate choice of substrates leads to increased energy production [191]. The substrate consumption and current generation rates by MFC follow Monod's equation under normal conditions. Frequently used substrates include:

(i) Acetate: a simple and extensively used substrate that is also used as the benchmark for new MFC design configurations because of its inertness towards fermentation and methanogenesis [192].

(ii) Lignocellulosic biomass: due to its abundance and renewability, lignocellulosic material gives cost-effective energy production but cannot be used directly; it has to be converted to monosaccharides to have low molecular weight [193].

(iii) Synthetic wastewater: the composition is known (well-defined composition) for easy control. Slowly, biodegradable waste gives higher current output than rapidly biodegradable waste [194].

(iv) Brewery wastewater: brewery wastewater is suitable due to its food-derived nature and low concentration of inhibitory substances. It has a high carbohydrate content. and low ammonium nitrogen concentration [195].

(v) Dye wastewater: using dye wastewater (Azo dyes) as substrates, with other co-substrates, leads to decolourisation. Experiments revealed that rapid decolourisation was achieved for active brilliant red X-3B (ABRX3) using glucose and confectionery wastewater as co-substrates [196].

(vi) Landfill leachates: these are heavily polluted effluents usually containing 4 groups of polluting agents, namely

(i) dissolved decomposable matter, (ii) inorganic matter, (iii) heavy metal ions and (iv) xenobiotic components [197].

Waste materials can be processed to yield carbonaceous mass that can further be utilised as precursors for the production of nanomaterials [41]. The carbonisation process yields fine carbon powder, which can be activated further [198]. Activated carbon refers to a range of carbonised materials having large surface areas and a high degree of porosity and finds many applications in both the environment and industry field [199]. Its major uses include the removal, retrieval, separation and modification of compounds in liquid as well as gas phases [200].

Advancements in nanoscience and nanotechnology have resulted in the fabrication of different classes of nanomaterials for use in BESs [201]. These broad classes of nanomaterials include metal/metal oxide and metal-based materials, carbon-based nanomaterials, and conjugated or composite materials. Table 2 lists some waste material sources that act as electrode material precursors [202]. For instance, Vishwanathan et al. used coconut husk as a precursor material for the synthesis of carbon dots and delivered a 172 % increase in power output of an MFC with mixed microbial culture [160]. Another report by Anusha et al. used tea waste ash with potter's clay to form functionalised electrode [203]. The material was low cost and provided with good performance under different ratios of mixtures. The unique molecular structure of precursor waste material can be exploited to form electrode modifiers. A report by Jaswal et al. utilised rice husk as silicon source and prepared waste derived silicon nanoparticles [204]. They reported a 7.6-fold increase in the power density obtained by MFC application when compared with control. In another report, a waste loofah sponge was used as electron collector and Japanese ink was coated on the sponge [205]. The Japanese ink alongside rice husk charcoal was used as electrode modifier and provided a low-cost solution for fuel cell application. Biomass waste like food content or algal biomass that are rich in carbon and nitrogen are used to develop in-situ N-doped carbon nanomaterials. Kumar et al. presented a report in which they used algal biomass to produce algal biochar via pyrolysis and used the biochar for electrode modification [206]. The table below (Table 2) holds some notable examples of reports where waste materials are reformed for MFC application.

Table 2: Use of waste as precursor molecules for electrode material synthesis.

Source	Electrode material	Synthesis method	Role in MFC fabrication	Power output	References
Coconut husk	C-dots	Hydrothermal	e^- mediator	126 mW/m^2	[160]
Orange peels	CQDs (N,S co-doped)/Cu2O-Cu NWs	-	Cathode	924.5 mW/m^2	[136]
Plastic	Fe-t-MOF/PANI on SSM	Alkaline hydrolysis	Electrode application	680 mW/m^2	[207]
Vehicle exhaust	Heteroatom-doped mesoporous	-	Electrode material	2200 mW/m^2	[208]

	Carbon nanoparticle				
Date seed, Banana peel powder	Powder coating of seed waste on MWCNT	-	Electrode material	1072 and 730 mW/m^3	[209]
Medicine wrapper waste	Metallic aluminium	-	Electrode application	27 mW/m^2	[73]
Loofah sponge and rice husk	Charcoal	-	Electrode application	16.1 μW/m^2	[205]
Palm kernel shell waste	Activated carbon	Pyrolysis and Hummer's method	Electrode application	24.17 mW/m^2	[210]
Archea nut husk	Activated carbon	Pyrolysis	Cathode material	590 mW/m^2	[211]
Tea waste ash with clay	-	-	Membrane separator		[203]
Food waste	Graphite	-	Fuel source	170.81 mW/m^2	[212]
Rice husk	Silicon nanoparticles	Pyrolysis	Electrode modification	190.5 mW/m^3	[204]
Corncob	SiO_2–incorporated graphite anode	Graphitisation	Electrode application	2010 mW/m^3	[213]
Avocado waste	Zn/Cu	-	Fuel source	566.80 mW/m^2	[11]
Biochar	AC-Cu	Carbonisation	Electrode application	173.20 mW/m^2	[214]
Biochar	AC-Co	Carbonisation	Electrode application	205.49 mW/m^2	[214]
Aquaculture waste	Carbon felt	Pyrolysis	biochar modification at chode	1693 mW/m^3	[215]
Algal Biomass to Biochar	Graphite	Pyrolysis	Electrode application	6.8 W/m^3	[206]

The biochar materials were found to be very useful as self-supported electrodes in order to improve microbial adhesion against the commercial carbon cloth/felt or as cathode catalysts vs. Pt/C commercial catalysts [201]. Biochar materials have been reported to increase the maximum power density when used as anode or cathode catalysts. Also, due to enhanced microbial adhesion and growth, direct interspecies electron transfer (DIET) was greatly enhanced compared to electron transfer intermediated by dissolved or immobilised mediators [216]. Whereas the use of doped biochar with dopants like transition metals and nitrogen atoms does not guarantee a straightforward improvement of power density when compared to a control (e.g., Pt/C) as the advantage lies in the substitution of Pt with low-cost catalysts to increase the cost-effectiveness rather than an absolute increase in power production [217]. The use of waste-derived materials for commercial applications decreases production costs immensely and presents a substitute for precious metals.

Vast research has been done to replicate the versatility of carbon. The coming section will briefly describe the application of carbon-based composite structures with different materials.

9 Carbon-based composite structures for electrode application

Carbon-based composite structures are a combination of carbon materials and other conducting materials [218]. Based on the conductivity, carbon-based composite materials can be further divided upon the materials used for modification. They can be (i) carbon-carbon composite [219-221], (ii) carbon-conducting polymer composite [222-224], and (iii) carbon-metal composite [225-227]. Some systems are reactive in nature and tend to improve their reactivity, while others are stable compounds that can be used as storage systems [228]. In this section, we will discuss the different carbon-based composite materials and highlight the enhancement strategies.

9.1 Carbon-Carbon composite

As discussed previously, graphene sheets have inherent stacking ability, which makes microbial adhesion a problem; on the other hand, CNTs have poor solubility and stability issues [221]. However, a composite of CNT and graphene results in the generation of a composite with much better properties. In this CNT/Graphene composite, CNTs prevent the stacking of graphene sheets, thus creating more surface area for microbes to adhere to, while graphene provides stability to the CNT mesh when CNTs are inserted through the plane [229]. This composite structure is both stable and adhesive, thus improving the material's efficiency and lifetime. A report by Zou et al. described the use of such CNT-graphene composite material for MFC application [162]. The material was prepared via solvent-processed method and the porous network was confirmed by electron microscopy. Doping of carbon nanomaterials has been of great virtue as the process not only preserves the advantages of carbon but also introduces the positive effects of nitrogen. Wu et al. developed a N-doped CNT/rGO composite material for anode application in MFC [163]. Using PANI as the N source, they demonstrated the superiority of N-doped CNT/rGO over N-CNTs, N-rGO and CNT/rGO materials. Alongside rGO, graphene oxide nanoribbons (GONR) have also been used in graphene-CNT composite material as it encourages entanglement between nanotubes and nanoribbons, providing more active surface area. Liu et al. synthesised and used N-doped MWCNT@GONR composite materials using microwave assisted synthesis method [230]. The doped composite material gave increased performance as compared to N-MWCNT, N-GONR, and MWCNT@GNOR composite material. The synergistic effects of using carbon based composite materials serves as an advantage over individual materials and further doping of these composite materials increases the power generation capability [231].

9.2 Carbon-conducting polymer composite

The use of conducting polymers in BES has widened owing to their durability and good conductivity [232]. Accordingly, the various conducting polymers have been used extensively to increase the efficiency of BES systems. For example, polyfuran, polyaniline, poly-para phenylene, polypyrrole, polyvinyl carbazole, polythiophene, and polyazulene are just to mention a few [233]. Among these, polyaniline (PANI) and polypyrrole (PPy) are the most widely used conducting polymers for composite formation with carbon-based materials [234]. Zou et al. demonstrated the use of PPy nanoparticles/MWCNTs in a mediator-less microbial fuel cell. The cell showed enhanced performance with a maximum power density of 228 mW/m^2 [235]. Yang et al. demonstrated the use of a 3-D graphene/PANI NP-modified electrodes using *S.oneidensis*MR-1-based MFC (figure), which reached a peak power density of 768 mW/m^2 [144]. Apart from PPy and PANI CPs, other polymers have also been used for anode modification and have been shown to increase bacterial adhesion on the anode surface. Chen et al. used novel poly(diallyldimethylammonium chloride) (PDDA) with rGO and prepared a modified carbon cloth electrode for anode application [236]. The electrode demonstrated an improved performance which was six-fold better than bare carbon cloth. In another study conducted by Li et al., polydopamine (PDA) was used with rGO and the composite was applied onto a carbon cloth [237]. PDA was chosen to increase hydrophilicity and microbial adhesion. These polymers have positive surface charges like PANI, thus following a similar mechanism for increasing microbial adhesion and charge transfer rate.

9.3 Carbon-Metal composite

Metal materials have always been a contender for electrode production and introduction of nanomaterials have been pivotal in material sciences. Metal nanoparticles have exceptional qualities as current collector and provide surface area enhancement. These materials have been used individually but their composite with carbon-based materials benefits them with enhanced biocompatibility and stability. Metal nanomaterials prepared via green synthesis methods have been a trending research topic. A report by Wu et al. used biogenic gold nanoparticles and prepared a composite material of Au NPs@MWCNT as electrode modifier [238]. The composite material gave a better performance than the individual materials, boasting a 1.8-fold performance boost. Another report by Zhao et al. demonstrated the use of platinum nanoparticles decorated graphene aerogel for anode applications [239]. The use of noble metal elements limits their application due to rising cost and scarcity in supply of these materials. Researchers pursued inorganic metallic compounds in order to construct carbon-metal composites. Song et al. prepared a composite material consisting of graphene and Fe_3O_4 for anode application [240]. They discovered the high affinity between Fe_3O_4 nanoparticles and *Shewanella* species that increased the bacteria hosting capability of the electrode. This was evident by the increase in power generation ability that was reported to be 2.8 times higher than that of graphene anode. Beside metal oxides as inorganic metallic compounds, other salts like nitrates, sulphides, carbides and carbonitrides have also been used in conjugation with carbon materials to produce carbon-metal composite materials. Wang et al. decorated graphene nanosheets with FeS2 in order to improve rGO performance in MFCs [142]. The study presented better interaction of anode with microbial species in case of composite material than only rGO. Another research by Zou et al., the decoration of rGO was done by Mo2C nanoparticles and the prepared electrode was used for anode application [241]. The decoration provided an increase in power density by 2 folds due to the excellent electrocatalytic properties of Mo2C. the electrocatalytic properties of metal nanomaterials clubbed with biocompatible carbon nanomaterials produce the composite materials that are cost efficient, easy to reproduce and enhances the application of BES.

The next section provides some notable examples of commercially used BES. Commercialisation of a technology refers to the use of pilot scale projects or the availability of technology in marketplace. Like many other commercialised technologies, BES have been commercialised while innovative research being underway.

10 Commercial aspects of BES

As discussed above, bioelectrochemical systems have diversified their use in real-world situations, such as energy production, wastewater treatment, bioremediation, biosensors, and product recovery applications [242]. Several corporations have tried and succeeded in commercialisation of this technology. A few notable examples would be,

- *M/s Cambrian Innovation (USA)*: The Boston-based company, M/s Cambrian Innovation specialises in providing sustainable wastewater treatment solutions using BES. The company’s technology, called EcoVolt, uses BES to treat wastewater while producing clean energy [243]. A conductive polymer matrix is used as an electrode material that promotes the growth of electroactive bacteria.
- *M/s Electrochaea (Germany)*: M/s Electrochaea, a Planegg-based company, uses BES to convert renewable energy into methane gas, which can be used as a renewable energy source [244]. The company’s technology, called Power-to-Gas, uses microorganisms to convert carbon dioxide and hydrogen to methane. The bioreactor contains electrodes that provide a source of electrons for the archaea to carry out their metabolism. The company has described their electrode material as “specially designed catalysts” that allow for efficient and effective transfer of electrons between the electrode and the microorganisms.
- *Emefcy (USA)*: The Minneapolis-based company, Emefcy provides wastewater treatment solutions using BES. The company's technology, called membrane aerated biofilm reactor (MABR), uses BES to reduce energy consumption and improve the efficiency of wastewater treatment [245]. In the MABR process, oxygen is supplied to the biofilm through the membranes, which are made of a flexible and durable polymer that allows for optimal oxygen transfer while preventing the growth of unwanted microorganisms.
- *Aqwise (Israel):* Aqwise firm, a Hertsliya-based company, uses BES to provide solutions for wastewater treatment, bioremediation, and biogas production. The company's technology, called attached growth airlift reactor (AGAR), uses microorganisms to remove contaminants from water and soil and to produce biogas from organic waste [246]. The media used in this technology has been described as a ‘patented plastic element’ that is designed to provide a large surface area for microbes to attach.
- *Pivot Bio (USA):* The California-based company, Pivot Bio uses BES to produce sustainable fertilizers for agriculture. The company uses Pivot Bio PROVEN technology that involves the use of microorganisms to synthesize nutrients to aid in the growth of crops, thereby reducing the dependence on synthetic fertilizers [247].

India is also not far behind in the practical and commercial applications of BES. There are several corporations in India that have applied bioelectrochemical systems (BES) for various practical applications. Here are some examples:

- *Graviky Labs*: Graviky Labs, a Bengaluru-based start-up, developed a technology called KAALINK, which uses BES to capture and convert air pollution into ink [248]. The company's technology uses carbon-capturing devices that can be attached to vehicles or chimneys, which capture the particulate matter in the air and convert it into ink that can be used for printing.
- *Tata Chemicals*: Tata Chemicals has developed a technology called Bioelektra, which uses BES to treat wastewater from its soda ash plant in Mithapur, Gujarat. The company's technology uses microorganisms to treat

the wastewater while generating electricity, reducing the plant's carbon footprint.

- *Indian Institute of Technology, Delhi*: Researchers at the Indian Institute of Technology, Delhi, have developed a technology called Microbial Fuel Cell (MFC) [249], which uses BES to generate electricity from organic waste. The technology has been tested in a variety of applications, including wastewater treatment and power generation.
- *National Environmental Engineering Research Institute* (*NEERI*): Researchers at NEERI have developed a technology called Bio-electro-Fenton (BEF), which uses BES to treat industrial wastewater [250]. The technology uses microorganisms to generate hydrogen peroxide, which is then used to treat the wastewater and remove contaminants.

These examples demonstrate the diverse applications of BES technology in India as well as around the world. As BES technology continues to develop and become more widely available, it has the potential to play an increasingly important role in addressing environmental and sustainability challenges in India and beyond.

11 Conclusion and Future Prospects

This review article shows the involvement of carbon-based nano-materials in BES and their ability to promote both EET and microbial growth. Carbon, being versatile in nature, can be employed as an anode and cathode electrode. At the macroscopic scale, it can be used as carbon cloth, felt, rod, brush, paper, etc., and as nanoparticles, nano-tubes/rods/wires at the microscopic scale. Carbon composite materials (carbon + metal + dopant (N, Cl, I, etc.)) have been extensively studied and have the benefits of both carbon-based materials as well as metal/metal oxide-based materials. Carbon composite structures can be (i) carbon-carbon, (ii) carbon-conducting polymer, (iii) carbon-metal NPs, and metal-organic hybrid structures, and (iv) MOFs. This combination reduces the cost of electrode material drastically and can be used as a replacement for costly metal electrodes that were conventionally used.

We have discussed the materials and their green replacements. Waste reduction is an important aspect of MFC as the waste acts as a fuel/microbial consortium source for the system. Despite the advancements in material research and the use of waste as electrode precursor material, the technology is still far from the commercialization process. Large-scale use of this technology is mainly prohibited due to high device cost, scalability issues and most importantly low power output owing to energy losses at every step. So, future research can focus on these aspects of the technology:

- *Microbiology aspect*: The microbial consortium used in this technology has seen a fair share of research trends, and new strains can be modified with genetic engineering in order to ascertain PilA microfilaments. The microbial species can be engineered for advancements in electrogenicity or can be used specifically for waste treatment. Pharmaceutical waste can be reduced by using resistant microbes prior to discharge. By doing this, microbes may be able to generate VAPs or at least be able to reduce the waste.
- *Electrode material aspect*: As discussed throughout this review, electrode materials are crucial aspects of BES fabrication as they govern the catalysis aspect of the system. They can be used in BPV as photocatalysts and in MFCs as both electrocatalysts and photocatalysts (in photo MFC). The precursor materials should be non-toxic and the synthesis route should be facile. Through material engineering, we will be able to produce low-cost electrode materials, which will be a giant leap

towards commercialization of this technology.

- *Biofilm formation aspect*: It has been discussed several times that biofilm formation enhances the EET rate of the species. Investigations in hybrid biofilm formation require attention as nanomaterials that induce biofilm formation can also enhance microbial adhesion and EET rate better than naturally induced biofilms. Unlike the attention given to nanomaterial research, only a few researches have been done in material-based hybrid biofilms, and this research area can give promising results regarding increasing the power density of the system.
- *Energy storage and lifetime aspects*: Despite poor energy output, a BES works without depending on an external energy source. This ability can be exploited by using energy storage devices, which will not only store energy but also allow a steady flow of output energy from a rather pulsated flow by a typical BES. Extending the life of the system is equally important, as waste reduction is a continuous process which requires long periods of time. Many reported works have demonstrated achieving extended lifetimes by using different materials, but the exact mechanism of the relationship between electrode materials and microbial species has yet to be discovered.

Credit authorship contribution statement:

Anuj Sharma: Conceptualization, Methodology, Writing – original draft, Investigation, Formal analysis. Aman Grewal – Writing – original draft, Investigation, Formal analysis, Shubham Patial: Writing – review & editing. Suman Singh: Idea conceptualisation, Supervision, Investigation, Writing – review & editing, Discussion. Amit Lochan Sharma: Supervision, Investigation, Writing – review & editing, Discussion.

Conflict of Interest:

The authors declare that they have no financial or personal conflicts of interest that could have impacted the article's findings or the authorship contributions.

Acknowledgements:

The authors are grateful to the Director, CSIR-CSIO, Chandigarh, India, for his constant support and encouragement during this work. The authors are grateful to the DBT-BET for the JRF fellowship. Authors also acknowledge the support of HCP52 W.P for financial support in the form of project.

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