

Review

Sustainable Syntheses and Sources of Nanomaterials for Microbial Fuel/Electrolysis Cell Applications: An Overview of Recent Progress

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Abstract: The use of microbial fuel cells (MFCs) is quickly spreading in the fields of bioenergy generation and wastewater treatment, as well as in the biosynthesis of valuable compounds for microbial electrolysis cells (MECs). MFCs and MECs have not been able to penetrate the market as economic feasibility is lost when their performances are boosted by nanomaterials. The nanoparticles used to realize or decorate the components (electrodes or the membrane) have expensive processing, purification, and raw resource costs. In recent decades, many studies have approached the problem of finding green synthesis routes and cheap sources for the most common nanoparticles employed in MFCs and MECs. These nanoparticles are essentially made of carbon, noble metals, and non-noble metals, together with a few other few doping elements. In this review, the most recent findings regarding the sustainable preparation of nanoparticles, in terms of syntheses and sources, are collected, commented, and proposed for applications in MFC and MEC devices. The use of naturally occurring, recycled, and alternative raw materials for nanoparticle synthesis is showcased in detail here. Several examples of how these naturally derived or sustainable nanoparticles have been employed in microbial devices are also examined. The results demonstrate that this approach is valuable and could represent a solid alternative to the expensive use of commercial nanoparticles.

Keywords: carbon nanomaterials; green syntheses; metal nanoparticles; microbial fuel cells; microbial electrolysis cells



Citation: Frattini, D.; Karunakaran, G.; Cho, E.-B.; Kwon, Y. Sustainable Syntheses and Sources of Nanomaterials for Microbial Fuel/Electrolysis Cell Applications: An Overview of Recent Progress. *Processes* **2021**, *9*, 1221. <https://doi.org/10.3390/pr9071221>

Academic Editor: Mohd Azlan Hussain

Received: 15 June 2021

Accepted: 12 July 2021

Published: 15 July 2021

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1. Introduction

In everyday life, energy plays an important part in sustaining processes required for life. Due to increased energy demands, researchers have focused on the research and development of low-cost and long-lasting energy sources [1]. In such efforts, microbial fuel cells (MFCs) potentially represent the best source of low-cost and eco-friendly (often referred to as “green”) energy production, where they operate by converting organic waste into electricity.

Over the last few decades, the development of microbial electrochemical technologies has been very active and productive and is mainly represented by MFCs and microbial electrolysis cells (MECs) [2,3]. These devices can use the organic matter in residual biomass or wastewater to either produce usable electricity (via MFCs) [4] or biosynthesize hydrogen [5] and other valuable chemicals (via MECs). Although the peculiar advantages of these devices are well-known and appreciated by scientists, market penetration and diffusion at the industrial level are inhibited by the problems related to high capital costs, increases in scale,

the multiplication/miniaturation approach [6] to maintain a suitable power density, COD (Chemical oxygen demand) removal rate, and value-added chemical production. Roughly, regardless of MFCs or MECs, the cost allocations for a device are represented by the anode, cathode, proton exchange membrane (PEM), reactor case, current collectors, and other costs (e.g., pumping, control systems, and assembly). The performance of MFC and MEC materials is dependent on several factors, such as the pH [7,8], temperature, cell design, surface structure [9], microbial inoculation [10,11], solution conductivity/nutrient concentration [12,13], and the efficiency of the charge transfer to/from electrodes. These issues are not exclusively related to MFCs and MECs, but also to other bioelectrochemical devices like microorganism-based sensors [14]. In a series of recent focused reviews, the emerging niche for the advantageous application of conducting polymers in biosensors and biofuel cells has been discussed [15], pointing out that these polymers possess biocompatibility, a fast transduction mechanism, and versatile synthesis processes. Moreover, it was found that they can greatly improve the electron transfer mechanism toward direct pathways [16], as shown in Figure 1. This is because conducting polymers such as polypyrrole [17] and MXenes [18] can be easily nanostructured and doped to obtain functional materials.

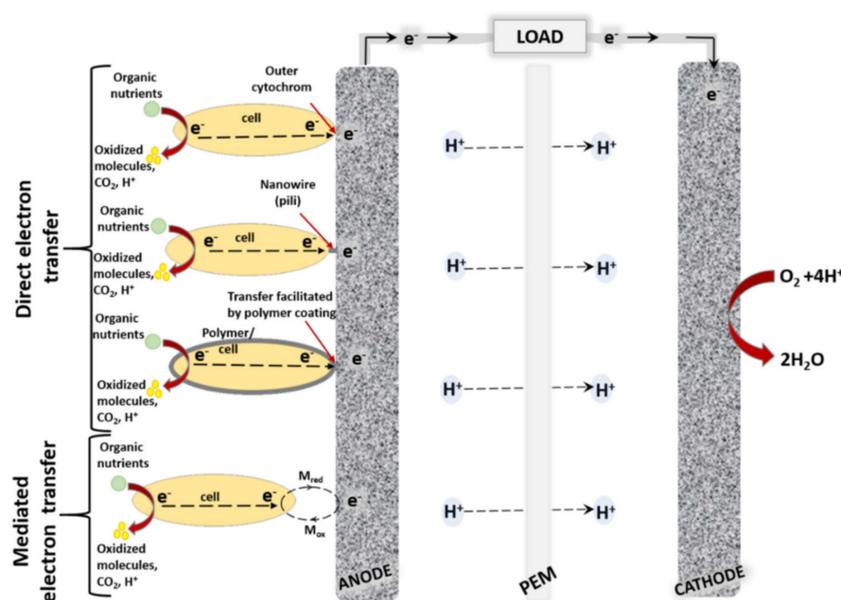


Figure 1. Direct and mediated electron transfer mechanism in bioelectrochemical devices and the facilitation offered by conducting polymers. Reproduced from [14] under a CC BY 4.0 license.

Large-scale and real-time applications of these devices are limited, for example, to small and wearable devices [19], whereas, for larger systems, one of the limits is the insufficient cost-effectiveness of electrode materials with low toxicity in neutral or near-neutral pH media. It has been reported in the literature that, for MFCs, the membrane and the cathode account for 85% of the total costs [20], while they should be around 30–40% of the total cost in order to be economically feasible. For MECs, the anode and the current collectors represent 94% of costs [21], while the cost should be less than 10–20% of the total cost to make a MEC device practical for use. Recently, regarding the membrane or separator, a successful trend has been substitute Nafion with porous ceramic materials [22–25], which have a lower cost, longer lifetime, and resistance to biofouling, whereas, for the electrode, the insufficient cost-effectiveness presents a more difficult challenge to overcome.

This is because electrodes usually entail the insertion of nanoscale and nanoengineered materials that can boost the performance [26], but also increase the fabrication costs. Furthermore, the use of nanomaterials may not always result in the desired boosting effect [27], particularly for cathodes [28], where the increase in performance can be quite modest in practical use. The main electrode materials for MFCs are carbon-based, but there are huge

differences in price between nanostructured and non-nanostructured materials [29]. Furthermore, MFC cathode catalysts are usually noble metals, i.e., Pt-based, whereas the use of non-Pt catalysts has been a longstanding challenge in reducing costs [30,31]. Recently, noble metals have been used to modify anode materials to impart an electrical bridging effect to improve electron transfer [32,33]. Non-noble metal nanoparticles will be widely used in the near future, thus creating a very interesting research niche. If this barrier is overcome, microbial electrochemical devices can potentially generate more profits and revenues than traditional wastewater treatments [34].

Reducing electrode material costs is critical for microbial electrochemical technologies to gain market attractiveness. The cost abatement needed to become feasible for use can only be achieved by excluding the use of noble metals and scavenging raw carbon materials from secondary or natural sources and then transforming them into performant nanostructured materials using green synthesis routes that are cheap and effective. Due to these driving reasons, and additionally to overcome the problems arising from toxicity and low performance, green synthesis approaches are developing are attractive solutions in this regard.

Two steps must be met for such an approach to be successful. The first step is to choose and control the synthesis routes that will convert a renewable, natural, and abundant source into a nanomaterial [35]. The second step is to use the eco-friendly synthesized materials as components in MFCs and MECs in order to demonstrate the real feasibility and performance that can be achieved with the simultaneous cost of these raw materials potentially being close to zero. As a result, this overview is divided into two main parts: The first part of the overview deals with some interesting examples of how eco-friendly syntheses and natural and recycled sources can produce nanostructured/nanosized materials, with the second part highlighting and discussing the performances of nanomaterials obtained from green, sustainable, or recycled sources in MFCs and MECs.

2. The Green and Sustainable Approach for Nanoparticles Production

2.1. Potential Renewable and Sustainable Raw Sources for Different Kinds of Nanoparticles

Even though different technologies may improve nanoparticle synthesis, nature itself is an especially prominent nanotechnologist, providing many naturally occurring nanoparticles in different processes, such as volcanic eruptions, iceberg sedimentation, umber, natural surface water, seawater, mineral wells, ore deposits, and particulates.

In volcanic eruptions, the occurrence of silica (SiO_2) nanoparticles has been extensively reported and such nanoparticles are well-known for their use in food additives, cellular imaging, and antireflection coating applications [36]. Iceberg sediments are also a good source of iron oxide (Fe_3O_4) nanoparticles, which are used in hyperthermia, medical diagnostics, biosensors, and drug delivery applications [37]. UMBER is also a good source for manganese oxide (MnO_2) nanoparticles, which are used for catalysis, remediation, and imaging. Natural surface water contains a large reservoir of different nanoparticles, such as calcium carbonate (CaCO_3), silicates (SiO_2), and alumina (Al_2O_3) [38]. Furthermore, seawater, mineral wells, ore deposits, and particulate represent potential reservoirs of silver (Ag), gold (Au), carbon (C), and sulfur (S) nanoparticles [39–42]. Some recent research performed by different researchers has shown how these natural renewable sources can be effectively utilized to produce different nanoparticles, such as metal titanates (FeTiO_3) from ilmenite sand, alumina (Al_2O_3) nanoparticles from bauxite, TiO_2 nanoparticles from natural ilmenite, and iron oxide nanoparticles (Fe_3O_4) from ironstone [43–46]. Iron oxide nanoparticles obtained from ironstone have been found to be in the order of 10 to 50 nm in size when obtained by a simple precipitation method using hydrochloric acid and an ammonia solution [43]. TiO_2 nanoparticles have been synthesized from raw ilmenite in multiple steps. Firstly, raw ilmenite has been treated with concentrated sulfuric acid and then treated with ferric sulfate to obtain titanium sulfate, which is converted to titanium hydroxide using ammonium hydroxide. The resulting titanium hydroxide has been sintered at 300 °C to obtain TiO_2 nanoparticles with a size of about 50 nm [44].

Furthermore, raw bauxite has been used to obtain alumina (Al_2O_3) nanoparticles via multiple steps, such as washing with sodium hydroxide to convert it into Bayer liquor, where the Bayer liquor was then treated with sulfuric acid to obtain an aluminum hydroxide precipitate. The obtained precipitate was calcined at $500\text{ }^\circ\text{C}$ to obtain spherical particles that were of the order of 50 nm in size on average [45]. FeTiO_3 nanoparticles (or metal titanates in general) can be synthesized by acid extraction followed by a precipitation method, and the resulting nanoparticles have been found to have a size between 50 to 100 nm [46]. It must be mentioned here that although these sources feature abundant amounts of minerals or mineral residues, the chemicals used in the extraction processes are harmful and are certainly not eco-friendly. This represents the aspect that must be improved when using natural sources for nanoparticle production.

The other primary class of materials used as electrode materials for MFCs and MECs is nanocarbons. While the sources of the previously mentioned nanoparticles are sometimes specialized inorganic residues, minerals, and sediments, carbon can be easily obtained from everyday organic biomass in the form of waste. Biochar is a solid residue that is produced with the high-temperature pyrolysis of any kind of organic biomass, and originally the term referred to the product used in agronomy and soil applications as a fertilizer and/or for biocompatible discharge/landfill with organic matter. Pyrolysis, along with other thermic procedures conceptually derived from it, is the primary method for converting biomass into biochar and involves prolonged heat treatment in an inert or oxygen-deficient atmosphere with a determined heating rate, dwell temperature and time, and additionally the separation of gaseous, liquid, and solid products. Such pyrolysis techniques have a background that arises from traditional industrial fossil coal processing techniques. This matter has a long story and has already been an object of concern in extensive studies, reviews, and books, like [47–49], and is still widely investigated nowadays.

When applied to microbial electrochemical cells, although mainly MFCs, biochar is receiving remarkable interest. This is because an engineered thermal process can provide conductive carbonaceous porous materials that are nanostructured and feature traces of other mineral elements when using practically any sort of waste biomass. This class of materials can be associated to the family of heteroatom-doped carbons because, as a result of the pyrolysis, the inorganic atoms (e.g., Fe, N, P, S, etc.) from trace minerals in the raw biomass turn into defective active sites in the carbon structure. In the literature, it is possible to find many exotic examples of waste biomass employed as raw material for pyrolysis and biochar production. Here, some examples of biochar explicitly tailored for microbial systems applications are reported (Table 1).

Table 1. Examples of biochar production from biomass when designed for MFC or MEC application.

N.	Source Material	Surface Area ($\text{m}^2\text{ g}^{-1}$)	Avg. Pore Size (nm)	Process Conditions	Trace Elements	Ref.
1	Water hyacinth (<i>Eichhornia crassipes</i>)	25.9 (BET) *	5.6 (BET)	Washing, sunlight drying, drying at $80\text{ }^\circ\text{C}$ for 1 h, pyrolysis at $900\text{ }^\circ\text{C}$ for 2 h at a rate of $25\text{ }^\circ\text{C min}^{-1}$	Al, Mg, Si, P, S, O, K, Ca, Fe, Cu, Zn (EDS) *	[50]
2	Bananas	105.1–172.3 (BET)	-	Hydrothermal treatment at $180\text{ }^\circ\text{C}$ for 12 h, filtration, washing, drying at $60\text{ }^\circ\text{C}$, pyrolysis at $900\text{ }^\circ\text{C}$ for 2 h in Ar, washing, drying at $100\text{ }^\circ\text{C}$ for 12 h, activation with KOH	O, N (EDS)	[51]
3	Alfalfa leaves	148–883 (BET)	-	Pyrolysis at $250\text{ }^\circ\text{C}$ for 2 h in N_2 , $\text{FeCl}_3/\text{KOH}/\text{ZnCl}_2$ activation, pyrolysis at $900\text{ }^\circ\text{C}$ for 2 h in N_2	O, N, P, S, Fe (EDS)	[52]

Table 1. Cont.

N.	Source Material	Surface Area (m ² g ⁻¹)	Avg. Pore Size (nm)	Process Conditions	Trace Elements	Ref.
4	Corncob	68.5–655.9 (CV) *	-	Sunlight drying for 5 days and pyrolysis at 750 °C for 2 h in N ₂	O, K, N, P (EDS)	[53]
5	Green algae (<i>Spirogyra</i>)	258 (BET)	4 (BET) 50–200 μm (SEM)	Washing, shaping, vacuum filtration, freeze-drying, and pyrolysis at 1100 °C for 2 h in N ₂	-	[54]
6	Pinewood lumber	42.4 (BET)	-	Gasification at 1000 °C at a rate of 17 °C min ⁻¹ in air, sonication 30 min, stirring at 80 °C for 2 h in 3 M KOH, filtering, washing, vacuum drying at 50 °C for 3 h, functionalization with Mn	Al, Ca, K, Mg, Mn, P, Si, Ti (ICP) *	[55]
7	Lotus leaves	611–909 (BET)	0.49–1.23 (BET)	Washing, ultrasonication for 2 h, drying at 40 °C for 12 h, hydrothermal treatment with ZnCl ₂ /(NH ₄) ₂ SO ₄ at 160 °C for 2 h, drying 60 °C for 24 h, pyrolysis at 1000 °C for 2 h in N ₂ , washing, drying at 60 °C for 24 h	Ca, N, O, S (XPS) *	[56]
8	Sewage Sludge	44 (BET)	0.8–8.6 (BET)	Drying, pyrolysis at 900 °C for 2 h at a rate of 5 °C min ⁻¹ in N ₂	N, O, Fe (XPS)	[57]
9	Coffee waste	3.5–428 (BET)	7.9–23.2 (BET)	Washing, filtering, drying, activation in KOH for 24 h, pyrolysis at 900 °C for 1 h in N ₂ , washing, drying for 24 h	-	[58]
10	Kapok tree fibres	-	10–20 μm (SEM) *	Washing, shaping, pyrolysis at 1100 °C for 2 h at a rate of 30/200 °C h ⁻¹ in 95% Ar and 5% H ₂ , washing, filtering	-	[59]
11	Eggplant	637–1181 (BET)	-	Peeling, shredding, washing, drying at 100 °C for 8 h, activation in K ₃ [Fe(C ₂ O ₄) ₃], drying, pyrolysis at 800 °C for 1 h at a rate of 5 °C min ⁻¹ N ₂ , washing in 2 M of HCl, washing, drying at 70 °C for 8 h	N, O (EDS)	[60]

Table 1. Cont.

12	Rice husk	1164–1809 (BET)	12.4–23.1 (BET)	Grinding, washing, drying at 105 °C for 12 h, washing in 98–54% wt H ₂ SO ₄ at 55 °C, filtration, washing, drying at 60 °C for 2 h, drying at 95 °C for 6 h, washing, drying at 120 °C for 12 h, pyrolysis at 500 °C for 0.5 h in N ₂ , activation with NaOH/KOH, pyrolysis at 400 °C for 0.5 h and then 800 °C for 1 h	-	[61]
13	Mixed microalgae	21 (BET)	-	Filtering, washing with HCl at 1 mM, centrifugation, drying at 60 °C, pyrolysis at 400 °C for 2 h at a rate of 10 °C min ⁻¹ , washing, drying at 60 °C, pyrolysis at 900 °C for 1 h at a rate of 5 °C min ⁻¹ in Ar, washing, drying at 60 °C overnight	N, O, P (XPS)	[62]
14	Watermelon rind	78–659 (CV)	-	Washing, drying at 40 °C for 72 h, sonication in 1 M of HCl for 5 h, filtering, washing, drying at 85 °C for 12 h, pyrolysis at 700 °C for 2 h at a rate of 5 °C min ⁻¹ in N ₂	N, O (XPS, EDS)	[63]
15	Sewage sludge/coconut shell	16–54 (BET)	-	Grinding, shaping, drying at 50 °C, pyrolysis at 900 °C for 2 h at a rate of 5 °C min ⁻¹ in N ₂	O, N, Fe, P (XPS, EDS)	[64]
16	Sludge from wastewater treatment	41.8 (BET)	-	Drying at 105 °C, pyrolysis at 500 °C for 1.5 h at a rate of 10 °C min ⁻¹ in N ₂ , HCl activation, drying at 105 °C	N, S, Si, Fe, Al, Ca, Mg, K, Na (elemental analysis)	[65]

* BET: Brunauer–Emmett–Teller; EDS: energy dispersive X-ray spectroscopy; CV: cyclic voltammetry; ICP: inductively-coupled plasma; XPS: X-ray photoelectron spectroscopy; SEM: scanning electron microscopy.

From Table 1, it is possible to observe that there are a plethora of recipes to obtain various forms of biochar from different biomasses, thus present several options for pre/post washing and drying of the fresh biomass, along with the use of a hydrothermal or alkaline solution for activation of the dried mass before the pyrolysis step. Some papers suggest that different parts of the same biomass, e.g., corncobs, sunflowers, woody sticks, etc., can lead to various biochar forms with different activities. This is an interesting perspective, but the real occurrence of a qualitative and quantitative remarkable variance of activity should be investigated more. What is well assessed in the various recipes is the effect of the pyrolysis temperature [66], which typically ranges between 750–950 °C, with N₂ and Ar as inert gases, an alkaline activation step, abundant washing steps to eliminate mineral ashes to reduce trace elements essential to N, O, and Fe, and the relevant volume variation as the final amount of obtained product is small and depends on the weight percentage of carbon and other inorganic elements present in the dried biomass. This can be evaluated by performing simple proximate/ultimate elemental analyses to provide an idea of the yield

of the process (which unfortunately has not always been reported in prior papers). This factor is important in determining process feasibility, as high yields may be associated with biomass that has a high content of carbon and is more easily processed, whereas low yields could be associated to waste biomass with a high volatile matter content, thus requiring large biomass volumes to be processed to obtain the same amount of biochar, consequently reducing the disposal volume required in landfills, although gas emissions could increase, and as such this presents a challenging trade-off. A good strategy is to add supporting biomass to increase the carbon content of the final biochar [64].

2.2. Green Routes for the Synthesis of Nanoparticles

Generally, nanoparticles are produced using harmful chemicals and highly sophisticated devices [67]. This could lead to the residual presence of chemicals in the final product and also increases the cost of production. To overcome such issues, green syntheses represent the best routes for the synthesis of nanoparticles and are typically relatively cheap and free from the use of harmful chemicals [68]. Recently, different biological components have been considered in order to elucidate the best components for the synthesis of different nanoparticle classes. The major biological components include marine organisms (green algae, brown algae, and seaweeds), micro-organisms, and plants (leaves, flowers, and fruits extracts) [69–73], as depicted in Figure 2.

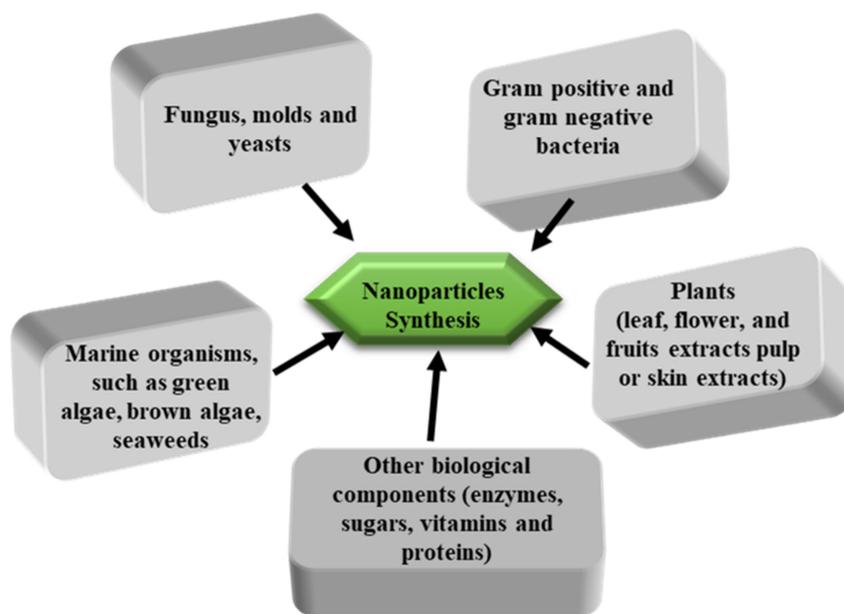


Figure 2. The major components used in the green synthesis of nanoparticles.

The synthesis of different metal and metal oxide nanoparticles by using some of the biological components mentioned above, from different sources, is represented in Table 2.

Generally, all the biosynthesis procedures are very simple. The methods of the aforementioned examples for synthesis generally consist of a few relatively simple steps. In general, when considering plant material as the biological source, plant material extracts are mixed with a precursor solution and kept for reaction from about 24 to 48 h to obtain a precipitate [84–89]. Plant extracts contain alkaloids, flavonoids, and other biological components which convert precursors into metal hydroxides or oxides. The obtained hydroxides are dried to obtain metal nanoparticles. The same procedure is followed for all the biological materials in biosynthesis after the stripping of extracts from them.

Table 2. Some representative examples of different metal and metal oxide nanoparticles synthesized from bacteria, fungi, and plants.

N.	Source Material	Nanoparticle	Size (nm)	Shape	Purity (%)	Ref.
1	Bacterium (<i>Bacillus cereus</i>)	Ag	20–40	Spherical	80	[74]
2	Bacterium (<i>Desulfovibrio desulfuricans</i>)	Au	5–50	Nanorods or nanoprisms	80	[75]
3	Bacterium (<i>Aquaspirillum magnetotacticum</i>)	Fe ₃ O ₄	10	Octahedral prism	70	[76]
4	Bacterium (<i>Shewanella oneidensis</i>)	UO ₂	-	-	-	[77]
5	Bacterium (<i>E. coli</i>)	CdS	2.9	Spherical	100	[78]
6	Fungus (<i>Rhizopus nigricans</i>)	Ag	13–74	Spherical	100	[79]
7	Fungus (<i>Verticillium luteoalbum</i>)	Au	~100	Spherical, triangular, hexagonal	-	[80]
8	Fungus (<i>Fusarium oxysporum</i>)	Au-Ag alloy	8–141	Spherical	98	[81]
9	Fungus (<i>Aspergillus terreus</i>)	ZnO	8.2	Spherical	100	[82]
10	Fungus (<i>Aspergillus flavus</i> TFR7)	TiO ₂	12–15	Spherical	80	[83]
11	Plant (<i>Acalypha indica</i>)	Ag	20–30	Spherical	80	[84]
12	Plant (<i>Avena sativa</i>)	Au	25–85	Spherical, triangular, hexagonal	78	[85]
13	Plant (<i>Gardenia jasminoides</i> Ellis)	Pd	3–5	Spherical, rod and three-dimensional polyhedral	80	[86]
14	Plant (<i>Medicago sativa</i>)	FeO	1–10	Spherical	-	[87]
15	Plant (<i>Sedum alfredii</i> Hance)	ZnO	53.7	Spherical	-	[88]
16	Plant (<i>Aloe barbadensis</i> Miller)	In ₂ O ₃	5–50	Spherical	-	[89]

The biosynthesis of nanoparticles utilizing bacteria can be performed in two major ways, where the first is intracellularly mediated synthesis and the second is extracellularly mediated synthesis. For example, the intracellularly mediated synthesis of AgNPs using *Bacillus cereus* was investigated in [74]. In this work, 1 g of bacterial biomass was mixed with a silver nitrate solution and incubated for 120 h, leading to the formation of AgNPs. In another method, *Desulfovibrio desulfuricans* was found to precipitate gold nanoparticles over its cellular membrane surface [76]. Magnetic Fe₃O₄ nanoparticles can be synthesized inside the cells of *Aquaspirillum magnetotacticum* by just providing the necessary precursor nutrients, where the bacteria then act as nanoparticle factories [76]. Similarly, an extracellular synthesis of nanoparticles was reported to produce UO₂ nanoparticles using *Shewanella oneidensis* [77]. Furthermore, fungal extracellular extracts are also often utilized for the synthesis of nanoparticles. For example, *Rhizopus nigricans* was utilized to synthesize Ag nanoparticles with a resulting size range of 13–74 nm [79]. *Verticillium luteoalbum* fungal extracellular extracts have also been found to produce gold nanoparticles in the order of 100 nm in size when simply mixing with an auric chloride solution [79].

A recent emerging niche is the microbially assisted synthesis of conducting polymers, mainly polypyrrole, which sufficiently interacts with cell walls to improve charge transfer [90]. It well-known that cell wall proteins do act as the main actors for exoelectrogenesis in microorganisms [91], but the direct transfer of electrons to an electrode surface needs a boost to become more efficient. Andriukonis et al. [92] and Ramanavicius et al. [93] have recently demonstrated that it is possible to polymerize pyrrole to obtain polypyrrole (PPy) via *S. Cerevisiae* yeast cells. The polymerization exploits the redox ability of the yeast

strain and the redox cycling of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$. The improved quantification methodology that was exposed was able to analyze the changes in mechanical properties of the cell walls and the biocompatibility of PPy. Later, it was confirmed that these in situ modifications of the cell wall by the conducting polymer improved the direct charge transfer [16,90] at the nanoscale level. In another work, *Streptomyces* ssp. bacteria were used for a totally natural and green synthesis of hollow PPy microspheres [94]. It was reported that no organic solvents and additives were used, and that the time needed to observe the sphere formation was 10 days. An environmentally friendly PPy form conjugated with a microorganism was obtained by a green method using *Aspergillus niger*, [95] a fungi that can release glucose oxidase and initiate PPy formation via an enzymatic reaction, as shown in Figure 3.

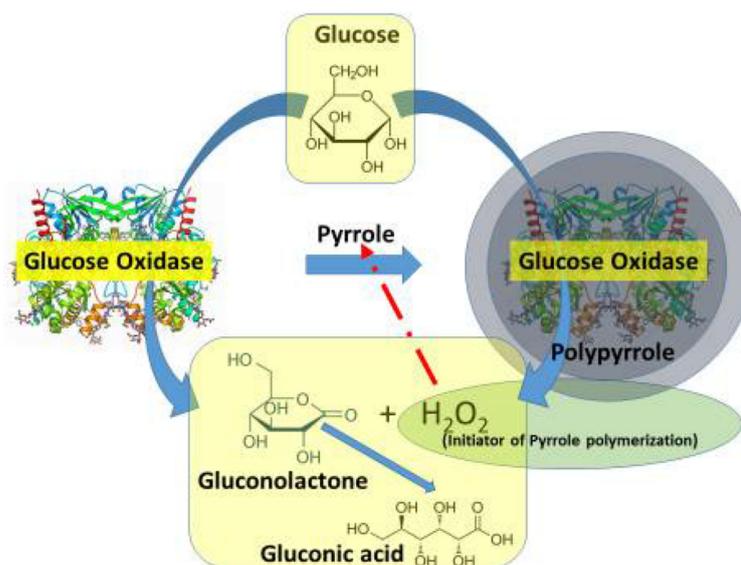


Figure 3. Biopolymerization of PPy in the presence of glucose oxidase, hydrogen peroxide, and glucose. Reproduced from [15] under a CC BY 4.0 license.

The authors compared this method with the chemical polymerization method and reported similar electrochemical properties for the obtained PPy chains. A similar result was obtained by the same group [96] when using a white-rot fungal strain from *Trametes* ssp., where the method was based on laccase enzyme release. In both cases, successful biopolymerization depended on the optimal concentration of the initiating enzyme, pH, and surrounding environment. Cultures with sufficient intracellular space provided the best PPy cell wall conjugate quality.

Several green synthesis methods are available for the production of a wide range of nanoparticles; however, there are also several limitations with the use of these green processes. The first major challenge is product recovery, which is critical to reduce impurities [86]. The second major challenge is size control, where there is a knowledge gap in the exact mechanisms of various synthesis procedures, as well as the correlations with particle size, which is still being discovered [87]. The third major challenge is the time-consuming nature of green synthesis, which depends on the specific bacteria and materials used [88].

2.3. Other Sustainable Unconventional Sources for Synthesis of Nanoparticles

Based on a recent environment survey program conducted by the United Nations, it was reported that around 11.2 billion tons of waste is produced every year, which leads to serious environmental pollution that is toxic to human health [97]. The majority of produced waste is classified as electronic waste (electronic boards, circuit boards, copper cables, etc.) and industrial waste (wastewater, rubber tires, batteries, etc.) [98]. These wastes can be converted into useful nanomaterials by using ad hoc recovery processes in

order to support the sustainable production of metal nanoparticles and, at the same time, the recycling and smart disposal of huge amounts of waste (Figure 4).

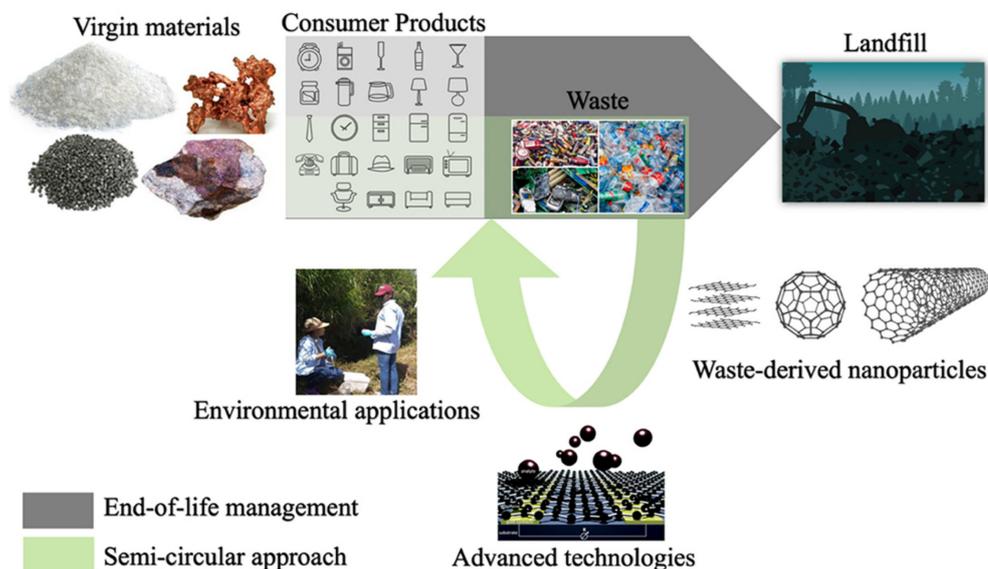


Figure 4. Conceptualization of recovery from electronic and domestic waste products as an alternative source of nanomaterials. Reproduced from [98] under a CC BY 4.0 license.

Cu_2O can be synthesized from discarded printed circuit boards using PVP as a stabilizer in an electrokinetic process. The prepared nanoparticles have been found to have an average size of 5 to 40 nm [99]. Cu nanoparticles with a particle size of about 100 nm with cylindrical and/or spherical morphologies have been obtained from the recovery of automobile residues [100]. Cu nanoparticles with a spherical size of 20–50 nm have also been synthesized from discarded circuit boards through a microemulsion process [101]. Copper-tin (Cu-Sn) nanoparticles have been synthesized using old computer motherboards with resulting particle sizes of about 500 nm [102]. The possibility to use electronic waste as a source of metal nanoparticles is very attractive due to the high available volume of electronic waste that is regularly produced, but the effective introduction of this practice is severely limited by the low demand for nanoparticles in commercial use, such as in MFCs (which is not a mature and widely commercialized technology) or other devices, as well as the high costs of the recovery processes. Hence, a clean and economically feasible process is required that can convert these waste products into more sustainable value-added materials.

Another large share of waste with high re-utilization potential is represented by plastics, metals, and batteries. Some studies have investigated such utilization for years to recover various metals and metal oxides as particles or nanoparticles. Most recently, copper, silver, and copper/silver nanoparticles of a 50–80 nm size were synthesized utilizing metalized acrylonitrile butadiene styrene (ABS) plastic waste [103]. Nanocrystalline γ - and α -alumina nanoparticles of about 36 to 200 nm in size were synthesized using aluminium foil waste by a co-precipitation method [104]. Furthermore, nanosized α - Fe_2O_3 particles with sizes ranging from 22 to 86 nm have been synthesized using ferrous sulfate waste obtained from the titanium industry [105]. Lead oxide nanoparticles of about 200 nm in size have been obtained from battery anode waste via a thermal evaporation method [106]. ZnO nanoparticles of about 100 to 300 nm in size have also been produced from zinc manganese battery waste by a vacuum evaporation method [107]. The sustainability of all of these processes relies upon the use of secondary raw materials and the production of waste originating from high-impact sectors like metallurgy, batteries, and plastics. The development, efficiency, and penetration of these technologies needs to be pursued in order to increase economic feasibility and profitability.

3. The Use of Green and Sustainable Nanoparticles and Materials in MFCs and MECs

Due to advancements in nanoscience and nanotechnology, different classes of nanomaterials have been synthesized for MFCs and MECs. The major broad categories of nanomaterials include metal oxide and metal-based materials, carbon-sourced nanomaterials, and conjugated or composite materials.

In this section, these nanomaterials, which have been obtained from green and sustainable processes/raw sources to the maximum extent possible, are showcased and considered in terms of their application in electrodes for MFCs and MECs. Conjugated or composite materials are not treated separately here but are instead included in the first two main classes because it is difficult to find real green and sustainable examples.

Works where green and sustainable nanoparticles have been synthesized, characterized, and employed in MFCs/MECs have been carried out, although sometimes the whole approach could not be completely green and sustainable in all of the required steps; however, the mentioned classes of nanomaterials and their impacts on device operations are reported in the context of the vision of substituting non-green nanoparticles (e.g., available as/or synthesized from commercial chemicals) with nanoparticles of the same kind, except obtained from green and sustainable processes as described above.

As the absolute values of power density or methane/hydrogen yields are dependent also on the substrate, inoculum, media composition, and cell architecture, which each may differ from article to article, what more important is a relative boost in performance for each condition between a device with the use of a nanomaterial in contrast to a device without one.

3.1. Metal Oxide and Metal-Based Materials

Metal oxides and metal nanomaterials have a high capacity to easily interact with the biological components, and, due to this, they can easily support electron transport towards electrodes. Electron transport is a key component for improving the efficiency of MFCs, especially on the anode side in order to achieve direct electron transport (DET) due to the intimate electrical bridging effect that can be obtained by stacking the carbon anode support, metal nanoparticles, and grown biofilm on top [32,108,109]. It is true that transition metals and transition metal oxides have a good and recognized catalytic activity [110] for the ORR (in MFCs) [111] and OER/HER (in MECs) [112], but this activity is limited in microbial devices by the temperature and pH, whereas the electrical bridging effect is not, showing a similar effect for bacteria with different DET characteristics [113]. Recent research by Wu et al. [114] showed that gold nanoparticles with *S. oneidensis* MR-1 bacteria could be very effective, potentially generating a power density of about $178.34 \pm 4.79 \text{ mW} \cdot \text{m}^{-2}$, which represents a 56.11% greater performance than that of the control cells. Another study of the biosynthesis of Pt/Pd bimetallic nanoparticles obtained by *E. coli* was also found to be very effective for expressing microbial NP biointerfaces for ORR, but the approach was not tested for MFC applications [115]. Saravanakumar et al. have shown that the effectiveness of Au and Ag nanoparticles obtained from *Trichoderma* sp. is effected for catalysis in MFCs under the aid of anaerobic conditions [116]. They have shown that the highest current extracted by the biosynthesized material was 342.80 mA. Plant-mediated (*Amaranthus dubius*) synthesis of iron oxide nanoparticles was found to be very effective in the MFC and showed a greater resulting power density of $145.5 \text{ mW} \cdot \text{m}^{-2}$ when compared to the control cell, which was deficient in nanoparticles [117]. Eucalyptus leaves were also used for the production of zerovalent iron nanoparticles so that they could be used for MFC applications [118]. The obtained results proved that the obtained zerovalent iron nanoparticles greatly improved the MFC performance. *Citrobacter* sp.-mediated synthesis of Pd nanoparticles has been shown to be very effective for MFC applications [119], where a higher power density of about $539.3 \text{ mW} \cdot \text{m}^{-3}$ was achieved. In another study by Tahernia et al., biogenic Pd nanoparticles were synthesized by using *S. oneidensis* MR-1, which was very effective and increased the performance by up to 75% [120]. Karim et al. showed that biogenic Au nanoparticles are also very effective for improving the performance of MFCs [121];

however, not all metal nanoparticles have the same effect as an electrical bridge in MFC anodes. It was reported in [122] that the highest power density in MFCs with a metal NP-decorated carbon anode was obtained with Ni nanoparticles rather than Au or Pt. This is potentially a great result that is worth of further investigation and development, as noble or precious metals could be efficiently substituted and cheaper metals might be preferred.

An interesting comparative list of precious/non-precious metal/metal oxide nanomaterials used in MFCs is briefly reported in Table 3. The green or sustainable origins of the nanomaterials are also indicated.

Table 3. Metal and metal oxide nanomaterials used in MFCs and their relative performances.

N.	Nanomaterial	Green/Sustainable (Y/N)	MFC Type	Component	Best Power Density (mW m ⁻²)	Control Power Density (mW m ⁻²)	Ref.
1	Pd NPs on carbon cloth	Y	Dual chamber	Anode	605	534	[123]
2	W/Co scraps	Y	Dual chamber	Cathode catalyst	36 W m ⁻³	3 W m ⁻³	[124]
3	Pd NPs on carbon cloth	Y	Dual chamber	Anode	824 ± 36		
4	MnO ₂ NPs on carbon cloth	N	Dual chamber	Anode	782 ± 37	680 ± 28	[125]
5	Fe ₃ O ₄ NPs on carbon cloth	N	Dual chamber	Anode	728 ± 33		
6	Fe nanorods	N	Dual chamber	Cathode catalyst	66.4 mW m ⁻³	10.6 mW m ⁻³	[126]
7	V ₂ O ₅ nanorods	N	Single chamber	Cathode catalyst	1073 ± 18	2067 ± 25	[127]
8	Au NPs on carbon paper	N	Dual chamber	Anode	346	174	[128]
9	MnO _x nanorods	N	Single chamber	Cathode catalyst	772.8 mW m ⁻³	236.7 mW m ⁻³	[129]
10	WO ₃ NPs on carbon felt	N	Single chamber	Anode	1280	490	[130]

From this table and the previously described works, it is possible to conclude that inserting metal or metal oxide nanoparticles in MFCs can effectively increase the resulting performance (except for the singular case of V₂O₅ nanorods in Table 3). The absolute electricity generation depends on the specific substrate, cell design, and operating conditions, but improvements can be obtained if either the nanomaterial is used as an anode decoration or as a cathode catalyst. For example, it is well-known that the extent of the improvement for NP anode decoration is greatly dependent on the size and shape [131], rather than NP loading, as it happens for cathodes. In Table 3, it was intentionally shown that the ratio between recent studies using/non-using green and sustainable NPs is still low and that non-precious metal/metal oxide NPs can compete with Au, Pd, and Pt NPs (Pt-based electrodes are often used as controls, where they are hence represented appropriately in the power density of control column of Table 3).

Conjugated or composite materials have also been shown to improve the performance of microbial electrochemical devices nowadays, which has led to advancement in this field with the aim of designing new materials [132]. Such aims have often been based on composite (metals/oxides/carbon-based) or conjugated (polymers, layer-by-layer structures) materials, mainly to exploit the interactions between carbons, polymers, and the particular

organism [133]. Qiao et al. developed mesoporous TiO₂/polyaniline composites and used them as anode materials in *E. coli*-based MFCs [134]. The MFC demonstrated a two-fold increase in the power density (1495 mW·m⁻²). Ma et al. showed that graphitized carbon and iron oxide nanocomposites are better cathode materials for improving the performance of MFCs [135]. Improved efficiency and higher stability were achieved after performance studies. Di Palma et al. showed that polyethersulfone/Fe₃O₄ nanocomposites can be an excellent membrane for MFCs [136]. These works are reported as examples as the metal oxide NPs that have been mentioned can be easily prepared in more than one of the green and sustainable synthesis routes detailed above.

A considerable amount of literature can be found regarding metal NPs employed as cathode catalysts in MECs for hydrogen production. For example, the use of Pd NPs, both in traditionally or bio-synthesized forms, has been reported since a decade ago [137,138]. Even a non-precious metal-based catalysts such as Fe@C and derivatives have been used in a MEC for hydrogen production [139], but the production was lower than that obtained with Pt-based catalysts, although the Fe-based catalyst was very cheap; however, since then, the challenges are still the maximization of hydrogen production, optimizing catalyst activity, and elucidating economic feasibility. The development of non-precious metal/metal oxide nanocatalysts, as well as the adoption of green syntheses and the use of sustainable sources, will help to overcome these existing challenges.

Briefly, some recent advances are reported here. Kim et al. [140] demonstrated an interesting hydrogen production of 0.95–1.55 m³ H₂ m⁻³ d⁻¹ from Makgeolli wastewater in a single chamber MEC without a membrane when using non-precious Cu₂O and MoS₂ NPs as cathode catalysts. In another interesting comparative work [141], several metal NP were loaded on carbon felt cathode with a hot-pressed membrane in a single chamber MEC using acetate as substrate. The results showed that when Pt/C, PtNi/C, and Ni/C cathode MECs were operated at the same low applied voltage of 0.4 V, hydrogen production was more or less the same (0.064–0.068 m³ H₂ m⁻³ d⁻¹), suggesting that, in these operating conditions, non-precious metal NPs can substitute Pt; however, the catalysts were prepared traditionally in both works. Looking at recent biogenic metal NPs, Wang et al. [142] investigated and compared Pd NPs deposited in situ on a carbon cloth cathode via an electrochemical or bio-assisted (*Shewanella oneidensis* MR-1) process. Under an applied voltage of 0.8 V, the biogenic Pd NPs produced 0.0618 m³ H₂ m⁻³ d⁻¹ of hydrogen, while the non-biogenic Pd NPs were limited to 0.0385 m³ H₂ m⁻³ d⁻¹. The authors suggested the addition of Nafion as a binder to strengthen the bond between the carbon fibres and the biogenic Pd NPs as, in the long term, the adherence and durability of electrochemically deposited Pd NPs is better as a result; however, it should not be forgotten that some precious metal NPs, like Ag, have a non-negligible antimicrobial effect and not all bacteria can tolerate such metals in the same way [143]. Conversely, some non-precious metal/metal oxide NPs, like magnetite, can improve and accelerate electrochemical reactions in MEC bioelectrodes [144]. In a stimulating work, Yuan et al. [145] demonstrated the possibility to prepare a “multi-catalyst” including several elements (i.e., C, O, S, P, Cr, Ni, Fe, Cu) distributed at the nanoscale by simply thermally treating an electroplating sludge, i.e., a hazardous waste that is very difficult to dispose of. Another interesting catalyst (unfortunately prepared with standard chemicals and methods) proposed recently is a Ni foam cathode decorated with NiMoO₄ NPs [146] to produce hydrogen at an interesting rate (0.12 L H₂ L⁻¹ d⁻¹) in a dual-chamber MEC fed by sugar industry wastewater. In conclusion, there are already many valid examples of metal/metal oxide NPs used in MECs, but systematic efforts aiming to identify a NP synthesis approach that is green, sustainable, and economically feasible should be intensified.

3.2. Carbon-Sourced Nanomaterials

Carbon-based nanostructured materials have also been used nowadays for application in the field of MFCs, progressing from their simple use as cheaper non-structured materials. Although carbon-based biomaterials can be used either as anodes or cathodes, usually, the

oxygen-defective and activated structure of biochar is often used as the cathode material, due to the high cost-share of this component. Biochar products are usually compared with Pt-C loaded carbon papers, cloths, or felts as these are the commercial and reference benchmark materials for cathodes.

Ngaw et al. showed that carbon nanotubes and graphene are very effective materials for use in MFCs [147]. The higher surface areas in graphene sheets and carbon nanotubes facilitate electron transport and thus better effectiveness in MFCs. Sharma et al. showed that carbon nanotubes and *E. coli* can be used together in MFCs [148]. The incorporation of carbon nanotubes has found the increase in the power density to be in the order of 6 times, i.e., $2470 \text{ mW}\cdot\text{m}^{-2}$ when compared to the $386 \text{ mW}\cdot\text{m}^{-2}$ of control cells. Quantum carbon dots have also been found to enhance MFC performance [149]. The improved performance in power density was 22.5% with that of the carbon quantum dots. Unfortunately, even if they can preserve catalytic activity [150], these carbon-based nanomaterials are expensive and are not derived from sustainable sources and processes.

Differently from metal/metal oxide NPs, the use of secondary raw material sources, mainly waste biomass, to prepare green and sustainable biochar products is more mature and has been well-reported through the years [151]. Briefly, continuing from Table 1, the performance of biochar materials from various sources is listed in Table 4. The biochar materials were discovered to be useful as self-supported anode electrodes to improve microbial adhesion vs. commercial carbon cloth/felt or as cathode catalyst powders to be dispersed on the cathode support vs. Pt/C commercial catalysts.

Table 4. Comparative performance of biochar materials from biomass as designed for MFC or MEC applications.

N.	Source Material	MFC/MEC Type	Component	Best Power Density (mW m^{-2})	Control Power Density (mW m^{-2})	Ref.
1	Water hyacinth (<i>Eichhornia crassipes</i>)	Single chamber	Cathode catalyst	12.3	24.7	[50]
2	Bananas	Single chamber	Cathode catalyst	528.2	695	[51]
3	Alfalfa leaves	Single chamber	Cathode catalyst	1328.9	1337.7	[52]
4	Corn cob	Single chamber	Cathode catalyst	458.8 mW m^{-3}	-	[53]
5	Green algae (<i>Spirogyra</i>)	Dual chamber	Anode electrode	408 ± 12	62	[54]
6	Pinewood lumber	Single chamber	Cathode catalyst	146.7	156.8	[55]
7	Lotus leaves	Single chamber	Cathode catalyst	511.5 ± 25.6	486.7 ± 23.3	[56]
8	Sewage Sludge	Single chamber	Cathode catalyst	500 ± 17	625 ± 17	[57]
9	Coffee waste	Single chamber	Anode electrode	3927	975	[58]
10	Kapok tree fibres	Single chamber	Anode	1738.1	1689.8	[59]
11	Eggplant	Single chamber	Cathode catalyst	667	621	[60]
12	Rice husk	Single chamber	Cathode catalyst	317.7 ± 0.4	367.8 ± 7.8	[61]
13	Mixed microalgae	Dual chamber	Cathode catalyst	$12.86 \pm 0.35 \text{ W m}^{-3}$	$13.52 \pm 0.05 \text{ W m}^{-3}$	[62]

Table 4. Cont.

N.	Source Material	MFC/MEC Type	Component	Best Power Density (mW m ⁻²)	Control Power Density (mW m ⁻²)	Ref.
14	Watermelon rind	Single chamber	Cathode catalyst	262 mW m ⁻³	-	[63]
15	Sewage sludge/coconut shell	Single chamber	Anode and cathode catalysts	969 ± 28	1069 ± 15	[64]
16	Sludge from wastewater treatment	Single chamber	Anode catalyst	(CH ₄ prod.) 110 mL _{CH₄} g ⁻¹ VS _{sadded}	(CH ₄ prod.) 80 mL _{CH₄} g ⁻¹ VS _{sadded}	[65]
17	Coconut shell	Dual chamber	Anode catalyst	(COD rem.) 71.4%	(COD rem.) 59.6%	[152]
18	Sugar industry filter cake	Dual chamber	Anode catalyst	(H ₂ prod.) 3.6 ± 0.4 mL _{H₂} L ⁻¹ h ⁻¹	-	[153]
19	Straw	Dual chamber	Anode catalyst	(COD rem.) 87.94%	(COD rem.) 57.58%	[154]

The increase in maximum power density appears to be greater when biochar materials are used as the anode because the cathode catalyst in those studies is usually Pt, and also because the adhesion, growth, and direct interspecies electron transfer (DIET) [155], compared to electron transfer intermediated by dissolved or immobilized mediators [156,157] is greatly enhanced when using biochar, whereas the use of biochar doped with transition metals and nitrogen atoms does not always show a straightforward improvement of power density when compared to a control (e.g., Pt/C) as the main advantage lies in the substitution of Pt with low-cost catalysts to increase the cost-effectiveness rather than an absolute increase in power production.

Carbon-based composites are widespread in microbial electrochemical devices. For example, Esmaeili et al. showed that biocomposites based on K-carrageenan/polypyrrole could be a better material to be used as a cathode in an MFC [158]. Hernández et al. showed that a PEDOT/nickel/graphene nanocomposite is a better composite for improving the performance of a MFC [159]. In a recent study, CoO/nitrogen/carbon nanotube-based nanocomposites have been demonstrated to be very effective cathode materials for use in MFCs. A maximal achieved power density of 1260 mW·m⁻² was observed [160]. Many of the biochar materials reported here can conveniently substitute graphene-based supports as they have a sufficient nanostructure, high surface area, active sites, and natural biocompatibility with the pertinent microorganisms. This is a very interesting field for investigation, especially for application in MECs.

4. Conclusions and Future Development

The collected and discussed literature demonstrate that many options have been explored to obtain major nanoparticle types by using either natural resources, waste materials, or green processes. This review has been carried out in order to encourage future research studies on these topics by covering the still present lack of literature for some unsolved issues concerning reliability and scalability, rather than proofs of concepts, as such proofs are already solid enough and accepted in the scientific community due to the high number of publications in the field.

The purity, quality, and size of the obtained nanoparticles is often good enough for the target application. Depending on the particular synthesis environment, different sizes and morphologies can be obtained, but the exact control of these parameters needs to be investigated further to unveil the precise mechanisms occurring in these complex

systems. This is particularly relevant when bacteria are used. Another bottleneck for such biosynthesis is the long time-to-product duration that is required, as sometimes two to three days are required to complete a reaction, apart from the separation and extraction steps. More reproducible and reliable processes are those based on mechanical or physical operations, but they appear to not be sustainable, even if they can recover, harvest, and valorize waste products. The gap for these approaches to reach industrial use is not narrow, and the missing steps seem to be a reliable scaling process for high throughput and the cheap production of valuable nanoparticles, as well as the standardization of sizes and morphologies and target properties like porosity and electrical conductivity, etc.

On the other hand, these types of nanomaterials can be efficiently used in MFCs and MECs with benefits from the point of view of economic feasibility. For example, MFCs containing nanocarbon materials or metal NPs from secondary sources have a potential power density boost ranging from a few hundred to a few thousand $\text{mW}\cdot\text{cm}^{-2}$. This implies that cheap and reliable production and the availability of such sustainable nanomaterials is crucial to propelling both fields further towards industrialization. Even for these devices, solid demonstrations of scaled-up systems that are capable of producing and supplying a sufficient amount of energy (MFC) or the production of convenient value-added products (MEC) are necessary. Indeed, there is a lack of works dealing with the intense use of biochar materials as bifunctional catalysts (i.e., anode and/or cathode) in MECs, considering that biochar materials have been widely proven to positively interact with biofilms. The progress described so far regarding the basic understanding, synthesis schemes, characterization, and testing of many kinds and types of sources, nanoparticles, and applications is very promising for further development of this field with the aim of a greener and cleaner utilization of material sources and resulting energy production.

Author Contributions: Conceptualization, D.F. and G.K.; methodology, D.F. G.K.; resources, Y.K. and E.-B.C.; writing—original draft preparation, D.F., G.K.; writing—review and editing, Y.K. and E.-B.C.; visualization, D.F.; supervision, Y.K., E.-B.C.; funding acquisition, Y.K. and E.-B.C.; All authors have read and agreed to the published version of the manuscript.

Funding: Domenico Frattini was supported by Brain Pool Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (Grant No. 2017H1D3A1A01013887). E.-B. Cho and Gopalu Karunakaran were supported by Brain Pool Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (Grant No. 2018H1D3A1A01037054). Gopalu Karunakaran also acknowledges supports under the Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education (NRF-2019R1I1A1A01062458).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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