Electronic Supplementary Material (ESI) for Materials Horizons.

Microbial Electrosynthesis: Carbonaceous Electrode Materials for CO_2 Conversion

Supporting Information

Table S1. A Comparison on the key features of various technologies for CO_2 conversion

CO_2 conversion methods	Thermocatalysis	Photoelectrochemical	Photocatalysis	Electrocatalysis	MES
Main products	MeOH, CH_4, C_{2+} products	Formate, HCHO, HCOOH, CH_4, CH_3OH, CH_3CH_2OH	MeOH, CH_4	C_{2+} products	Organic acids, alcohols, fatty acids, lipids, etc.
Advantages	Large output of products. Tandem routes for value-added products. Appropriate to use at the industrial level.	Product selectivity can be controlled. The utilization of renewable solar energy. Operating at room temperature and pressure.	Simple reactor designs. Utilization of sunlight. Operating at room temperature and pressure.	An effective method of storing electrical energy. Operating at room temperature and pressure.	Unaffected by system fluctuations. Higher conversion efficiency. Capable of self-healing. Operating at room temperature and pressure. Good product selectivity.

Challenges	The consumption of excessive energy. Poor product selectivity. The chances of coke formation are higher. High temperature and/or pressure operations are required.	Lack of stability. Low yield and selectivity.	Low energy efficiency. Poor product selectivity and stability.	Requires high overpotential. More complex reaction pathways. The liquid electrolyte has a low CO_2 solubility, which reduces the current density. Poor yield and product selectivity.	Requires high overpotential for long-chain products. Rising costs are experienced because of the high energy required to activate the bacterial pathway for autotrophic development Needs a particular growing medium. Membrane biofouling is susceptible.

Table S2. The key findings of the state-of-the-art of carbonaceous electrodes for MES-based CO_2 conversion.

Electrode Material	Surface area	Microbe/Medium	Biofilm thickness	Faradaic /Coulombic Efficiency (%)	Current Density	Over potential required for the product yield	Product Yield	Reference
CNT-MXene	8.66 m^2 g^{-1}	Mixed microbial consortium	___	7	− 324 mA m^{-2}	-800 mV (vs. Ag/AgCl)	Butyrate (780 mg/L)	Tahil et al., 2022 [1]
Graphene-CNTs	344.17 m^2 g^{-1}	*Clostridium ljungdahlii* (DSM13528)	___	83 ± 11	595 ± 77 mA m^{-2}	-600 mV vs. SHE	Acetate (278 ± 44 mM m^{-2} d^{-1})	Han et al., 2019 [2]
CF/rGO-Magnetite	0.824 cm^{-2}	*Rhodopseudomonas palustris* TIE-1	___	9.05 ±0.2	−11.7± 0.1 µA cm^{-2}	−1.212 V vs. SHE	Polyhydroxybutyrate (91.31 ± 0.9 mg l^{-1})	Rengasamy et al., 2020 [3]
Graphite and Carbon cloth	49.5 cm^2	*Sporomusa ovata*	___	80	-20 A m^{-2}	−0.9 V vs Ag/AgCl	Acetate (∼11 g/L)	Bajracharya et al., 2022 [4]
Co-Pi/GF		*Rhodobacter sphaeroides* 2.4.1	___	58.3	___	−1.0 to +1.0 V (vs. Ag/AgCl)	Malate (1.7 ± 0.2 mg L^{-1}) Succinate (5.7 ± 0.1 mg L^{-1}) Total carotenoids (1.7 ± 0.1 mg L^{-1})	Fitriana et al., 2022 [5]
Activated carbon fiber-supported g-C_3N_4-$NiCoWO_4$	65 m^2/g	*Escherichia coli*	___	56.6	640 mA/m^2 (light) 316 mA/m^2 (dark)	−1.0 V vs AgCl	Formate (12.8 mM)	Gupta and Verma, 2022 [6]
N-doped Fe_3O_4@CDs	___	*Geobacter sulfurreducens*		30	~8 mA	−1.0 V vs AgCl	Methane (222.52 mL)	Cheng et al., 2022 [7]
Carbon fibers	___	*Methanobacterium*	___	68.5 ± 4.8	___	−1.0 V vs. Ag/AgCl	Methane (298.0 ± 46.7 mL L^{-1} d^{-1})	Zhang et al., 2022 [8]
Carbon brush	___	*Methanothrix*	___	18.8 %	∼4.07 × 10^{-4} A/m^2	−0.5 V vs. SHE	Methane (5.2 mmol day^{-1})	Liu et al., 2020 [9]

RVC	___	Mixed microbial consortium	5 ± 2 µm	~100	-37 A m^{-2}	-0.85 V (vs SHE)	Acetate (1330 g m^{-2} day^{-1})	Flexer and Jourdin, 2020 [10]
MXene coated Biochar	64.05 m^2 g−1	*Firmicutes* (66 %), *Proteobacteria* (13%), and *Bacteroidetes* (12%)	___	12	-239.4 m^{-2}	−800 mv (vs AgCl)	Butyrate (~1000 mg L^{-1})	Tahir et al., 2021 [11]
Carbon paper	___	Enriched anaerobic sludge	___	74.15 ± 5	14.26 A m^{-2}	-0.85 V vs SHE	Acetic acid (197.50 ± 10 g m^{-2} day^{-1})	Answer et al., 2021 [12]
3D bioprinted Carbon cloth	___	*Sporomusa ovata*	~1 mm	62.7±15.4	14.8 A m^{-2}	−800 mV vs Ag/AgCl	Acetate (104 g day^{-1} m^{-2})	Krige et al., 2021 [13]

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Table S3. Comparison of advantages and disadvantages of various carbonaceous electrode materials

Cathode Material	**Advantages**	**Disadvantages**
Carnon nanotubes	High specific surface area, excellent mesopore density, and large current-carrying capacity.	Inadequate catalytic activity
Graphene	Promotes bacterial proliferation, large surface area, great electrical conductivity, high carrier mobility, exceptional intrinsic mechanical strength, and chemical stability.	Fragility in oxidative conditions
Graphene oxide	Promotes the development of a thick electroactive biofilm.	Less electrical conductivity, the more the chances of agglomeration.
Reduced Graphene oxide	Enables highly efficient bidirectional electron transfers among both bacteria and electrodes, cheaper, and good surface area.	Less conductivity than graphene, poor water affinity, and dispersibility.
Graphite	Affordable, porous conductive material, good biofilm adherence, preferential electroactive bacterium attachment, conductive.	Low oxidation rate, lower power density, strong contact resistance, and hydrophobicity.
Graphite felt	Good biofilm growth, surface area, porous nature, encourage direct electron transfer, cost-effective, reasonably high overpotentials.	Challenges with polarisation
g-C_3N_4	Superior chemical stability, relative affordability, and intriguing electronic band structure.	Minimal surface area and less charge carrier movement.
Activated carbon	Significant surface area for microbial colonisation,	Can result in clogs, and Combustion danger

	cheap, high surface area, is readily available in market, is simple to process, has high porosity, and is extremely scalable	
Carbon felt	Sufficient contact area and volume for microbial colonization, transportation of microbes, and increased electroactivity.	Reduced catalytic efficiency and anode conductivity.
Carbon dots	Development of promising nano-bio interfaces by conjugation with biomolecules, great photostability, compact diameters, strong biocompatibility, and minimal toxicity.	Agglomeration.
Carbon fibers	Fibrous structure, high porosity, quick adsorption kinetics, and porous storage capacity.	Expensive, and complicated synthesis procedures.
Carbon brush	Porous surface area, low resistance, and good electrical conductivity. The dense morphology can prevent the biofouling of electrode materials.	Increased interface resistance and poor current density.
Reticulated vitreous carbon foam	Highly porous morphology, excellent conductivity, and large surface area promote mass dispersion and microbial development, low price, and simple handling.	Poor product yield and selectivity
MXenes	Exceptional conductivity, ion intercalation behaviour, and hydrophilicity.	Not enough ecological resilience.
Biochar	High porosity, low cost for physical activation,	Chemical activation is expensive

	and renewability.	