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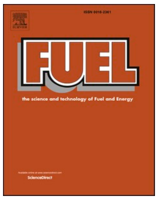

Review article

Bioelectrochemical conversion of carbon dioxide into hydrocarbons and other sustainable renewable fuels

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ABSTRACT

Bioelectrocatalysis provides sustainable and efficient methods for generating chemical compounds from CO_2, thereby reducing CO_2 emissions. Enzymes and microorganisms have been utilized to transform CO_2 into carbon-containing compounds with enhanced selectivity and catalytic efficiency. Challenges related to enzyme immobilization, the application of redox mediators, and the incorporation of conductive nanomaterials, which enhance direct electron transfer, are discussed. However, charge transfer efficiency significantly limits the efficiency of enzymatic bioelectrocatalysis. Therefore, the advancement of bioelectrocatalysis based on the application of nanocatalysts and/or charge transfer mediators is an important issue during the development of electrochemical systems dedicated to CO_2 reduction. Modifications of electrocatalysts and bioelectrocatalysts by homo- or heterostructures, which advance electron transfer kinetics, are discussed. Strategies that improve compatibility between electrode materials and biomaterials are reviewed. The application of solar-powered photoelectrochemical techniques, which are suitable for electrocatalysis and biocatalysis, is outlined. These techniques enable the synthesis of valuable chemicals from CO2 under favorable and cost-effective conditions. Prospective carbon-valued products efficiently formed by bioelectrocatalysis under mild conditions are outlined.

1. Introduction

The Earth has insufficient power sources, and climate change has emerged as one of the primary environmental issues. Therefore, sustainable alternatives should be explored, and new energy sources to replace fossil fuels are essential for future generations [1-3]. In addition, current methods for the conversion of CO_2 into non-harmful compounds include photocatalysis, chemical catalysis, biocatalysis, and electrocatalysis [4,5]. The combination of enzymatic and microbial reactions, as well as electrochemical processes, is an attractive research area primarily related to bioelectrocatalysis. From the perspective of green chemistry, bioelectrocatalysis is the most attractive of the aforementioned methods due to the possibility of generating renewable and/or eco-friendly electricity at relatively low costs, derived from an increasing number of abundant resources [6]. It is remarkable that bioelectrocatalytic electricity generation can be performed at ambient conditions, including pressure and temperature, which enable environmentally friendly and sustainable development. In the subsequent procedure, 'blue hydrogen' can be generated directly through water electrolysis, eliminating the need for hydrogen derived from another source [5-9]. Additionally, bioelectrocatalysis-based enzymatic reactions offer several unique advantages, including high activity and exclusivity, in electrocatalysis, a process that enables the production of valuable hydrocarbon compounds [7,8].

Bioelectrocatalysis based systems are suitable for decentralized organizations and have immense commercial potential due to an estimated surplus of inexpensive electrical power from an extensively transported and fluctuating sustainable source that would be challenging to store [9]. Despite the significant C–C coupling potential limitation, obtaining carbon long-chain compounds with high selectivity *via* direct CO_2 electrocatalysis is remarkably challenging whenever the hydrogen evolution reaction (HER) begins to emerge. Bioelectrocatalysis produces

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an abundance of ‘C_{2+} products, which are based on more than two carbon atoms, due to the great effectiveness and selectivity of biocatalysts. The incorporation of bioelectrocatalysts, designed through the rational selection of electrode and catalyst materials, which utilize carbon dioxide and renewable energy, has spurred renewed interest in research. Conventional electrocatalysis suitable for the fixation of CO_2 produces acetate, butyrate, alcohols, polyhydroxybutyrate, methane, methanol, and formic acid [10]. The contributing pathways applied to decrease carbon dioxide generation also led to various chemicals exhibiting comparable applicability [11,12]. Combining VFe nitrogenate with cobaltocenium, 1-carboxycobaltocenium, and 1,1′-dicarboxycobaltocenium enabled the electroenzymatic production of ethylene, propane, and methane by the reduction of CO_2, therefore, the average cost of electricity produced using renewable resources has decreased significantly [13]. To capture CO_2 more rapidly and effectively, experts have developed a combination of more sophisticated electrochemical technologies and multifaceted electrode materials [14,15]. Hybrid frameworks based on enzymes are closely related to metabolic engineering and have contributed to the advancement of certain bioelectrocatalytic systems [16-18]. The utilization of digestive enzymes, mechanisms, and microbial cells presents ample opportunities for bioelectrocatalysis, leading to the commercialization of certain C_{2+} products [5,19–22]. The process for electron transfer in bioelectrocatalytic systems is being extensively investigated. The enzymatic contribution to the electrocatalytic conversion of CO_2 into pyruvic acid has been reported [23]. The incorporation of various CO_2-reducing microbiological mechanisms, which include the tricarboxylic acid (TCA) cycle, acetyl-CoA carboxylate method, Wood-Ljungdahl process, Calvin-Benson-Bassham process, and reducing acetyl-CoA process, facilitated the creation of new bioelectrocatalytic methods for the fixation of CO_2 [24]. Bioelectrocatalysis offers numerous advantages over conventional enzymatic and microbiological methods. Improvements in CO_2 reduction into multi-carbon chemical synthesis have spurred the extent of bioelectrocatalysis. The combination of enzyme-based hybrids with metabolically engineered microbes, and the modification of bio-based interfaces with nanomaterials, conductive polymers, or functional moieties, it is possible to facilitate electron transfer rate, improve the biocompatibility and advance long-term stability [25–30]. The incorporation of bioelectrocatalysis for CO_2 reduction is crucial for designing long-lasting bioelectrochemical systems. Over the past two decades, hybrid bioelectrocatalytic systems have been developed, mainly through the combination of fermentation with electrochemistry [31,32]. The field is advancing rapidly, expanding the spectrum of products achievable through bioelectrocatalysis from poly(3-hydroxybutyrate) (PHB) to long-chain molecules containing great energetic value, including saccharides and fatty acids. Despite significant advancements in the formation of intricate organic molecules, the reduction of CO_2 by bioelectrocatalytic systems still requires improvement due to the complex nature of electron transfer pathways [9,16]. Consequently, fundamental design principles governing the electrocatalytic reduction of CO_2 and the primary impediments to advancements in enzymatic and microbial electrocatalysis should be designed [7,23,24].

In this review, we provide an overview of the application of traditional electrocatalysis, bioelectrocatalysis, and microbial electrosynthesis for reducing CO_2 emissions and fixing CO_2. We also address the fundamental features of both approaches. An overview of the most significant advancements in the structure and the integration of charge transfer materials into enzymatic, photocatalytic, and microbial systems suitable for the fixation of CO_2 is presented in Fig. 1.

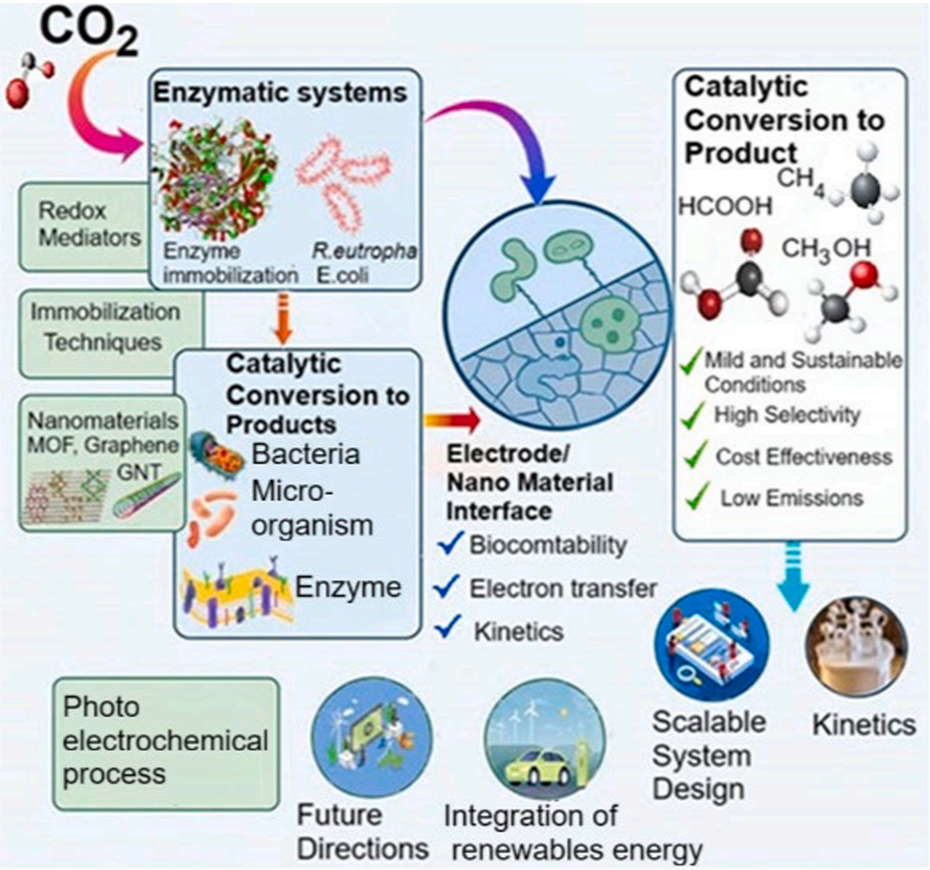

Fig. 1. Overview of bioelectrocatalytic CO_2 reduction strategies and pathways, including biocompatibility, integration, and microorganisms.

2. Optimization of electrocatalysis for CO_2 reduction

Potential advantages and challenges in CO_2 conversion via biocatalysis are depicted in Fig. 2, which highlights the use of natural enzymes with high specificity, mild operating conditions, and an eco-friendly nature. The schematic also highlights key challenges, including enzyme stability, cofactor dependency, and scalability limitations, and provides a roadmap for addressing these issues and enhancing comprehension. Natural enzymes exhibit high substrate specificity, operate under mild conditions, and are environmentally friendly, which facilitates their integration into sustainable biocatalytic processes (Fig. 2).

Due to thermodynamic restrictions, which cannot be overcome spontaneously during CO_2 reduction, the fixation of CO_2 requires external electrical power. Simply combining experimental and theoretical studies in advantageous integrative trends, considerable efforts have been devoted to elucidating CO_2 reduction processes. Fig. 1 illustrates the synthesis of copper-based materials, with their valence states highlighted, and the production of highly selective CO_2 reduction products [24].

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O\ \Delta G^\circ = 102.274\ \text{kJ mol-1},\ E^{\circ\prime}\ \text{redox} = -0.53\ \text{V} \tag{1}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH\ \Delta G^\circ = 117.712\ \text{kJ mol-1},\ E^{\circ\prime}\ \text{redox} = -0.61\ \text{V} \tag{2}$$

$$2CO_2 + 2H + 2e^- \rightarrow H_2C_2O_4\ \Delta G^\circ = 176.182\ \text{kJ mol-1},\ E^{\circ\prime}\ \text{redox} = -0.91\ \text{V} \tag{3}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O\ \Delta G^\circ = 185.251\ \text{kJ mol-1},\ E^{\circ\prime}\ \text{redox} = -0.48\ \text{V} \tag{4}$$

$$CO_2 + 6H^+ + 6e \rightarrow CH_3OH + H_2O\ \Delta G^\circ = 219.986\ \text{kJ mol}^{-1},\ E^{\circ\prime}\ \text{redox} = -\ 0.38\ \text{V} \tag{5}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O\ \Delta G^\circ = 185.251\ \text{kJ mol}^{-1},\quad E^{\circ\prime}\ \text{redox} = -\ 0.24\ \text{V} \tag{6}$$

$$CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O\ \Delta G^\circ = 404.079\ \text{kJ mol}^{-1},\ E^{\circ\prime}\ \text{redox} = -\ 0.35\ \text{V} \tag{7}$$

$$2CO_2 + 12H^+ + 12e \rightarrow C_2H_5OH + 3H_2O\ \Delta G^\circ = 380.923\ \text{kJ mol}^{-1},\ E^{\circ\prime}\ \text{redox} = -\ 0.33\ \text{V} \tag{8}$$

$$2CO_2 + 14H^{+} + 14e^- \rightarrow C_2H_6 + 4H_2O\ \Delta G^\circ = 364.713\ \text{kJ mol}^{-1},\quad E^{\circ\prime}\ \text{redox} = -\ 0.27\ \text{V} \tag{9}$$

$$3CO_2 + 18H^+ + 8e^- \rightarrow C_3H_7OH + H_2O\ \Delta G^\circ = 538.386\ \text{kJ mol}^{-1,}\ E^{\circ\prime}\ \text{redox} = -\ 0.31\ \text{V} \tag{10}$$

Both proton and electron transfers are simultaneous components inherent in the CO_2 reduction process. The driving forces influencing CO_2 reduction are based on the involvement of both electrons and protons [25]. During the reduction of CO_2, several hydrocarbons, including methane, methanol, formic acid, ethylene, carbon monoxide, and ethanol, can be produced. The Gibbs free energy (at 298 degrees Celsius, 1 atmosphere) and reducing potential vs. standard hydrogen electrode (SHE) at pH = 7 are represented in Eqs. (1)–(10). The following equations represent various stages of CO_2 reduction processes involving distinct products [31]. Changes in Gibbs free energy (ΔG°) indicate that none of these reactions can occur spontaneously, without external energy.

The formation of long-chain carbon products demands excessive energy; therefore, the formation of long-chain carbon products is more challenging in comparison to the generation of one-carbon-atom-containing reaction products (C_1 products). Additionally, bio-electrocatalysis could reduce CO_2 by utilizing renewable energy from sustainable sources, which may minimize fuel costs and the overall CO_2 conversion process and produce C_{2+} products with high conversion efficiencies. The incorporation of bio-catalysis increases the potential to exploit sustainable energy sources required for CO_2 fixation.

2.1. Classic bioelectrocatalysis for CO_2 reduction

In conventional electrocatalysis applied for CO_2 reduction, the electrolyte plays a crucial role, as its interaction with the electrocatalytic surface significantly influences the reaction outcome, while CO_2 can further alter key properties of the electrolytic solution, making it essential to understand electrolyte effects for designing efficient and selective electrochemical devices capable of converting CO_2 into valuable products (Fig. 2) [31-33]. Then, CO_2 binds to the active sites of the catalysts, followed by the formation of the radical anion $CO\bullet^+$ (CO*). Due to the short half-life of CO*, the phenomenon protonates quickly to

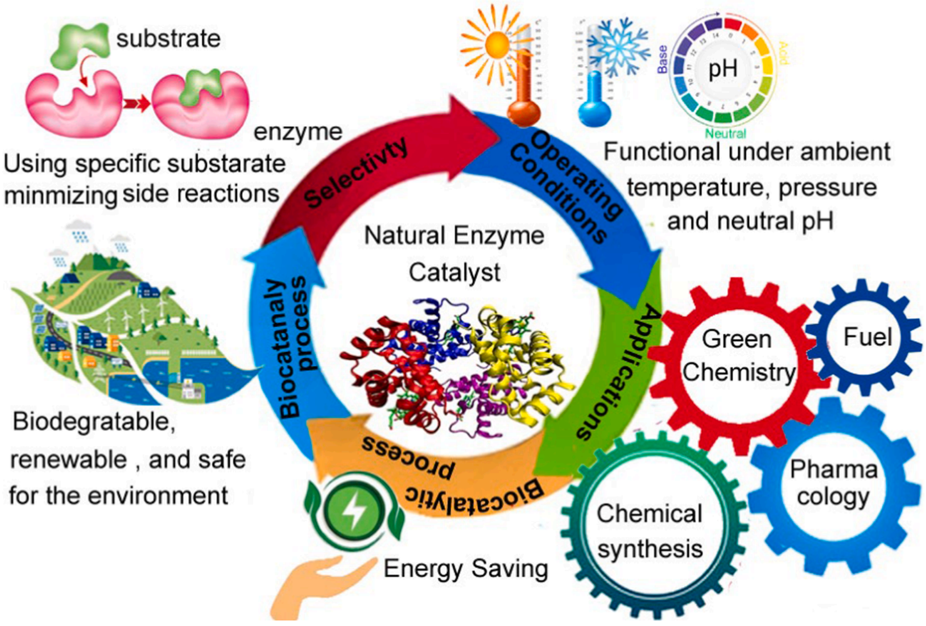

Fig. 2. The application areas of natural enzymes.

generate *COOH or *OCHO. For instance, the CO* intermediate can transform into either COH* or CHO*, and both intermediates are subsequently reduced to methanol through sequential proton and electron transfers (Fig. 3). The product facilitates the development of the C_2 compound through a carbon–carbon bond. In contrast, various C_2 products undergo a higher percentage of oxidation–reduction reactions. Based on these processes, standard electrocatalytic fixation of CO_2 is possible, generating a wide range of products, including CO, methanol, formic acid, methane, ethylene, and ethanol [34,35]. However, the equilibrium of attainable substances is shifted towards the formation of C_1 products because the formation of C_{2+} compounds is thermodynamically less favourable.

2.2. *The application of volcano phase diagram and scalar correlation for the characterization of CO_2 reduction reactions*

Sabatier's principle states that the interaction of a perfect catalyst with a substrate occurs in two ways: weak (i.e., significant interaction for the reactants) and strongly effective (i.e., outcomes with inadequate binding, which facilitates the product's degradation). An excessive binding strength results in external poisoning of the catalyst, whereas an excessively inadequate absorption leads to inadequate diffusion, which leads to an insufficient reaction rate. A'volcano-shaped' graphic is observed whenever catalytic effectiveness is plotted regarding the binding energy of reactants [36,37]. The following information could be used as an intuitive tool for comparing the thermodynamic properties of various catalysts, which assists in understanding and forecasting active prospects that might be approaching the heights or base of the volcano. The'volcano-shaped' elevation represents the action of catalysts that facilitate interaction and are either excessively powerful (left slope) or insufficiently firm (proper slope). The essential facilitator to stay the explosion diagram for CO_2 reduction reactions varies depending on the characteristics of the catalysed reaction.

Based on that identical surface-carbon interactions are formed despite the decrease in CO_2 capturing stages (*CO, *COOH, and *the COH, for illustration), where symbol '*' demonstrates retained domain, the study immense obstruction persists in the form of optimizing a binding ability of initial intermediate. It is suggested that the hydrogenation process for CO to CHO occurs during the potential-determining stages involved in the reduction of CO_2 into CH_4 [38-40]. The substantial free energy shift of the above step (0.74 eV) can be attributed to the weaker binding of *CHO compared to that of *CO. Nonetheless, the proportional relationship renders it challenging to obtain *CHO (i.e., additional adverse) to bind more strongly than *CO for the preferential production of CH_4 [36,37,41,42]. For instance, the proportional growth of COOH and CO causes COOH to couple unfavourably with CO. The consequence of these reactions is characterized by an elevated overpotential and reduced CO_2 to CO conversion rate on Ag and Au electrodes [42,43]. Therefore, the reduction overpotentials is an important issue. For this objective, some effective strategies are based on the application of alloys with numerous active sites and the involvement of active ligands that generate active reaction promoters [43,44].

2.3. *Factors affecting CO_2 reduction and hydrogen evolution*

The strategy for the reduction and activation of CO_2 is frequently impeded by the simultaneous occurrence of the HER-reduced protons and water in protic solvents. In most cases, the HER exhibits significantly faster kinetics and an advantage comparable to, or even more rapid than, CO_2 reductions. Moreover, the sequential coupling of hydrogen (*H) with the stage involved in CO_2 reduction can affect the adsorption energies and the kinetics of the CO_2 reduction reaction. Accessibility of protons towards the electrode and electrolyte composition is important for CO_2 reduction thermodynamics and reaction rate. Meanwhile, reaction conditions could be altered by reducing the adverse HER. The following can be accomplished by (i) employing an electrolyte that has reduced contribution to the activity of reacting chemicals, and this can be achieved by the combination of different solvents, which can be aprotic solvents with poor diffusion ability or cationic solutions [45]; (ii) optimization of reaction conditions [46]; (iii) the adjustment of efficient electrode design [47]; (iv) activity of applied electrocatalysts to promote CO_2 adsorption and binding with hydrogen atoms [48].

2.4. *Bioelectrocatalysis-based CO_2 reduction*

Enzyme- and microorganism-based bioelectrocatalytical systems are used for the selective and efficient production of C_{2+} compounds. Due to the limited charge transfer efficiency of some enzymes, nanostructures that enhance charge transfer are beneficial, as highlighted in a comprehensive table summarizing key charge-transfer materials, their properties, and relevant performance metrics (Table S1). In contrast, biocatalytic systems are rather selective and even stereoselective, allowing them to produce specific compounds [48–50]. Most enzymes, which utilize C2 + compounds and directly generate electricity in

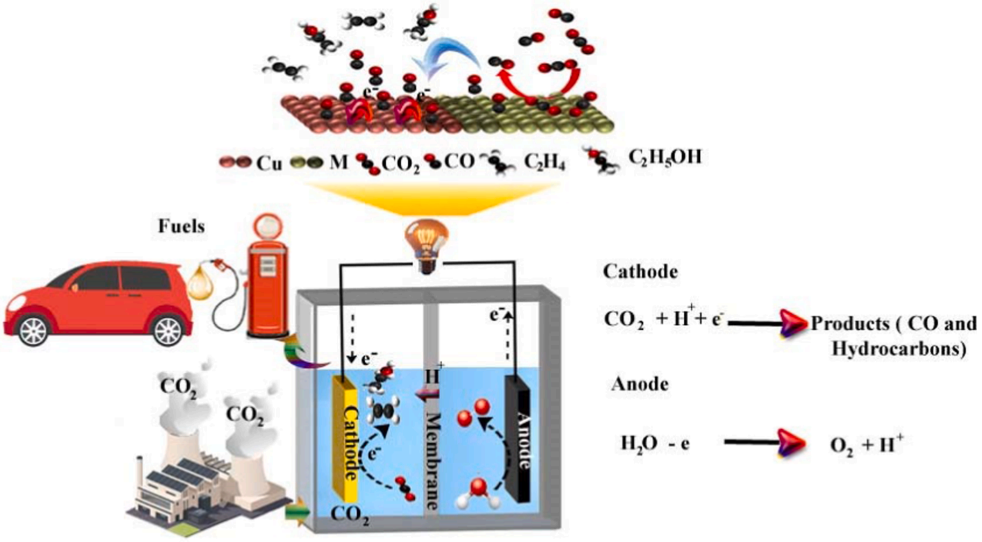

Fig. 3. Traditional design and strategies of copper-based nanomaterials by electrochemical reducing CO_2 in an aqueous medium, accompanied by the corresponding reactions at their electrodes [36].

enzymatic biofuel cells, belong to the class of oxidoreductases [51,52]. Bioelectrocatalysis can generate a wide range of C_{2+} products and compounds using the materials produced by conventional electrocatalysis [53,54]. The microorganisms relied on in biocatalysis can be characterized as self-regenerating accelerators due to their increased stability and reliability. Bioelectrocatalysis can be described based on the direct or indirect charge-transfer of electrons [54,55]. Microorganisms capable of exploiting C_1 and C_2 fuels remain widespread and diverse [52,56-61].

In most electrocatalytic systems, enzymatic and electrocatalytic processes are performed in separate compartments or electrochemical cells based on different electrodes. In some bioelectrocatalytic systems, redox mediators [57], metallic nanoparticles [61-65], coenzymes PQQ [6], NADH and/or NADPH [55,66] are applied for the facilitation of charge transfer between electrodes and enzymes [6,56,61]. Electrode immobilization can enhance stability, catalytic activity, and flow compatibility; however, the most optimal technique must be chosen based on the enzyme's unique structure and properties [67]. To solve these challenges, supports like polymers, MOFs, metallic nanoparticles, and carbon nanomaterials have been studied. Due to their fragile nature, enzymes require carefully designed matrices and gentle immobilization methods that enhance stability while preserving their catalytic performance. A primary challenge in immobilizing redox-active enzymes is ensuring compatibility between the enzyme and the supporting matrix. The pyrene-modified linear poly(ethylenimine) hydrogel is used for the immobilization of oxidoreductases on a carbon electrode. This approach enables the positioning of enzymatic redox-active sites close to conducting parts of electrode, which enables direct electron transfer without the application of any redox mediators [68,69]. However, this approach is not universal, and most enzymes may denature or lose catalytic activity when encapsulated in the hydrogel due to unfavourable microenvironments or restricted mobility. To overcome this limitation, ferrocene-based redox hydrogels have been utilized to immobilize glucose oxidase for gluconate synthesis, thereby trapping the enzyme near the electrode and allowing ferrocene moieties to facilitate efficient electron transfer [70]. The resulting bioanodes maintained stability for over 24 h at 0.7 V vs. Ag/AgCl, indicating potential for industrial applications that require enhanced hydrogel stability. In addition to hydrogels, MOFs are increasingly employed for enzyme immobilization due to their tunable design. For example, pepsin anchored on ZIF-8 through Ni^{2+} ions enabled the oxygen evolution reaction at 127 mV (compared to 690 mV without Ni^{2+}), demonstrating a strategy to enhance the electrocatalytic efficiency of various enzymes [71]. Advances in enzyme immobilization are crucial for industrial applications and the development of improved bioelectrocatalytic systems. Future work includes spatially arranging multiple immobilized enzymes on a single electrode for "one-pot" multi-step catalysis [72]. Recent studies have shown that a non-native carbon-binding peptide (SBP) fused to NAD^+/NADH-dependent CO_2 reductase can catalyze electrocatalytic CO_2 conversion into formate. Site-specific SBP fusion affects enzyme/cofactor orientation and electron transfer at the electrode interface. Structural, enzymatic, and electrochemical analysis of C-terminal SBP-fused reductase (CR-GrC) showed enhanced electrocatalysis, efficient hydride and NADH/NAD^+ transfer, and more efficient electron transfer. SBP-linker-controlled cofactor orientation on graphite enabled low-cost, scalable bioelectronic CO_2 reduction [73]. In most oxidoreductases, catalytic and/or redox sites are deeply embedded within a protein globule; therefore, charge exchange with an electrode is complicated and rather slow, which mainly limits the applicability of these enzymes in electrocatalytic systems [74]. In order to facilitate charge transfer in such systems artificial [75] or natural [76] redox mediators are applied. The same principles of indirect charge transfer are applied in bioelectrocatalytic systems, which convert CO_2 into C_{2+} hydrocarbons and other C_{2+}-based organic materials.

It is notable that enzymes can be applied in the further conversion of C_{2+} hydrocarbons and other C_{2+}-based organic materials, suitable for various technological purposes. For example, *Clostridia* and other bacteria, which are capable of C_{2+} organic compounds, have been utilized in the production of many organic compounds using indirect (mediated) electron transfer strategies [64]. However, the application of artificial intermediaries, as shown in Table 1, can incur significant costs and pose additional challenges. In pursuit of cost-effective CO_2 conversion, many different strategies have been developed. Some of these strategies involve the regeneration of redox sites of oxidoreductases by redox mediators or by other redox enzymes, which possess the propensity to facilitate charge transfer between the corresponding redox site and the electrode.

3. The most important challenges of bioelectrocatalysis

Bioelectrocatalysis requires the enhancement of the range of products and the improvement of overall effectiveness by integrating the redox mediators of traditional electrocatalysts with biocatalysis. Differences in mechanisms, catalyst types, and reaction environments are observed (Table S2). The integration of catalysts comprising one-dimensional (1D), two-dimensional (2D)], or three-dimensional (3D) composites containing charge transport compounds is a critical issue in most bioelectrocatalytic systems. Furthermore, different microorganisms, enzymes, redox mediators, and electrochemical reactor configurations have been combined into bioelectrochemical systems capable of fixing CO_2.

3.1. The application of charge transfer materials in bioelectrocatalysis-based systems

In various electrochemical and bioelectrochemical systems, different charge transfer materials are employed to facilitate electron transfer, hole transfer, ion transfer, or charge transfer through an electron hopping mechanism. All these materials are used to facilitate electrical conduction and charge transfer. Materials that possess electrical conductivity are mainly based on metals, semiconductors, metal–organic frameworks (MOFs), carbon-based materials, conducting polymers [6] MXenes [], and many other materials and composites [75,76,119]. The primary factors influencing the efficiency of electron transferable materials are based on their electrical conductivity and resistance. The most advantageous electron transfer materials are characterized by low Ohmic resistance. Metallic components such as Ag, Cu, Au, and Pt are known for their outstanding electrical conductivity; therefore, they are often used as electrode materials [120–123]. In addition to conductivity, polarization ability, catalytic properties, and hydrophobicity, among other aspects, are crucial for efficient charge transfer between electrodes and other elements of bioelectrochemical systems [124].

Carbon-based materials are also promising in the development of various bioelectrochemical systems [15]. Carbon-based materials are classified into several groups, including reduced graphene oxide (rGO), graphene (G), carbon nanotubes (CNTs), and composites based on these materials [119,125,126]. Carbon nanotubes are often used in the design of composites with advanced catalytic properties due to their large surface area (1,315 m^2 g^{-1}), high electrical conductivity (5,000 S cm^{-1}), and excellent stability at ambient conditions [127]. CNTs are frequently used in bioelectrochemical systems []; therefore, they can serve as electron conduits that facilitate and sustain catalytically active sites while engaging in the process of CO_2 transformation [127]. In CO_2 electrocatalysis, N-doped carbon nanotubes (N-CNTs) are highly efficient, facilitating the formation of CO with 80 % faradaic performance at 0.78 V vs. reversible hydrogen electrode (RHE) [128–130]. N-CNTs contain a large number of active sites, which are available for: (i) CO_2 reduction, (ii) binding of COOH, and (iii) thermodynamically favorable CO production. Moreover, pyridinic and pyrrolidine N-CNTs facilitate thermodynamically favorable CO desorption, which is advantageous for gaseous CO formation [131,132]. Graphene is a primary carbon-derived material characterized by a high surface area (2630 m^2 g^{-1}), good

Table 1
A Summary of Major Contributors to Electrochemical Catalysts.

Type	Materials	Major product	Potential	Faradaic efficiency %	Ref.
Metalic	Au	CO	−0.6 V/RHE	83.0	[77]
	Au-Zn	CO	−0.6 V/RHE	95.9	[78]
	Au-Cu	CO	−0.4 V/RHE	94.0	[79]
	Cu@Sn	HCOOH	−1.3 V/RHE	100.0	[80]
	Ag-Cu/p-Si	CH_4	−0.9 V/RHE	18	[81]
	Sn-Bi	COOH	−0.8 V/RHE	96.4	[82]
	3D Au	CO	−0.6 V/RHE	83.5	[83]
	Au_4-Ni_2	CO	−0.76 V/RHE	93.0	[84]
	BiOX	HCOOH	−1.1 V/RHE	85.0	[85]
	BiNPs/GaN NWs	HCOOH	−0.3 V/RHE	98	[86]
	Cu hollow	CO	−1.2 V/RHE	75.0	[87]
	Bi-Pd/SAA	CO	−0.31 V/RHE	91.1	[88]
	3D Ag–Pd	CO	−0.6 V/. RHE	91.5	[89]
	PdH	CO	−0.7 V/RHE	93.4	[90]
	PdH/C	HCOOH	−0.4 V/RHE	93.1	[91]
	Pd_2	CO	−0.9 V/RHE	98.2	[92]
	Sn/Cl	HCOOH	−0.9 V/RHE	96.1	[93]
	Ag 3D Cu foam	HCOOH	−1.0 V/RHE	35.1	[94]
Oxide-based	Cu-TiO_2	CH_3-OH	−1.4 V/SCE	70	[95]
	β-Bi_2O_3-DCNT	HCOOH	−0.6 V/RHE	91	[96]
	CuO_2/TiO_2 NPs	C_2H_5OH	−0.9 V/RHE	47.4	[97]
	CuO_2–CeO_x	CO	−0.98 V/RHE	81.8	[98]
	Au_3Cu	CO	−0.7 V/RHE	98.1	[99]
	Cu_2O-Cu	C_2H_4	−1.0 V/RHE	77.4	[100]
	Cu/CeO_x	CH_4	−0.1 V/RHE	38.6	[101]
	Ag–CuO	C_2H_5OH	−0.6 V/RHE	80.1	[102]
	3D Cu–Cu_2O	C_2H_5OH	−0.4 V/RHE	80.0	[103]
	CuO_x/Cu/C	C_2H_4	−0.3 V/RHE	40.0	[104]
Alloy	Pd-Cu	C_2H_4	−1.1 V/RHE	33.1	[105]
	Cu–Au	HCOOH	−1.0 V/. RHE	40.0	[106]
	Sb-Bi alloy	HCOOH	−0.9 V/RHE	96.0	[107]
	In Bi NS	HCOOH	−0.9 V/RHE	96.3	[108]
	PdAg nanosphere	CO	−0.2 V/. RHE	87.5	[109]
	AgCu	CO	−1.0 V/. RHE	54.6	[110]
	BiCu-SAA	C_2H_4	−0.8 V/RHE	73.4	[111]
	CuNS	CH_4	−1.2 V/RHE	70.1	[112]
	Ga-CuAl	CH_4	−1.4 V/. RHE	53.0	[113]
	Ag-Cu	C_2H_5OH	−1.0 V/RHE	52.6	[114]
	Pd–Cu	HCOOH	−0.6 V/. RHE	50.0	[115]
	CuIr	−BuOH	−0.9 V/RHE	14.8	[116]
	InBi	HCOOH	−0.9 V/RHE	14.1	[117]
	CuNiZn	CO	−2.0 VRHE	80.0	[118]

electrical conductivity (106 S cm^{-1}), high thermal conductivity (5000 W m-1 K^{-1}), and sufficient mechanical rigidity [133,134]. Graphene-based composites can be utilized in electrochemical CO_2 reduction to CO with a remarkable 84 % faradaic efficiency at −0.6 V vs. RHE. The structural flaws in graphene form active catalytic sites suitable for the reduction of CO_2 [135]. Chae et al. examined different types of composites based on particulate-activated carbon doped with Ni nanoparticles in a bio-electrochemical reactor, achieving a methane yield of 40.6 % [136]. The high surface area of granular activated carbon enables the transfer of electrons and protons between microorganisms and the electrode. Ni-based active sites in the composite also exhibit catalytic activity and are non-toxic toward the applied microorganisms, which is advantageous for promoting methanogenesis in these microorganisms.

MOFs are chemical compounds suitable for various electrochemical systems due to their diverse structures and stable porosity. Incorporating metallic substances with organic ligands produces an adaptable and highly reactive framework [137–142]. Metal organic frameworks (MOFs) demonstrate exceptional selectivity attributed to the presence of specific functional groups [139]. Furthermore, their extensive structural tunability and high porosity endow them with a high density of catalytically active sites and a large number of accessible pores, thereby enhancing their capacity for CO_2 adsorption [142–147]. Indium-doped bismuth-based MOFs were involved in the formation of BiIn5-500@C composite, which exhibited remarkable catalytic activity, resulting in the electrochemical reduction of CO_2 and the formation of HCOO-with the faradaic efficiency of 97.5 % and 13.5 mA cm^2 current density at −0.86 V vs. reference hydrogen electrode (RHE) [148]. Bi_2O_3 improves the effectiveness of MOF-based electroreduction of CO_2 [149]. Targeted fuel production has been enhanced by hybrid MOFs, which combine a coordinated cube-shaped pyrazolate structure and metal featuring asymmetric, potentially charged Ni-Cu centers under MOF-based catalyst conditions. This MOF-based composite was applied for C_2H_4 formation from CO_2 at −1.3 V vs. RHE, achieving a Faradaic efficiency of 52.7 % [150].

Enzymatic cofactors, specifically FMNH2/FADH2 and NAD/$NADH^+$, can serve as redox mediators in bioelectrochemical systems, as applied in bioelectrochemical CO_2 reduction (Fig. 4) [144]. Redox mediators are vital in proton and electron transfer in microorganism- and enzyme-based electrochemical systems [145–147,151]. Mediated electron transfer (MET) and direct electron transfer (DET) are both exploited in bioelectrochemical systems, as depicted in Fig. 3a and b. In DET schemes, electrons are directly transferred to/from catalytic sites of oxidoreductase enzymes and/or electrochemically active proteins anchored to membranes of microorganisms [152]. Externally soluble redox-active intermediaries are essential for transferring electrons between electrodes and oxidoreductase in MET schemes (Fig. 4b). The most frequently used redox mediators in bioelectrocatalysis are methyl viologen, anthraquinone-2,6-disulfonate, flavin adenine dinucleotide (FAD), haem, pyrroloquinoline quinone, neutral red (NR), NAD(P)H,

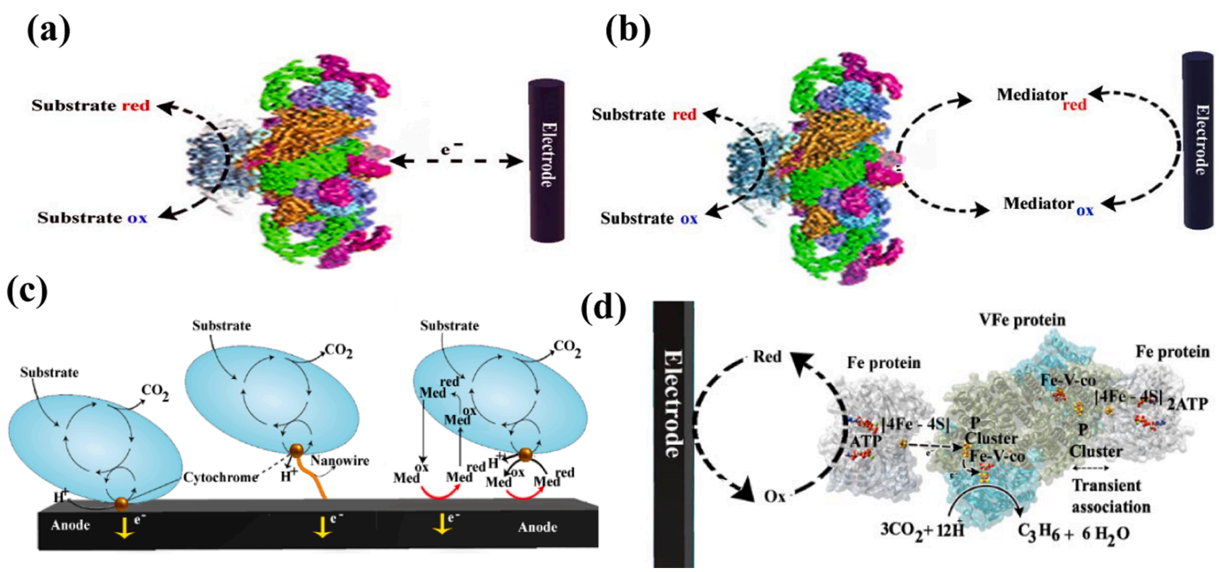

Fig. 4. Direct and mediated microbial and enzymatic electrocatalysis, which encompass direct electron transfer: (a) DET in enzyme electrocatalysis; (b) MET in enzyme electrocatalysis; (c) DET and MET combined at microorganism electrocatalysis; (d) the connection of vanadium nitrogenase (VnfDKG VFe) with FeVco in Azotobacter vinelandii, forming VnfH Fe enzymatic complex. The VFe protein structure is , while the VnfH Fe protein is represented using the molybdenum nitrogenase Fe protein (NifH), for which the structure remains undetermined (PDB). Copy right permission from the Royal Society of Chemistry (2022) a, b, and c [] d and Journal of American Chemistry (2018) []
adapted from PDB 5N6Y4WZA1312.

flavin mononucleotide (FMN), and further transfer metal compounds (Fig. 4c and d) [153]. Although MET might result in substantial thermodynamic losses, it facilitates long-distance charge transfer and cascading reactions [154].

3.2. Catalysts applied in CO_2 reduction systems

Some electrocatalytic systems utilize specific catalysts to accelerate the reduction of CO_2. Metals, metal oxides, and enzymes are the most

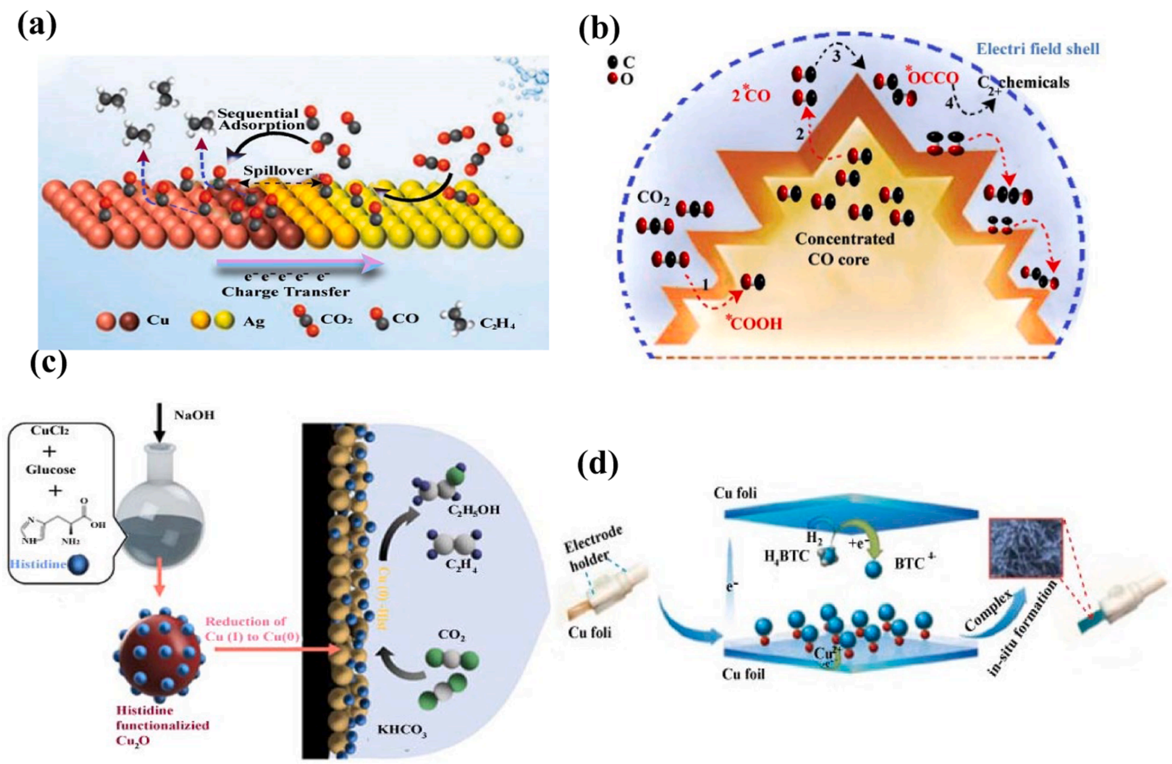

Fig. 5. (a) A schematic illustration is provided to illustrate the proposed mechanism by which ethylene is facilitated with Ag-CuNDs. (b) The simplified diagrammatic representation for the electroreduction activities of CO_2 in hollow hierarchical Cu/Cu_2O. (c) The reaction's selectivity toward C_{2+} products are enhanced after the in-situ reduction of Cu_2O to Cu under catalytic conditions, as the histidine remains on the surface. (d) A schematic diagram illustrating the assembly of a Cu-Complex-1 layer from a Cu substrate demonstrates the in situ anodic growth of a copper complex at the electrode position over a copper foil. Copyright permission from the American Chemical Society (2019), [161](a), Nature (2023), [118] (b), Nature (2019) [159] (c) and Nature (2019), [162] (d).

frequently used catalyst types employed in electrocatalysis. Classifications of catalysts based on metals, metal oxides, and their composites are presented in Table 1.

3.3. Metallic catalysts

Metal-based catalysts such as gold (Au), silver (Ag), and zinc (Zn) can convert CO_2 into CO [155]. Tin (Sn), lead (Pb), indium (In), and bismuth (Bi) possess a d^0 electronic structure, which facilitates the conversion of CO_2 into formic acid. Au nanoparticles (AuNPs) have demonstrated an impressive 97.3 % faradaic efficiency in transforming CO_2 into CO [156].

The addition of carbon layers to the Au-Ag bimetallic catalyst altered the arrangement of atoms in the alloy structure, thereby enhancing its efficiency for electrocatalysis. Moreover, the structural ordering of atoms within both the Au and AgCl domains was altered by reducing the AgCl to form the active site of Au-Ag, which improved carbon monoxide production [157]. Additionally, the partial current density for CO_2 reduction was doubled in the composite configuration.

Electrochemical synthesis, as shown in Fig. 5a, ensured a Faradaic efficiency FE of 40 % for C_2H_4 when a −1.1 V voltage was applied vs. the reversible hydrogen electrode (RHE) [24]. A catalyst based on the Bi monolayer has exhibited a remarkable FE of 99 % in the transformation of CO_2 into formic acid [158]. Thermodynamically and kinetically advantageous selective C_1 and C_2 production is shown in Fig. 5b. Cu-based catalysts have attracted considerable attention in many technological applications [112]. Moreover, Cu-based catalysts have the ability to convert CO_2 into C_2– and C_3-based products; therefore, they are used for the production of several compounds, including ethanol and ethylene [159,160].

Various modifications of the electrode surface are employed to improve their performance. Electrodes modified with porous nanoparticles exhibit advanced efficiency due to increased surface area and cavities, which provide a confined environment required for the reduction of CO_2 [163]. Electrodes modified with ‘Cu-based foam’ are achieving a 55 % Faradaic efficiency in converting CO_2 into ethane and ethylene. A three-dimensional nanostructure and a mixture of metallic copper (Cu^0) and copper(I) oxide were used for a simple electrochemical in-situ reduction of CO_2. Fig. 5c shows that the 3D dendritic structure has more active sites, which advances Faradaic efficiency of C_{2+} compound generation to up to 80 % [162]. Furthermore, electrodes functionalized with organic compounds exhibit advanced catalytic properties in oxidation/reduction reactions involving copper forms or compounds at different oxidation levels ($Cu^0/Cu^+/Cu^{2+}$) [164,165]. Cu modification by Histidine implements surface changes in the catalyst, resulting in the shift of cathodic potentials that defined alternative reaction pathways, as shown in Fig. 5d [159]. Fig. 3 examined various cathode materials, such as bare stainless steel felt, heat-treated stainless steel felt, and graphite felt, which were both cost-effective and biocompatible. According to some research, the efficiency of an energy and current sensor made of heated metal material across a biocathode was 21.9 % and 60.8 %, respectively [166,167].

3.4. The application of metal oxides in electrocatalytic reduction of CO_2

Transition metal oxides such as TiO_2 and RuO_2 can be used for CO_2 reduction, while SnO_2 and Bi_2O_3 could be applied for the formation of HCOOH. Further, the main output of CO_2 reduction by MoO_2 and ZnO catalysts is CO [168,169]. In addition, Cu_2O displays a significant formation of C_{2+} compounds, along with the formation of C_3– and C_4-based compounds [170,171]. During the action, Cu^+ species and CO interact more efficiently, and the coverage by intermediate species remains more stable, which facilitates the development of C_3 and C_4 products [103]. The structure and morphological behavior of the electrode characteristics might impact the efficiency of electrocatalytic reduction of CO_2. Cheng et al. assessed active sites and active regions of Cu oxide-based catalyst during the electro-reduction of CO_2 by integrating a structural kinetic model, which was based on the action of step-square fields that promote alcoholic generation. In contrast, planar-square and convex-square catalytic sites produce ethylene [170].

In contrast to electrodes featuring a smooth surface, electrodes exhibiting an increased surface area have a higher number of active sites with coordinated CO_2 adsorption, a higher frequency, and enhance the high selectivity of hydrocarbons and catalysts exhibiting sharpened nanoneedles, nanowhiskers, and nano-dendrites is more likely to produce C_{2+} [172,173]. Enhancing gas nucleation, stabilizing cations, and increasing localized pH are claimed to be key factors in preventing the protonation of linked CO and improving the selectivity of generating multi-carbon products [37,174]. Cu(OH)BTA has a monoactive site of copper integration polymers, which are required for the carbon–carbon (C–C) coupling that generates products with increased multicarbon (C_{2+}) yields and have been observed to transform into metallic agglomerations during operation to enhance the structural stability and active side following a rate-determining process of CO hydrogenation, a *OCCHO intermediate and also improve the production for the design of polymer composites with single-site Cu catalysts [175]. Improving healing interactions between C–C groups on Cu/ceria catalyst enabled high-selective C_{2+} production due to the significant role of ceria in weakening the neighboring Cu atom’s hydrogen binding energy, thereby stabilizing CO-CO. Based on this approach, the development of the cathode using rGO and WO_3 led to an increase in the generation of acetates by 41 % [176]. Titanium oxides, especially various forms of TiO_2 [128,177] and zinc oxide (ZnO) [65] also shows applicability in catalytic processes, required for CO_2 fixation and/or conversion into C_{2+} organic compounds. Furthermore, RuO_2/TiO_2 catalysts can be used with mixed-metal oxides to achieve the synergistic effect of RuO_2 on the TiO_2 side that requires modification to enhance the features of transport of electrons on the defective active side and alter the amount of RuO_2 on the active side to raise the apparent reaction barrier of CO oxidation [178].

3.5. The application of alloys in electrocatalytic reduction of CO_2

Some alloys can enhance the faradaic efficiency of CO_2 reduction in comparison to respective primary metals. The incorporation of other metals within copper (Cu)-based structures affects the electronic configuration of the resulting structure. A Catalyst based on a gallium-copper alloy facilitates the electrochemical formation of C_1 compounds with a Faradaic efficiency of 79 % and makes the generation of C_{2+} compounds (e.g., 2-propanol) more thermodynamically favorable for C_1 yields, exhibiting reliability and a long-lasting lifetime of 20 h [167,175,179]. A silver-copper alloy led to a 56.7 % faradaic efficiency in ethanol production [180]. Polycrystalline and shape-controlled single-atom composites (SACs) based on a Pd-Cu alloy have been demonstrated to enhance hydrogen evolution, resulting in the formation of CH_4 or C_2H_4 [181].

3.6. The facilitation of electro-reduction of CO_2 by charge transfer materials

A promising strategy for converting renewable energy into valuable hydrocarbon derivatives is electrochemical CO_2 reduction and remediation (Fig. 4). The conversion process typically occurs in an electrochemical device, where CO_2 is located at the cathode and converted into a different form with the assistance of a metal-based catalyst and a suitable electrolyte. The reaction pathway varies depending on the catalyst type, electrode potential, electrolyte composition, and reaction conditions [103,167]. Key intermediates, such as carbonate, bicarbonate, carboxylate, and formate, significantly influence selectivity, efficiency, and reaction kinetics. The optimization of catalysts to facilitate CO production necessitates a comprehension of the chemical structure of these stages. Optimum catalysts exhibit a significant attraction to

*COOH, while their affinity for CO and H is inadequate and suppresses the competing hydrogen evolution reaction (HER) [182]. This principle has guided the development of nanostructured catalysts, which facilitate charge transfer, promote mass transport, and increase surface area. Chemical vapor deposition, sol–gel, electrochemical deposition, and template-assisted methods are controlled synthesis techniques that precisely adjust catalyst morphology and active site distribution [179,183].

Surface modification approaches such as activation, chelation, and combination improve efficiency. Besides the natural features of the nanostructure, links to support materials or molecular stabilizers can impact the efficiency of adsorption and the movement of electrons, which influence the stability of the intermediate phase [184]. Despite substantial advancements, long-term catalyst reliability and flexible fabrication challenges continue. Current studies focus on enhancing strength selectivity and cooperation with alternative power sources [185,186]. Nanostructured catalysts possess significant potential for advancing environmentally friendly and efficient CO_2 reduction technologies.

3.7. *The application of one-dimensional composites for electrochemical reduction of CO_2*

Recently, structures such as nanowires, microfibers, nanotubes, and nanorods are collectively referred to as one-dimensional materials (1D composites). These one-dimensional materials are currently utilized in the formation of various composite materials, which possess an extensive surface area, a high abundance of catalytically active sites, attractive crystalline structures, advanced energy, and electron transfer capabilities, among other properties [112,164,187,188]. During CO_2 electroreduction, the increased surface area of one-dimensional materials facilitates the additional exposure of catalyst areas, which are exceptionally active and contribute towards the production of essential intermediates and their absorption. Due to their ability to distribute electrons and protons along a streamlined trajectory, one-dimensional materials are more capable of converting CO_2 into other compounds due to their nanotube-like structures. Furthermore, 1D substances might be produced from material composites over the combination of factors to produce advanced hybrid material electrodes for CO_2 electroreduction [189,190]. Significant advancements are made possible by heteroatom-containing 1D materials for electrodes that enable the electrochemical reduction of CO_2, combined with other extraordinarily effective drivers, thereby leading to reactivity across crystal surfaces. For example, CNTs derived from nitrogen exhibit enhanced catalytic properties due to nitrogen deficiencies, which can influence the electronic configuration and determine the surface atomic composition of the complex [189,191]. 1D SnO_2 incorporating a wire-in-tube (WIT) design, which might have enhanced electrocatalytic performance by synthesized electrospinning technology and show increased grain bounties, can effectively improve the selectivity for formic acid products and achieve Faraday efficiency of 80 % [192]. Recently, the electrochemical performance of Ag and Cu wires functionalized with various nanowire morphologies, with a focus on their effects, was investigated. This exploration aims to progress electronic catalysts that are exceptionally strong, exclusive, and effective in reducing CO_2, paving the way for the next generation of electrocatalyst material [193] and a more stable CO_2 intermediate to increase the electroactive sites on the surface and enabling process of reducing CO_2 to CO with a 90 % FE.

Design and strategy of the single-metal-atom catalysts (SACs) on N-doped CNT electrodes on the carbon fiber paper with self-standing array structure increase regarding obtaining a significant FE of 97.2 % during the process of transformation of CO_2 to CO effectively combining protoporphyrin IX complex and cobalt ions (CoPP) and carbon nanotubes (CNT) were able to achieve an outstanding 98.3 % Faraday efficiency for CO products during CO_2 electro reduction [194–196]. A hybrid graphite felt biocathode with −1.4 V electrode voltage in interaction with Ag/AgCl could produce 80.9 % methane, demonstrating that a substantial amount of methane could be produced, and described one-dimensional composites-based conversion, summarized as depicted in Table 2.

3.8. *The application of 2D composites in electroreduction of CO_2*

2D materials comprise a single layer or a collection of particles or elements. In most cases, composites exhibiting a membrane layer, a nanosheet, and a geometrical lattice phase are considered 2D materials [215,216]. In 2D composites, uniform geometrical structures could expose catalytically active areas, and their flatness increases the number of elements contained on the surface and at peripheral regions, thereby enhancing their distinctive properties and electrocatalytic capability to reduce CO_2 [217-219] Table 3.

3.9. *The application of 3D composites in electrochemical reduction of CO_2*

3D composites typically have an extraordinary structure and increased surface area, making the forming charges easier and exposing their more catalytically active center, where CO_2 can be adsorbed. Since the present moment, the development and construction of 3D electrode materials for reducing CO_2 are of paramount importance and involve the categorization of nanostructures (Fig. 6). These nanostructures include arrangements, designs of core–shell, equivalent to sandwiches, composed of padding, and the structure of polyhedrons. Table 4 summarizes the facilitated 3D composite materials and their electrocatalysis applications.

A substrate facilitates the vertical growth of nanowires, leading to an array of nanostructures. Whenever vertical channels are present in a nanostructure array, the length of the diffusion path is shortened, the efficiency of electron transfer is increased, and catalyst nanoparticles can be added to either the interior or exterior of the channels, thereby contributing to the overall improvement of electrode performance [245,246]. 3D Cu nanoarrays are designed explicitly for CO_2 reduction, and Cu arrays are efficient conduits for transporting charge and CO_2 molecules. In addition, Cu's high electrocatalytic activity enables the formation of ethanol and propanol separately, which has a FE of 67 % [261,262].

In core–shell nanostructures, the highly active nanoparticles are shielded by a shell to prevent their inactivity during the reduction process [263]. Furthermore, the shell hybridizes the catalyst's electronic

Table 2
An overview of 1D Composites applied in electroreduction of CO_2.

Materials	Product	Potential	F.E.%	Reference
NCNT/PEI	HCOOH	−1.8 V/SCE	87.0	[197]
CoPc@MWCNT	CO	−0.6 V/RHE	95.0	[194]
Ni-N/NCNT	CO	−2.0 V/RHE	93.5	[198]
Ag–S–C_3N_4/CNT	CO	−0.8 V/RHE	80.0	[199]
CoPP@CNT	CH_3-OH	−0.6 V/RHE	98.3	[195]
CoTAP/CNT	CO	−1.2 V/NHE	85.0	[187]
NCNTs-ACN-850	CO	−1.0 V/RHE	80.1	[200]
CdS-CNT	CO	−1.2 V/RHE	92.3	[201]
CoPc-py-CNT	CO	−0.6 V/RHE	98.1	[196]
V-doped Cu_2Se	C_2H_5OH	−0.8 V/RHE	63.8	[202]
CuNi/NCNT	CO	−1.1 V/RHE	92.8	[203]
Ni@N-CNT	CO	−0.8 V/RHE	93.0	[204]
MWCNTs/BiCu-MOFs	HCOOH	−0.86 V/RHE	100	[205]
NiPPc/CNT	CO	−0.9 V/RHE	99.8	[206]
Ni-N/NCNT	CO	−0.9 V/RHE	96.7	[207]
NiFe@NCNTs/Ni HF	CO	−1.0 V/RHE	90.9	[208]
CNT/Cu	HCOOH	−0.9 V/RHE	90.1	[189]
Ni@N-C	CO	−1.3 V/RHE	98.5	[209]
Ni@NCNT-C	CO	−0.3 V/RHE	90.1	[191]
Sn@CNT	C_2H_4	−2–2 V/RHE	85.1	[210]
Ni-N-CNS/CNT-5	CO	−0.7 V/RHE	81.3	[211]
NC-CNT/Ni	CO	−1.0 V/RHE	90.1	[212]
NiN_x/NCNT	CO	−0.8 V/RHE	86.9	[213]
Mel/CNT	CO	−0.8 V/RHE	99.1	[214]

Table 3
Overview of two-dimensional composites applied in electroreduction of CO_2.

Materials	Structure	Product	Potential	F.E. %	Ref
Cu/a-In_2O_3	Nanosheet	C_2H_5-OH	−1.2 V RHE	98.0	[220]
Cu_2SN/Cu	Nanosheet	C_2H_5-OH	−1.2 V RHE	46.0	[221]
mBi-DETA NSs	Nanosheet	HCOOH	−0.8 VRHE	96.8	[222]
Bi_2O_3@PPy NSs)	Nanosheet	HCOOH	−0.8 VRHE	95.8	[223]
Ultrathin Co_3O_4 Layers	Nanosheets	HCOOH	−0.8 V/RHE	51.2	[224]
Co/MOF	Nanosheets	CH_4	−0.4 V/RHE	22.4	[225]
AEI-OD-Cu	Nanosheets	C_2H_4	−0.6 V/RHE	85.1	[226]
Bi Nanosheets	Nanosheets	HCOOH	−1.2 V/RHE	27.4	[227]
BIF-102NSs	Nanosheets	C_2H_4	−0.8 V/RHE	11.3	[228]
Cu_2O/MOF	Nanosheets	C_2H_4	−1.1 V/RHE	52.1	[229]
CuS Nanosheet Arrays	Nanosheets	HCOOH	−0.7 V/RHE	70.0	[230]
a/c-BiB NAs/CF	Nanosheets	HCOOH	−0.8 V/RHE	99.9	[231]
Fe_2P2S_6	Nanosheets	CH_3-OH	−0.2 V/RHE	65.2	[232]
1 T/1H-SnS_2	Nanosheets	HCOOH	−1.1 V/RHE	63.3	[233]
$SnSe_2$/Graphene	Nanosheets	HCOOH	−0.9 V/RHE	93.1	[234]
(Ni(OH)2/NC)	Nanosheets	CO	−0.5 V/RHE	84.3	[235]
Multilayer Zn	Nanosheets	CO	−1.1 V/RHE	86.6	[236]
Bi_2O_3NSs@MCCM	Nanosheets	HCOOH	−1.3 V/RHE	93.8	[237]
Vo-ZnO nanosheets	Nanosheets	CO	−1.1 V/RHE	83.1	[238]
AgZn bimetal	Nanosheets	CO	− 1.3 V/RHE	82.5	[239]
Cu/Cu_2O sheet	Nanosheets	CO	− 0.7 V/RHE	93.5	[240]
Pd-Zn nanosheets	Nanosheets	CO	− 1.1 V/RHE	88.5	[241]
Hcp-Co	Nanosheet	C_2H_5-OH	−0.4 V/RHE	60.2	[242]
Hcp CuBi	Nanosheets	HCOOH	−0.6 V/RHE	90.5	[243]
Ag-G-NCF	Nanosheets	C_2H_5-OH	−0.6 V/RHE	82.1	[244]
CuNi	Nanosheet	Ethanol	−1.5 V/RHE	80.5	[245]

structure, enhancing the catalyst's catalytic performance. Additionally, the shell exhibits more excellent activity than its core, and its surface can be modified more readily than that of other nanostructures.

Due to their unique crystal facets, polyhedron nanostructures are commonly employed in metal electrodes [264,265]. The simple and effective layer structure prepared by the in-situ topotactic approach as developed on bismuth oxidize nanosheets based electrocatalyst for CO_2 reduction that contains excellent tin metallic layers that are capable of plenty of areas for the diffusion of electrolytes and demonstrates numerous exterior atoms function as catalysts or regions as a catalyst for CO_2 adhesion [266,267].

Silver (Ag) foam demonstrates high selectivity ($j_{(CO)}$ value of -17.658 mA/cm^2), CO occupancy at low to moderate overpotentials, and CH_4 efficiencies of 51 %. The enhanced *CO energy of binding versus Ag film could contribute to the copper-like performance observed in the following silver foams [244]. Meanwhile, the accessible patterns mentioned keep CO maintaining active positions for extended periods, which causes the C–C coupling response and the production of C_2H_4. From metallic foams, it can be challenging to obtain multicarbon compounds (C_2, C_3, etc.) [268]. Additionally, 3D G-doped N foam was developed for CO_2 reduction. An extensive surface area is displayed at interfaces in hierarchical foam, such as numerous effectively active areas for CO_2 absorption and electrolyte advancement [269,270]. The foam-like catalyst's maximal CO output FE was 85 % at a potential voltage of −0.47 V over at least 5 h [271].

During the reaction, the catalytic performance can be enhanced by utilizing 3D arrays, sandwich-like structures, foam nanostructures, and core–shell configurations, which expose a large active area and an abundance of effectively active sites. The development of hierarchical three-dimensional (3D) nanostructures has garnered significant attention for the fabrication of advanced 3D catalysts, which facilitate highly selective electrochemical reduction of CO_2. This performance can be further enhanced by optimizing parameters such as surface area and pore volume [249,272,273]. It is evident that ensuring catalytic activity for CO_2 reduction requires.

lowering contact resistance, promoting efficient electron and mass transport, and successfully reducing the development of active sites.

The design of a 3D Cu nanofoam with nanoscale dendritic walls, achieved through a simple hydrothermal procedure, aims to explore its potential application in CO_2 reduction processes, due to the increased active sites, improved surface variation, and hierarchical porosity [249]. Compared to bulk Cu, the electrochemical results showed a notable improvement in the kinetics of the HER, and evidence rates for the pursuit of C_1-C_3 hydrocarbons were substantially reduced as a structural effect [274]. Designed the 3D cathode comprised of a long chain of carbon compounds coated using Ni/Fe/Mn-based nanomaterials that exhibited extraordinary stability and consistently produced 50 ml d^{-1} of CH_4 and 185 mg d^{-1} of CH_3-COO– with an approximate current efficiency of 100 % [275]. To improve the efficacy of electrocatalysis, it is necessary to concentrate on developing and fabricating novel electrode materials. This paper asserts that a geometrically structured combination of electronic transfer materials and catalysts should constitute the subsequent generation of electrode materials. Catalytic efficiency and product selectivity must be enhanced with the aid of this combination. The process requires catalysts extracted from nanoparticles and crystallographic dimensions, respectively. The catalytic behavior of nanoparticles may fluctuate considerably between their various crystal planes. Hence, it is essential to conduct exhaustive studies that evaluate the effect of different crystal planes on catalytic activity. Enhancing the efficiency of electron transmission is the primary goal when developing materials for electron transfer. Improving electron transfer efficiency, designing and modifying nanomaterials, and the future advancement in CO_2 electroreduction will depend on this methodology.

3.10. Dimensional electrocatalytic components of structure

D factor significantly affects the catalytic activity and selectivity of electrode materials. For example, Au nanoparticles with dimensions equal to 5 nm can generate H_2; on the other hand, 8-nanometer gold nanoparticles exhibit more excellent selectivity in CO formation. This is attributed to the rise of cost-effective, coordinated sites on reduced-sized nanoparticles, which inhibits the CO formation process [276]. Nanoparticles made of Bi, Sn, and Pb spread well inside electrodes due to their small surface. However, catalysts with higher macroscopic sizes benefit from the nanostructure of these particles, which expands their surface as components get closer. Catalysts can expose additional active regions for CO_2 adsorption due to their respective positions and increased active surface, which facilitates the reduction of CO_2 to various chemical compounds and enables more selective manufacturing. A nanostructure electrocatalyst was developed by integrating N-doped PC61BM (N-C61), the leading catalyst consistently demonstrated a FE of 91.2 % in HCOO production at a sufficient overpotential of 700 mV [272]. Their outcomes indicated that the nanostructure performed significantly better in reducing CO_2. Since Sn particles can interact more closely with an electrolyte at the nanoscale, these features can potentially increase

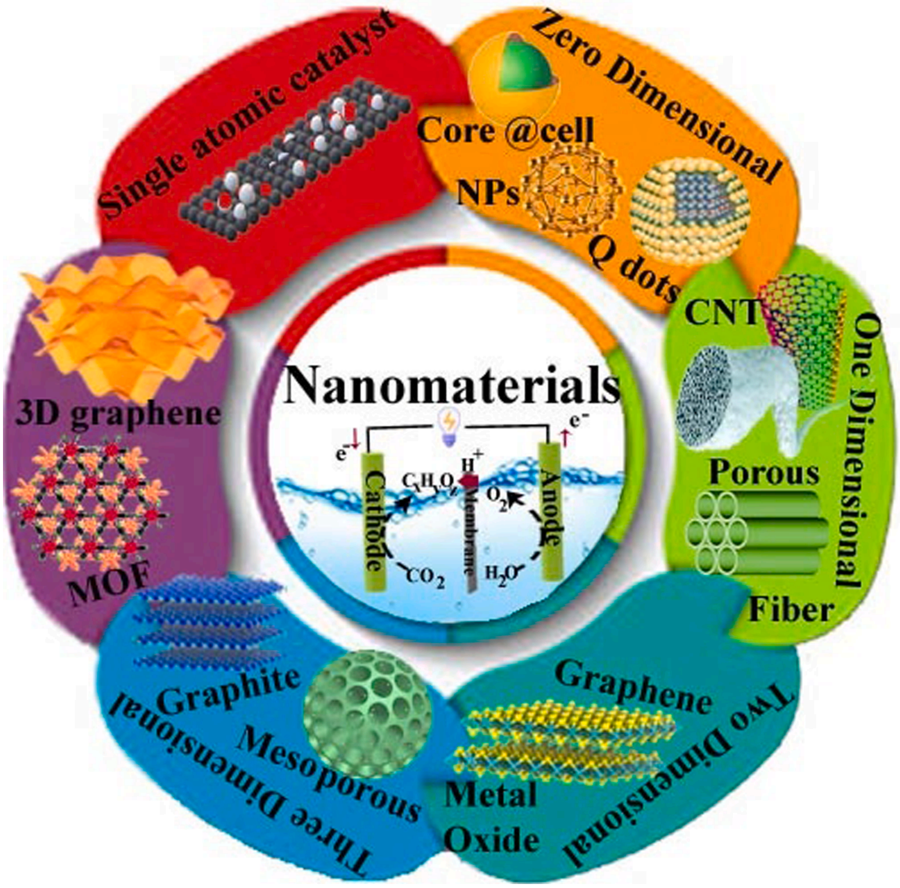

Fig. 6. Application of various nanomaterials in electrochemical reduction of CO_2. The copyright for the publications from Journal of Elsevier in 2021 [246].

Table 4
Overview of 3D composite materials in the electrochemical reduction of CO_2.

Materials	Structures	Product	Potential	F.E. %	Ref
Al–Cu_2O	Octahedral	Ethylene	−1.2 V/RHE	44.9	[247]
AgCl NWs	Nanowire	CO	−0.8 V/RHE	97.0	[248]
3D Cu	Foams	CO	−0.3 V/RHE	59.8	[249]
3Cu	Nanodendrites	CH_4	−1.2 V/RHE	45.0	[250]
3ZnBi	Nanodendrites	HCOO–	−0.75 V/ RHE	85.0	[251]
Porphyrin/Gr	3D Hydrogels	CO	−0.49 V/ RHE	96.4	[252]
Co(III)TPPCl/ GO	3D CoTPP	CO	−0.8 V/RHE	90.1	[253]
Cu/C	Octahedron	CH_4	− 1.3 V/RHE	55.2	[254]
NGQDs	Quantum dots	CH_4	−0.1 V/RHE	70.2	[255]
Bi_2O_3/NGQDs	Quantum dots	HCOOH	−1.0 V/RHE	29.3	[256]
CQDs	Quantum dots	CH_4	−1.6 V/RHE	52.0	[257]
Sn QDs	Quantum dots	HCOOH	−1.1 V/RHE	95.0	[258]
Co–N5/HNPCSs	Core@shell	CO	−0.7 V/RHE	99.2	[259]
Cu in NGQDs	Quantum dots	CO	−0.9 V/RHE	54.2	[260]

electron transfer efficiency. **Guo et al.** further investigated how the particle size of Pd impacts the catalyst's function in CO_2 electroreduction. The dimensions of the Pd nanoparticles were reduced from 10.3 nm to 3.7 nm, and the researchers determined that the overall faradaic efficiency, enabling CO generation, increased by 5.8 % to 91.2 % [273]. Smaller nanoparticles may expose more catalytic sites for CO_2 electroreduction intermediate adsorption, thereby enhancing the electrocatalytic efficiency required for carbon dioxide reduction. Size regulation might impact the ratio of edge-to-platform sites and the electronic structure of nanoparticles. Influencing the crystal's facets is a viable alternative method to accomplish CO_2 reduction with substantial selectivity and electrocatalytic effectiveness. These distinctive, stunning patterns of equivalent catalysts can occur when developing various products. Ag wires that possess Ag (211) feature an improved ability to attract COOH-based intermediates, which could enhance the electroreduction of CO_2, enabling high-selective CO generation rates [276]. Cu-based accelerators with an extensive number of Cu (100) aspects, resulting in the creation of C_{2+} products with an efficiency of conversion of 40.5 % while electroreducing CO_2 and It has been demonstrated that Cu (100) facets can lower the dimerization energy barrier, offer robust stability for CO intermediates on catalytic surfaces, and consequently promote the expansion of the chain of carbons [254,277]. The Zn (101) aspect seems more advantageous for reducing CO_2 into CO, whereas the Zn (002) component prefers to form H_2. The reduction potential decrease induced by the Zn (101) facet, from CO_2 to CO, may facilitate the stabilization of COOH intermediates, thus enhancing the electrocatalytic activity of the electrode material [251].

Since most CO_2 electrocatalysis reactions comprise the solid, liquid, and gas phases, interfacial change has attracted increasing recognition. Modifying the interfaces might improve the electrocatalytic performance of the electrode materials. Aqueous electrolytes are typically present during CO_2 electrolysis, and due to the lower overpotential of the hydrogen evolution process, this phenomenon competes with the production of selective products. Certain electrode materials have undergone surface modifications to enhance interface control in electrocatalysis. The nitrogen-doped carbon coating onto the Cu surface, the formation of a thin carbon layer induced numerous active sites, enabling the presence of nitrogen defects as a barrier, preventing the catalytically active Cu from altering its shape, which would otherwise facilitate an astounding 90 % FE act of transforming carbon dioxide to C_2 outcomes [256].

Coating the electrode surface with polytetrafluoroethylene (PTFE) on the Cu nanoarray encapsulated led to increased electrocatalytic effectiveness. Since most CO_2 electrocatalysis reactions comprise the solid, liquid, and gas phases, interfacial change has attracted growing recognition [278]. Modifying the interfaces might improve the electrocatalytic performance of the electrode materials. Aqueous electrolytes are typically present during CO_2 electrolysis, and due to the lower overpotential of the hydrogen evolution process, this phenomenon competes with the production of selective products. Certain electrode materials have undergone surface modifications to enhance interface control in electrocatalysis. The nitrogen-doped carbon coating onto the Cu surface, the formation of a thin carbon layer induced numerous active sites, enabling the presence of nitrogen defects as a barrier, preventing the catalytically active Cu from altering its shape, which would otherwise facilitate an astounding 90 % FE act of transforming carbon dioxide to C_2 outcomes [278]. The increase in electrocatalytic effectiveness was achieved by coating the electrode surface on the Cu nanoarray encapsulated with polytetrafluoroethylene (PTFE) to render it hydrophobic[279], and the improvement resulted in a 67 % FE to reduce CO_2 using propanol as well as ethanol [280]. The electrocatalytic efficacy was increased by substituting carbon nanotubes (CNT) with an epichlorohydrin dimethylamine copolymer (EDC) electrode. To improve electrocatalytic performance, we propose the following: electrode generation materials that incorporate nanostructure design, control size effects, select specific crystal faces, and modify interfaces [281]. For achieving high conversion efficiencies for products with added value, materials used in electrodes are necessary to remove the faces of crystals and nanoparticles for optimal catalytic activity and product selectivity [282,283]. Further research should investigate the effects that different crystal planes suffer from on catalysis. The primary objective of interface modification should be to increase the hydrophobic/hydrophilic or aerophobic/aerophilic characteristics of the electrode surface to enhance its effectiveness.

4. Electrolysers used in CO_2 capturing systems

Bioelectrocatalysis relies on electrolysis, which functions as an inhibitor of the external environment of the electrode[121,284]. The primary objective remains to utilize electrical energy to drive reduction–oxidation reactions, which typically culminate in oxygen generation and the decomposition of CO_2 [283,285,286]. Different cell designs, including H-cell, flow-cell, and bilayer electrode assembly cells, are frequently used to extract and produce electrolytes [287]. Due to its accuracy and ease of operation with a wide range of catalysts and electrodes, the H-cell electrolyzer has been widely adopted. However, the dissolution of CO_2 into the electrolyte and subsequent transportation of that material to the cathode for reduction is crucial to enable the technology to produce electricity [288,289].

Moreover, the limited mass transfer of CO_2 reduces the prospective current density and hinders the process's economic viability[56,290]. Both the transfer-cell electrolyzer and the MEA-cell electrolyzer utilize gas diffusion electrodes to ensure a consistent electrolyte flow throughout the system. This setup enables real-time adjustments to operational parameters while also improving current density and mass transfer [291]. Flow-cell electrolyzers, on the other hand, rely on the combined conductive and anodized products and have limited essential electrolyte stability, diminishing their overall effectiveness and undermining their ability to conserve energy [292]. As an alternative, the MEA-cell electrolyzer implements an alternate strategy by firmly integrating the interaction between the bipolar membrane and the catalytic layer, which occurs through the cathodic gas diffusion electrode, thereby eradicating the need for catholyte. The configuration reduces ohmic losses, prevents catalyst contamination, and improves the system's sustainability and dependability [293,294]. As a result, MEA-cell electrolysis facilities have garnered more enthusiasm, particularly for C_{2+} products and promotional purposes[295]. Copper catalyst by incorporating organic coatings containing nitrogen-4,4′-bipyridine that has been 'sulphurized'. Following the subsequent conditions for 190 h at a current density of 80 mA cm^{-2}, ethylene was produced with an FE of 64 % and energy efficiency of 20 % [165,296]. Designed with a multilayer electrolyzer intended for producing CO by connecting MEA units sequentially, thereby increasing the electrochemical surface-active area, and their design yielded the transfer efficacy of CO_2 of 40 %, a FE of 95 % and densities of currents reaching 250 mA cm^{-2} [297]. The representatives for the MEA-cell are described in detail in Table 4.

5. Prospective strategies for electrochemical reduction of CO_2

5.1. Advancements desired for bioelectrocatalytic reduction of CO_2

Biocatalysis displays remarkable efficiency under gentle operating conditions. While this aspect promotes sustainability and affordability, it simultaneously imposes limitations when discussing bioelectrocatalysis characteristics [48,298,299]. Digestive enzymes in distinct active parts, including peroxidase, cytochrome *C*, and ferredoxin, are excellent options for promoting DET [300–302]. Subsequently, achieving the equilibrium and appropriate operation of enzymes near an electrode is relatively challenging. While mediators possess the capacity for increased electron transportation performance, they also remain able to be harmful to biocatalysts, particularly enzymes [300,301]. Co-assembling biocatalysts and electron mediators using redox polymers and biofilms can enhance communication between electrodes and biocatalysts at nanometer and micrometer scales, thereby improving their biocompatibility, conductivity, and mass transfer efficiency [20]. Integrating sophisticated electrochemical methodologies, nanomaterials, enzymes, and microbiological electrosynthesis can optimize the manufacturing process of commercially viable compounds and biofuels derived from alternative energy resources. Furthermore, this could result in a decrease in energy usage [288,303,304].

In addition, microbe colonies that can enhance electric acceptance for bioelectrocatalysis generation have been reported. Hogan estimated that the methanogenesis assessment revealed a methane production rate of 0.72 mg L^{-1} day. Additionally, evidence from the microbial community indicated a significant association between the methane production and the abundance of *Euryarchaeota* and the *Desulfovibrionaceae* phylotype [63,305]. In addition, it demonstrated that particular species in the community that cannot generate methane on their own may contribute to improving the transfer of electrons and ultimate synthesis.

The modification of electrodes can improve the bio-catalytic properties and their applicability for bio-electrochemical purposes [20,306]. Despite considerable emphasis on the appealing attributes of electrochemical technologies, there have been significant developments in innovations and viewpoints concerning the most promising electrochemical instruments for wastewater remediation [290,306]. Moreover, the effectiveness of electrocatalytic anodes could be enhanced through integrated methodologies that merge homogeneous and heterogeneous catalysis with simultaneous anodic and cathodic processes. Electrochemically produced reactive chlorine facilitates oxidation, while electrocatalysis achieves reduction [307]. *Ralstonia eutropha H16* was induced to generate isobutanol and 3-methyl-1-butanol in an electron bioreactor predominantly powered by carbon dioxide and electricity via substantial genetic modification. This procedure combines the production of formate electrochemically with the biological fixation of CO_2 and increased alcohol production to transform CO_2 into marketable compounds via electricity-driven fermentation [308]. Consuming the systematic integration of conductors into an ultrathin silica membrane, chemical separation between abiotic and biotic elements is accomplished with their electrochemical interactions preserved [305,309]. Implement enabling interaction directly with gaseous CO_2 via the diffusion cathode. Based on the innovation, a substantial acceleration of the mass transfer process of CO_2 in salt-based electrolytes was achieved [310]. Biocompatible perfluorocarbon nanoemulsion as the carrier for H_2, which stands, and their innovative strategy caused a remarkable increase in acetate production, attaining an overall reported increase in productivity [306,311]. The development of photoelectrodes that directly harvest solar energy to generate electrical current [312], has facilitated the fixation and conversion of CO_2. Combining synthetic biology with the design techniques for establishing redox-enabling processes facilitates interaction between biotic and abiotic components. Besides using artificial light-harvesting complexes, we can enhance the transfer of electrons and improve solar energy production/conversion processes [313,314]. Such integration of diverse technologies provides potent instruments for advancing solar energy usage. Using a polyphenol-based assembly method, integrating yeast cell factories with indium phosphide-based light-harvesting nanoparticles facilitates shikimic acid's carbon- and energy-efficient production [315]. These findings are expected to advance the practical applications of semi-artificial photosynthesis significantly. Combining CdS nanoparticles with a synthetic CO_2-fixing *E. coli* pathway enhances anaerobic L-malate and butyrate production, showcasing the synergy of nanotechnology and synthetic biology in generating valuable compounds [316]. To advance enzymatic electrosynthesis, it is crucial to explore the adaptation of this apparatus to non-biological reactions and conditions. Directed evolution, known for its effectiveness in creating new biocatalysts, holds significant potential for improving bioelectrochemical systems [314,317]. We can indicate a new era of inventive synthetic reactivity [318].

Some modifications can enhance the functions of enzymes by designing the active site, proposing new reactions, and conferring redox behavior on non-redox enzymes. It significantly exceeds current limitations and offers intriguing reaction-design possibilities. Enzymatic electrosynthesis can also be achieved through the design of non-traditional reaction media, which helps create new and sustainable reaction processes [319,320]. While biphasic systems for electrosynthesis have shown promise, it is crucial to remain aware that as enzymatic systems are used for more complex redox reactions, the reaction medium becomes complex [284,321]. The continued extensive use and design of reliable artificial enzymatic organisms in non-aqueous environments present a promising solution, particularly when coupled with integration into renewable energy systems, scaling-up strategies, techno-economic considerations, and the potential role of artificial intelligence in advancing bioelectrocatalysis. The investigation into hybridized biological cascading processes over electrosynthesis, which involves separate enzymes, catalyzes redox reactions in aqueous solutions [322].

In contrast, molecules of organic compounds or transition metal complexes are typically engaged in non-aqueous solutions, which have proven to be limited. In comparison, bioorthogonal methods have attracted considerable interest and had a significant impact [323]. However, as electroorganic synthetic methods gain popularity, enzymatic electrosynthesis is anticipated to expand into these fields as a complementary synthetic resource.

5.2. Enhancing electron transfer efficiency in electrochemical reduction of CO_2

Optimizing the electron transfer rate and increasing multi-electron transfer efficiency in bioelectrocatalysis is paramount [324]. In instances where oxidoreductases are utilized in enzymatic electrocatalysis, active sites tend to be concealed within the complex enzyme structure. This results in greater control over intra-enzyme electron transfer, decreasing the electron transfer efficiency between electrodes and enzymes [57,58]. Enhanced connectivity between electrodes and oxidoreductases has been achieved through the application of enzyme engineering, which includes truncating proteins to eliminate non-essential peptides and reveal active sites, modifying surface properties (such as de-glycosylation) to reduce protein dimensions and promote electron transfer, and modifying active sites to optimize the channellings of electrons [325,326]. In some cases, enzymes can be modified by conducting polymers [6,63,305]. A redox polymer and a tethering motif can be used to anchor oxidoreductases onto the electrode surface, thereby increasing local enzyme concentrations [52,61,64,66]. However, the formation enzyme of monolayers may reduce the total catalyst concentration [327].

A substantial proportion of membranes in cells exploited in microbial electrocatalysis lack conductivity. In addition, the microbial pathways of a microbial system are complex and necessitate the presence of multiple cofactors that facilitate the transfer of electrons as the driving force [58,321]. Future research could determine that placing these protein nanowires on the surfaces of microbial cell factories facilitates the effective transfer of electrons [327]. Cytochromes and conductive nanowires, as well as redox intermediaries or carriers of energies, are among the technologies used to connect electronic devices with microbial cell factories [327–329]. The extracellular electron transfer of the atomic structure of the electron-conducting outer membrane protein complex – MtrAB – and the structures span the outer protective membranes of *Shewanella* species and assist in connecting cells to extracellular electrodes to facilitate electron transfer [330]. Surface charge generation of cytochrome OmcZ nanowires with remarkable conductivity and rigidity. Based on these nanowires, electricity activated the biofilms of *Geobacter sulfurreducens* [331]. Subsequently, it remains possible to create synthetic channels with effective biological pathways to produce significant products, enabling the direct collection of electrons for biosynthesis (Fig. 7(1)). Thus, the reliance on additives and overall energy usage would drastically decrease. Indirect electron transfers often involve various carriers and intermediaries. These include electron-carrying cofactors (H_2 and formate) and native mediators such as flavins and quinine. Natural and synthetic substances, such as humic acid and neutral red, also contribute.

Enzymes such as hydrogenases and formate hydrogenases additionally impact these processes [336]. Consequently, it was initially suggested that improving the methods of the bound flavin could significantly increase the extracellular transfer of electrons [337]. Bimetallic Pt- and Ni-based electrocatalysts for the hydrogen evolution reaction in *Methanosarcina barkeri* to turn CO_2 into methane with an impressive 81 % faradic efficiency [338]. A single enzyme or a combination of multiple enzymes can efficiently catalyze the electro-enzyme coupling conversion of CO_2 into hydrocarbon products, including formate, CO, methanol, and C_2 chemicals, as depicted in Fig. 7 (2). *Cupriavidus necator* integrated catalysis into C. necator, resulting in the efficient production of cellular mass, fuel alcohols, and PHB [339]. *S. oneidensis MR-1* essential genes associated with NAD + biosynthesis in Shewanella oneidensis, leading to an impressive rise of 2.1-incorporate in the intracellular NAD(H) concentration [340]. Furthermore, the Flavia-generation mechanism, initially present in *Bacillus subtilis*, was successfully transferred to *S. oneidensis* by incorporating nanomaterials, leading to an impressive 15.5-fold enhancement in internal current density [341]. Fig. 7(3) provides a comprehensive overview of the essential elements and future paths for MES feature enhancement, emphasizing the necessity for varied study endeavors consistent with the abovementioned works. MES's further development and industrialization remain contingent upon technological advances and accomplishments in material science, mass transfer, and biocatalysis. Notwithstanding the considerable and valuable insights that have been amassed in recent times concerning the operational parameters of MES, including the influence of cathode potential, C source type, and reactivity conditions, this remained the case. Future research in plant MES will focus on optimizing plant reactors through engineering in order to improve performance and overcome obstacles. Alternative bioelectrochemical systems have been devised to produce electric power through solar radiation-induced biological alignment between organisms and microbes, including plant microbial fuel cells (PMFCs), as shown in Fig. 7(4). To investigate and improve the implementation of PMFCs using naturally occurring vegetation to generate sustainable

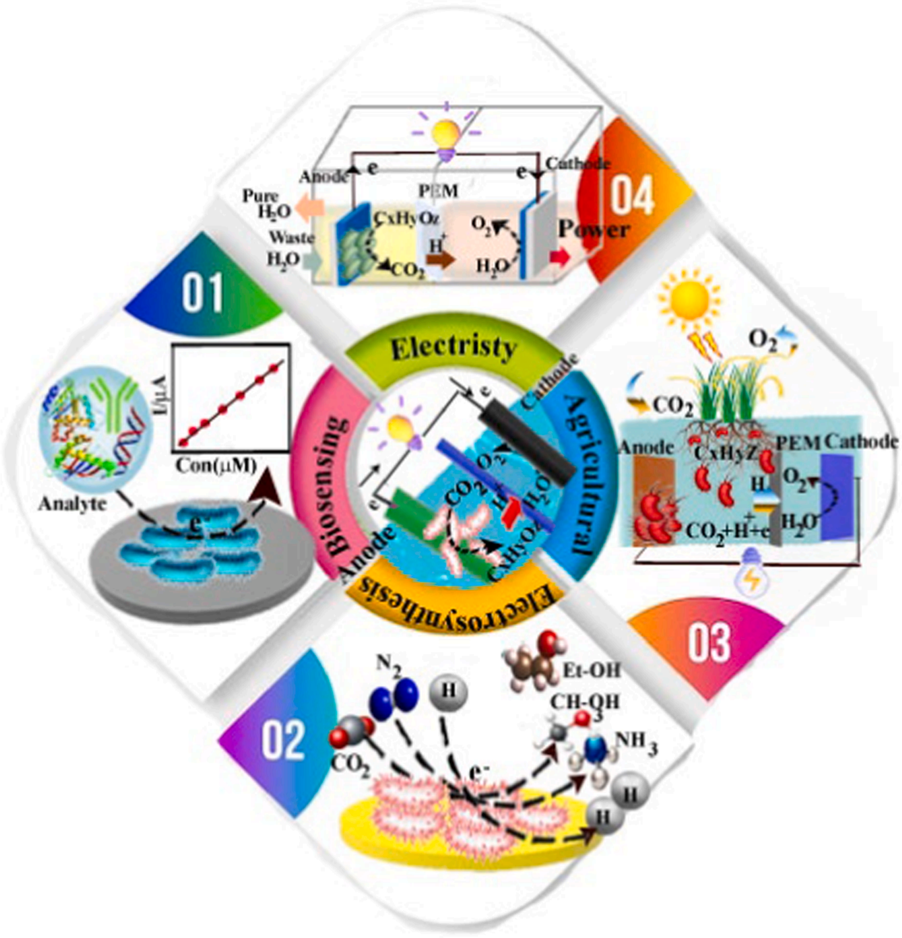

Fig. 7. The schematic diagram for microbial electrochemical systems encompasses a multitude of applications, including electricity generation, the advancement of biosensor technology for monitoring hazardous and potentially hazardous composite materials, the generation of electrictricity on agricultural and arable land, and the establishment of bioelectrosynthetic factories. Copy right of the paper Elsevier, 2022, [332,333], Springer 2020 reference [334,335].

electricity, the fundamentals of PFCs have been studied. Vascular plants, macrophytes, and bryophytes find applications in various environmental processes, including wastewater treatment, remediation of contaminated drinking water and detritus, reduction of greenhouse gas emissions, and biological sensing [153,342]. Genetic modification and regulation of microbes and enzymes are essential for adapting reactor configurations and modifying operational parameters within MES systems. As MES advancements progress over the next decade, there will be a growing demand for robust biocatalysts, efficient reactors, and systems capable of operating in adverse conditions. Therefore, it is critical to integrate multidisciplinary research from synthetic biology, biochemistry, electrochemistry, process engineering, chemistry, microbiology, and multiscale simulation for a comprehensive understanding of the efficiency and yield constraints imposed by MES platforms.

These variables, which vary across fields of study, contribute to the advancement of MES technology. Based on the investigated research, non-biological advancement is notably feasible. Future MES advancements can be driven by computational modelling and scalable reactor/electrode design [343]. Genetic engineering techniques have been exploited to enhance bacterial resistance to more demanding conditions, including increased temperatures and sodium concentrations, and to extend the range of value-added products manufactured by MES [344]. With electrosynthesis, the genetic engineering of microorganisms for MES applications impacts the field. Indeed, computational biology research has focused on creating synthetic biological processes or altering organic methods to manufacture sophisticated natural products, pharmaceuticals, and biochemicals [320,345]. Exploiting strategies from synthetic biology to enhance microbes' intercellular electron transmission, a crucial factor via the performance of bioelectrochemical systems signifies extremely extensive progress within the area of study. Establishing a dependable and effective electrochemical interface is critical in implementing bioelectrochemical strategies that leverage synthetic biology technologies. This involves optimizing interactions across the surfaces of electrodes and bacteria, particularly non-electroactive microorganisms. The integration of the outer membrane protein complex (Mtr) based pathway, sourced from *S. oneidensis*, into the *E. coli* has been achieved through the application of genetic engineering methods. This modified *E. coli* can efficiently harness external electrons from the electrode to initiate desired reactions [343–346]. In a distinct instance, incorporated artificial networks into electrochemical cells using a particular method. Precisely, their engineered *E. coli* cells convert carbon dioxide into n-butanol, polyhydroxybutyrate, and natural products [347]. Enhancing the movement of electrons outside cells is necessary to achieve the high current densities required for long-lasting microorganism-based electrosynthesis platforms.

In contrast, research has demonstrated enhanced extracellular electron transfer, and future demands novel approaches that blend electrode design with materials for biological replication in advanced, reliable MES platforms. Diverse analytical techniques, including tissue cell analysis, biological sensors, and mass spectrometry, will be crucial for determining the expression levels of heterologous proteins and understanding the functional dynamics and behavior of designed biological catalysts. These insights will facilitate the optimization of future MES systems' performance.

6. Outlook and concluding remarks

The evolution of CO_2 capturing technologies shows real potential to slow down climate change and further the development of the circular economy. Consequently, there is an increasing emphasis on recent advancements in converting CO_2 into fuels and other valuable chemical compounds. Bioelectrocatalytic systems dedicated to CO_2 capturing still need significant improvements in subsequent aspects: (i) advancements in integrating bioelectrocatalysis on the electrode surface, application of porous conducting/electro-catalysing nanomaterials and enhanced discrimination of reducing and oxidizing products, and formation of final C_{2+} product with increased stability; (ii) increased selectivity, extended stability, enhanced adaptability for the generation of tailor-made products, and greater diversity of formed C_{2+} products, particularly those with longer chain lengths, including biopolymers and biofuels; (iii) bioelectrocatalysis outperforms bio-catalysis in two crucial stages: facilitation of CO_2 fixation and the improvement of charge transfer between components of bioelectrochemical system.

The most promising advancements could be based on the application of conducting nanowires and metabolic frameworks, which utilize CO_2 as a reactant. The advanced combination of photocatalytic materials and microbes enables a significant reduction of energy consumption and will provide cost-effective CO_2 conversion into valuable organic compounds such as formate, which in the future could be applied as a base material in the formate-based economy'. However, some intracellular electron transfer pathways in redox enzymes and other biocatalytic systems remain insufficiently explored. Therefore, an advanced understanding of intracellular charge transfer pathways and charge transfer heterogeneous boundaries is essential for further developments in this area. The advancement in the above-mentioned areas will enable the improvement of CO_2 conversion and facilitate the production of desired C_{2+} products. Recently, two main factors have been identified as limiting the efficiency of electrocatalysis: (i) the rate of charge transfer and (ii) the efficiency of CO_2 mass transfer. For improvement, advanced electrode materials (e.g., core–shell structures, arrays, foam compositions, sandwich-like configurations, and polyhedra in 3D, as well as their combinations) are utilized. The MEAN-cell electrolyzer, which is being extensively advanced as a route toward the commercialization of bioelectrocatalysis, also provides a platform to specifically address the decline in selectivity during large-scale production caused by mass transfer limitations, as well as the broader scalability challenges inherent to enzymatic and microbial systems. To mitigate these issues, we present optimization strategies such as designing hierarchical porous structures to improve reactant accessibility, employing flow reactors to enhance mass transport, and applying catalyst surface engineering to sustain high selectivity under industrial conditions [348]. Furthermore, reactor design and process modifications are highlighted as crucial measures for overcoming mass transfer limitations and improving efficiency. For instance, microreactors and flow reactors provide extremely high surface-area-to-volume ratios, enabling efficient heat and mass transfer and offering better control and selectivity. Similarly, structured catalytic packings enhance flow distribution and mass transfer coefficients compared with traditional packed beds. Advances in catalyst and process engineering, including the design of catalysts with reduced particle sizes or porous architectures, improve internal mass transfer, while the use of high-efficiency impellers or static mixers enhances bulk mixing and minimizes concentration gradients [349]. In addition, multistage reactor configurations maintain optimal conditions by controlling reactant concentrations across each stage. Alongside these developments, advanced monitoring and control systems, such as real-time in-situ CO_2 reduction technique and advanced process control techniques, enable dynamic adjustments and predictive management of process variables, ensuring stable performance and reducing the effects of mass transfer limitations [350]. To mitigate this, we present optimization strategies such as designing hierarchical porous structures to improve reactant accessibility, employing flow reactors to enhance mass transport, and applying catalyst surface engineering to sustain high selectivity under industrial conditions [351]. Furthermore, reactor design and process modifications are highlighted as crucial measures for overcoming mass transfer limitations and improving efficiency. For instance, microreactors and flow reactors provide extremely high surface-area-to-volume ratios, enabling efficient heat and mass transfer and offering better control and selectivity [352]. Similarly, structured catalytic packings enhance flow distribution and mass transfer coefficients compared with traditional packed beds. Advances in catalyst and process engineering, including the design of catalysts with reduced particle sizes or porous architectures, improve internal mass transfer, while the use of high-efficiency impellers or static mixers enhances bulk mixing and minimizes concentration gradients [353]. In addition, multistage reactor configurations maintain optimal conditions by controlling reactant concentrations across each stage. Alongside these developments, advanced monitoring and control systems, such as real-time in-situ CO_2 reduction and advanced process control techniques, enable dynamic adjustments and predictive management of process variables, ensuring stable performance and reducing the effects of mass transfer limitations [354].

Collectively, these revisions provide a more comprehensive analysis of the challenges and solutions associated with scaling up these technologies; in parallel, we emphasize that scaling enzymatic and microbial systems, from fuel cells for electricity generation to microbial electrosynthesis of value-added chemicals, faces distinct biological and economic barriers. Microbial fuel cells, for example, suffer from sharp declines in power density at larger scales due to ohmic losses, inefficient electron transfer, mass transport barriers, and biofilm instability, while microbial electrosynthesis systems struggle with low energy efficiency and limited product selectivity in CO_2 reduction [355]. Addressing these biological and operational challenges in parallel with engineering innovations such as improved catalyst utilization and large-scale production is essential, as these strategies are projected to reduce costs below $200 per kW, thereby aligning with practical deployment targets. This integration of performance improvements and cost reduction underscores the economic feasibility of MEA-based bioelectrocatalytic systems and their potential to accelerate commercialization[356]. Addressing these constraints requires innovations in electrode engineering, biofilm stabilization, and standardized performance metrics, as well as integration of advanced materials to improve efficiency and reduce fabrication costs. Looking ahead, biohybrid catalysts that couple enzymes or microbes with nanostructured synthetic materials, together with synthetic biology tools such as CRISPR-Cas-enabled pathway engineering, offer promising strategies to improve enzyme stability, electron transfer efficiency, and product specificity [357]. Collectively, these revisions provide a more comprehensive and balanced analysis of the technological, biological, and economic challenges of scaling up bioelectrocatalytic systems, while highlighting current advances and future opportunities for achieving industrial translation.

Moreover, advancing theoretical calculations of modified nanomaterials interacting with bacterial metabolic pathways is essential in order to facilitate the development of the most efficient systems for CO_2 conversion. This review highlights technological advancements that suggest bioelectrocatalysis will drive notable progress in the generation of renewable energy and the synthesis of valuable chemical compounds.

CRediT authorship contribution statement

Kumarasamy Jayakumar: Writing – original draft, Visualization, Formal analysis, Conceptualization. **Huangxian Ju:** Writing – original draft, Conceptualization. **Simonas Ramanavicius:** Writing – review & editing, Resources, Conceptualization. **Arunas Ramanavicius:** Writing – review & editing, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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Data availability

Data will be made available on request.

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