



## Review

# Role of the cathode chamber in microbial electrosynthesis: A comprehensive review of key factors

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## ARTICLE INFO

## Keywords:

Microbial electrosynthesis  
Energy regeneration  
CO<sub>2</sub> reduction  
Cathode chamber  
Electroactive bacteria

## ABSTRACT

The consumption of non-renewable fossil fuels has directly contributed to a dramatic rise in global carbon dioxide (CO<sub>2</sub>) emissions, posing an ongoing threat to the ecological security of the Earth. Microbial electrosynthesis (MES) is an innovative energy regeneration strategy that offers a gentle and efficient approach to converting CO<sub>2</sub> into high-value products. The cathode chamber is a vital component of an MES system and its internal factors play crucial roles in improving the performance of the MES system. Therefore, this review aimed to provide a detailed analysis of the key factors related to the cathode chamber in the MES system. The topics covered include inward extracellular electron transfer pathways, cathode materials, applied cathode potentials, catholyte pH, and reactor configuration. In addition, this review analyzes and discusses the challenges and promising avenues for improving the conversion of CO<sub>2</sub> into high-value products via MES.

## 1. Introduction

Since the advent of the industrial revolution, non-renewable fossil fuels including coal, petroleum, and natural gas have served as crucial underpinnings for the progress of human society. As global energy demand continues to increase, these fuel resources are rapidly depleting and proving to be unsustainable. Moreover, the widespread utilization of fossil fuels persistently jeopardizes global ecological safety through the emission of toxic and hazardous gases [1,2]. By the end of 2018, global energy consumption had increased by 2.3%, which was nearly double the average growth rate since 2010. This surge in global fossil fuel consumption has directly contributed to a significant rise in the cumulative global CO<sub>2</sub> emissions, reaching a staggering 33.1 Gt [3]. Currently, anthropogenic activities continue to release CO<sub>2</sub> into the atmosphere at an alarming annual growth rate of 4%. Projections from the International Energy Agency indicate that the cumulative global CO<sub>2</sub> emissions are expected to reach 40.2 Gt by 2030 [4,5]. According to the estimates of the Intergovernmental Panel on Climate Change, atmospheric CO<sub>2</sub> levels could potentially reach as high as 570 ppm by 2100, resulting in an average global temperature increase of approximately 1.9°C and a sea level rise of 3.8 m [6]. Excess CO<sub>2</sub> will worsen ocean acidification and may result in a dramatic decline in marine species diversity, including the complete extinction of some species [7]. By 2060–2080, 5–13% of

terrestrial tetrapods and 2–6% of marine animals are estimated to become extinct, with global warming caused by CO<sub>2</sub> emissions being one of the major causes [8]. From a sustainability perspective, CO<sub>2</sub> is also recognized as the most abundant and cost-effective C1 resource in the environment [9,10]. Therefore, the development of efficient and economically viable technologies for CO<sub>2</sub> capture, sequestration, and utilization holds immense importance. These technologies not only offer the potential to mitigate the worsening effects of global warming but also reduce the dependence on and consumption of fossil fuels. However, converting CO<sub>2</sub> into complex molecules remains a formidable challenge, owing to its inherently strong C=O bond, with a bond energy as high as 750 kJ mol<sup>-1</sup> [11].

Currently, the utilization of CO<sub>2</sub> is primarily categorized into two major classes: physicochemical conversion [12–17] and biological conversion [18,19]. Non-biological conversion processes require the precise control of reaction conditions and the use of expensive catalysts. Many known catalysts are yet to address certain challenges, such as low selectivity, low Faradaic efficiency, and difficulties in catalyst recovery [12,20]. Additionally, the chemical conversion pathway still relies on non-renewable resources and has a negative environmental impact [21], making non-biological carbon fixation economically unfeasible. In contrast, traditional biological carbon fixation processes, such as photosynthesis, require arable land and solar energy, posing limita-

**Abbreviations:** CO<sub>2</sub>, carbon dioxide; MES, microbial electrosynthesis; EAB, electroactive bacteria; EET, extracellular electron transfer; DET, direct electron transfer; IET, indirect electron transfer; H<sub>2</sub>, hydrogen; SH, soluble hydrogenase; MBH, membrane-bound hydrogenase; SHE, standard hydrogen electrode; PFC, perfluorocarbon; FDH, formate dehydrogenase; RM, redox mediator; 2D, two-dimensional; 3D, three-dimensional; Rubisco, ribulose-1,5-bisphosphate carboxylase.

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<https://doi.org/10.1016/j.engmic.2024.100141>

Received 23 October 2023; Received in revised form 14 February 2024; Accepted 16 February 2024

Available online 17 February 2024

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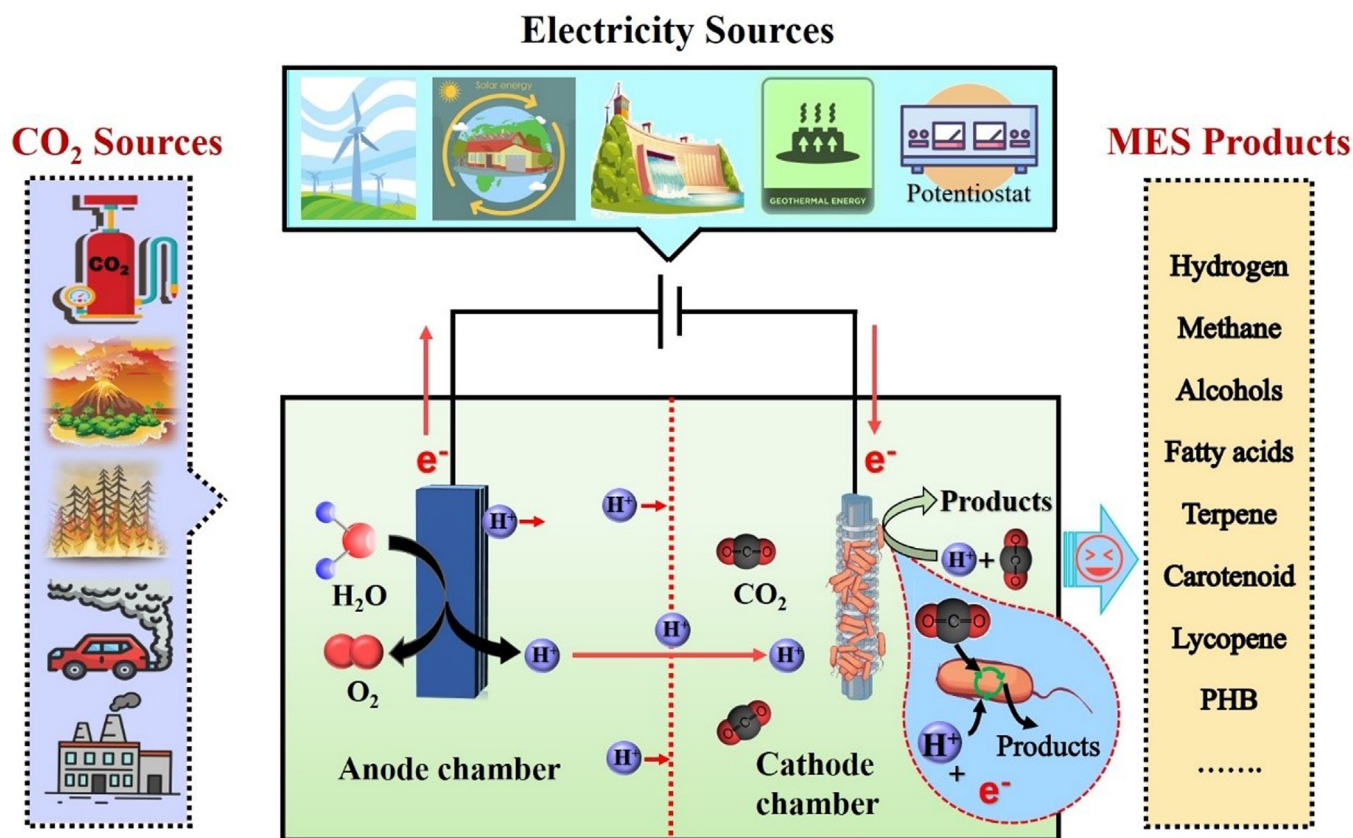


Fig. 1. Schematic of a typical two-chamber MES system.

tions for its widespread application. These limitations of physicochemical and traditional biological carbon fixation processes can be overcome by employing microbial electrosynthesis (MES), an emerging interdisciplinary technology that combines microbiology, electrochemistry, and engineering [22]. This technology has remarkable advantages in efficiently synthesizing high-value products from  $\text{CO}_2$  or organic waste by utilizing the microbial internal metabolic pathways coupled with external energy or bioelectricity [23–26]. Therefore, MES is an efficient, environmentally friendly, and sustainable bioenergy regeneration strategy.

The cathode chamber is the core part of an MES system and its internal factors are closely related to its performance. However, few reviews have systematically summarized and analyzed these key factors affecting the catalytic conversion of  $\text{CO}_2$  via MES in recent years, as well as the challenges and breakthroughs in improving the conversion capability of high-value products. This will help researchers understand the progress, challenges, and opportunities for  $\text{CO}_2$  conversion in MES.

## 2. The microbial electrosynthesis system

### 2.1. Principles and components of MES

The MES is a bioelectrochemical system that utilizes microorganisms as biocatalysts to convert  $\text{CO}_2$  or other organic compounds into high-value products by integrating electric energy with microbial intracellular metabolism. A typical MES system consists of an anode chamber (non-biological compartment) and a cathode chamber (biological compartment) separated by a proton exchange membrane, as illustrated in Fig. 1 [27]. The microbial component in the biocathode chamber can either be pure or mixed cultures. Pure cultures mainly employ au-

totrophic microorganisms with high electron utilization efficiencies, including acetogens, methanogens (such as *Sporomusa ovata*, *Clostridium ljungdahlii*, and *Moorella thermoacetica*), and hydrogen-oxidizing bacteria (such as *Ralstonia eutropha*) [28]. Additionally, mixed cultures have also been widely used as they have higher production rates, like in producing volatile fatty acids, and greater potential for practical applications [29,30]. Applying a negative potential to the cathode drives the electrochemical synthesis reaction and protons generated via water electrolysis in the anode chamber migrate across the proton exchange membrane into the biological cathode chamber. In the cathode chamber, biocatalysts can regenerate the reducing power using the cathode and sustain a series of metabolic processes. These include the Calvin–Benson–Bassham cycle [31], the Wood–Ljungdahl pathway [32], the reverse  $\beta$ -oxidation pathway [33], and other non-autotrophic bacterial pathways that require the assistance of special materials [34,35].

### 2.2. The unique advantages of MES

The MES is a carbon recycling system and an energy storage technology that produces high-value products. For example, the electric conversion efficiency of MES for acetate can exceed 80% [36]. Meanwhile, MES is compatible with various forms of electrical energy input, ranging from conventional electricity to unstable and renewable clean energy sources such as solar, wind, and tidal power, and even bioelectricity [37–40]. Although enzymes and organelles may provide high reaction specificity and controllability, the utilization of microorganisms in bioelectrosynthesis presents several unique benefits, such as the self-regeneration of the catalyst, adaptability of the number of catalysts to the desired conversion activity, having a flexible and wide substrate spectrum, and more versatile product synthesis pathways than those of enzymes or organelles [22]. Additionally, the enzymatic nature of cellular metabolism greatly reduces the difficulty and energy consump-

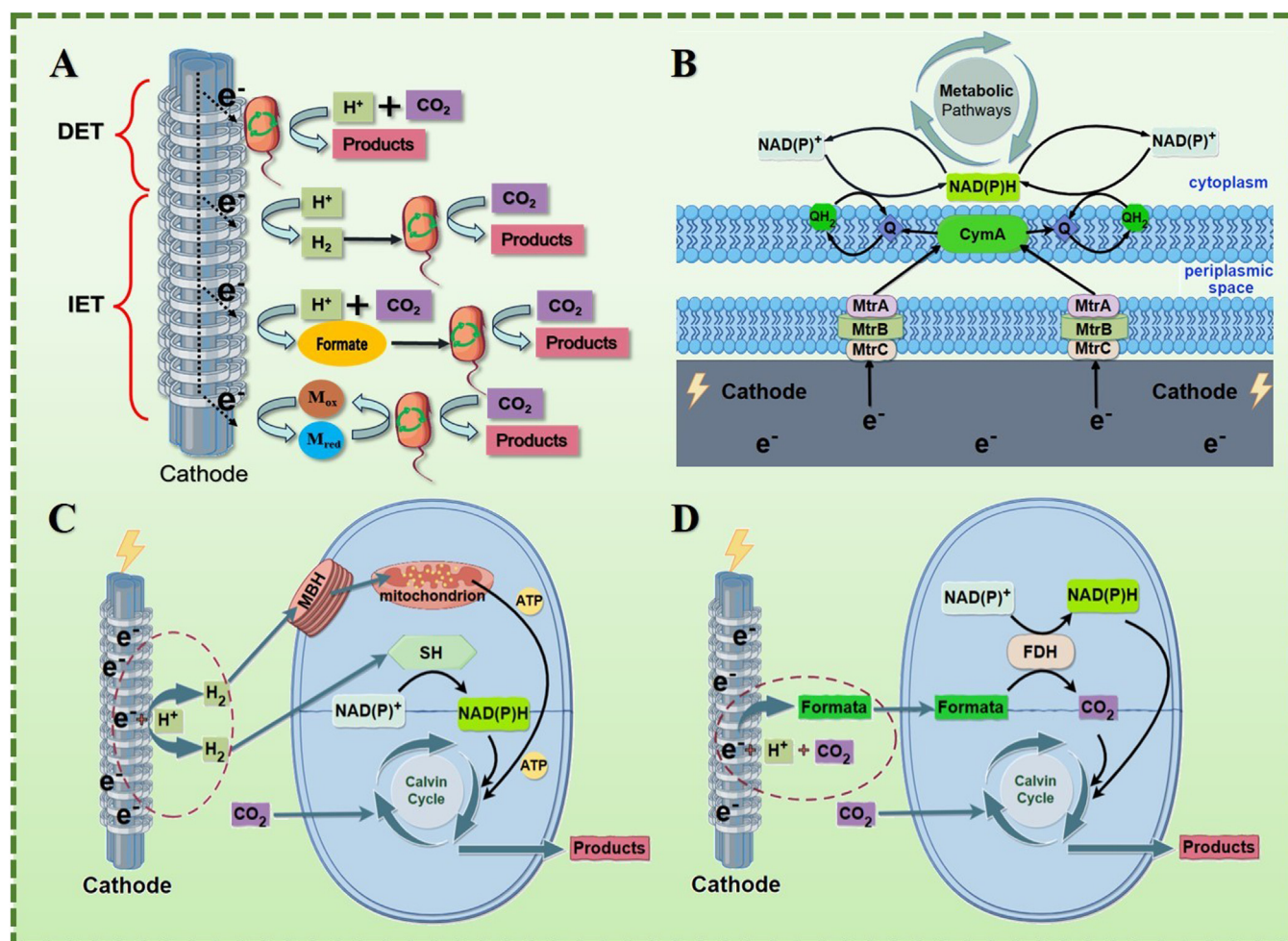


Fig. 2. (A) Schematic of extracellular electron transfer (EET) pathways of microorganisms. (B) Inward direct electron transfer (DET) pathway performed using the MtrCBA complex. (C)  $H_2$ -mediated indirect electron transfer (IET) pathway. (D) Formate-mediated IET pathway.

tion required for  $CO_2$  reduction, enabling the efficient and targeted conversion of  $CO_2$  into various high-value products under mild conditions using low-quality energy sources. While the primary products of MES remain short-chain fatty acids and alcohols, applying synthetic biology techniques has enabled the successful synthesis of complex compounds, including terpenes, carotenoids, lycopene, and poly- $\beta$ -hydroxybutyrate. Therefore, MES offers a groundbreaking platform for the utilization of  $CO_2$ .

### 3. Key factors for catalytic $CO_2$ conversion in an MES system

#### 3.1. Extracellular electron transfer pathway

In the cathode chamber of an MES system, electroactive bacteria (EAB), also known as electrotophs, take up electrons from the cathode as an energy source to convert  $CO_2$  into high-value products [41,42]. Therefore, the extracellular electron transfer (EET) pathway between the cathode and EAB becomes a crucial factor in improving the rate of cathodic microbial electron uptake and achieving high MES productivity. Currently, EET pathways are primarily categorized into two classes: direct electron transfer (DET), mediated by membrane-bound redox proteins, and indirect electron transfer (IET), mediated by substances such as hydrogen ( $H_2$ ), formate, and redox mediators (Fig. 2A). Table 1 summarizes the EET pathways of various microorganisms used in MES system reported in recent years.

#### 3.1.1. Direct electron transfer pathway

The DET pathway is a process in which EABs directly uptake electrons from the electrode surface without the involvement of any external mediators or additional components; it only requires physical contact between the EABs and the electrode. The metal-reducing MtrCBA pathway in *Shewanella oneidensis* is currently the most extensively studied DET pathway (Fig. 2B). EABs that utilize the DET pathway typically adhere to solid electrode surfaces and form biofilms, relying on redox proteins located in their extracellular membrane to facilitate inward electron transfer, like c-type cytochrome. As shown in Table 1, most EABs used in MES systems can acquire electrons from electrodes through the DET pathway.

Researches on the DET pathway started relatively early. In 2009, *Methanobacterium palustre* was reported to directly take up electrons from the cathode and convert  $CO_2$  into methane [46]. In 2010, the term ‘‘MES’’ was proposed for the first time when Nevin et al. [43] reported the carbon fixation of the acetogenic microorganism *S. ovata* by relying on the DET pathway. Subsequently, Nevin et al. significantly expanded the selection range of biocatalysts for MES systems by further identifying other organisms that drive  $CO_2$  reduction through the DET pathway: *C. aceticum*, *S.phaeroides*, *M. thermoacetica*, and *C. ljungdahlii* [44]. The DET pathway has also been discovered in the photosynthetic autotrophic bacterium *Rhodospseudomonas palustris*, an excellent MES biocatalyst capable of converting  $CO_2$  by taking up electrons from the cathode using various functional proteins in its own photosynthetic electron transfer chain [25,57]. *R. palustris* was revealed to utilize electrodes and light as



**Table 1**  
The electron transport mechanisms of various strains used in MES systems in recent years.

| Electron transport mechanism  | Mediator | Strain                    | Substrate        | Products                       | Engineering transformation                                      | References |
|-------------------------------|----------|---------------------------|------------------|--------------------------------|---|------------|
| DET                           | No       | <i>S. ovata</i>           | CO <sub>2</sub>  | Acetate                        | –   | [43]       |
|                               | No       | <i>C. acetatum</i>        | CO <sub>2</sub>  | Acetate, 2-Oxybutrate          | –   | [44]       |
|                               | No       | <i>S. sphaeroides</i>     | CO <sub>2</sub>  | Acetate                        | –   | [44]       |
|                               | No       | <i>M. thermoacetica</i>   | CO <sub>2</sub>  | Acetate                        | –   | [44]       |
|                               | No       | <i>C. ljungdahlii</i>     | CO <sub>2</sub>  | Acetate, 2-Oxybutrate          | –   | [44]       |
|                               | No       | <i>M. vannielii</i>       | CO <sub>2</sub>  | CH <sub>4</sub>                | –   | [45]       |
|                               | No       | <i>M. maripaludis</i>     | CO <sub>2</sub>  | CH <sub>4</sub>                | –   | [45]       |
|                               | No       | <i>M. petrolearia</i>     | CO <sub>2</sub>  | CH <sub>4</sub>                | –   | [45]       |
|                               | No       | <i>M. congolense</i>      | CO <sub>2</sub>  | CH <sub>4</sub>                | –   | [45]       |
|                               | No       | <i>M. submarinus</i>      | CO <sub>2</sub>  | CH <sub>4</sub>                | –   | [45]       |
|                               | No       | <i>M. palustre</i>        | CO <sub>2</sub>  | CH <sub>4</sub>                | –   | [46]       |
|                               | No       | <i>R. palustris</i>       | CO <sub>2</sub>  | n-Butanol                      | Introduce the n-butanol synthesis pathway                       | [25]       |
|                               | No       | <i>S. oneidensis</i>      | Acetoin          | 2,3-Butanediol                 | Introduce proteorhodopsin and butanediol dehydrogenase proteins | [47]       |
|                               | No       | Engineered <i>E. coli</i> | Fumarate         | Succinate                      | Introduce the MtrCBA pathway from <i>S. oneidensis</i> MR-1     | [48]       |
|                               | IET      | H <sub>2</sub>            | <i>A. woodii</i> | CO <sub>2</sub>                | Acetate   | –          |
| H <sub>2</sub>                |          | <i>M. maripaludis</i>     | CO <sub>2</sub>  | CH <sub>4</sub>                | –   | [50]       |
| H <sub>2</sub>                |          | <i>R. eutropha</i>        | CO <sub>2</sub>  | Lycopene                       | –   | [11]       |
| H <sub>2</sub>                |          | <i>S. ovata</i>           | CO <sub>2</sub>  | Lycopene                       | –   | [51,52]    |
| H <sub>2</sub>                |          | <i>M. barkeri</i>         | CO <sub>2</sub>  | CH <sub>4</sub>                | –   | [63]       |
| Formate                       |          | <i>R. eutropha</i>        | CO <sub>2</sub>  | Isobutanol, 3-Methyl-1-butanol | Introduce the isobutanol synthesis pathway                      | [53]       |
| Anthraquinone-2,6-disulfonate |          | <i>C. glutamicum</i>      | Glucose          | Lactate                        | –   | [54]       |
| Neutral red                   |          | <i>M. extorquens</i>      | CO <sub>2</sub>  | Formate                        | –   | [55]       |
| Neutral red                   |          | <i>R. eutropha</i>        | CO <sub>2</sub>  | Poly-3-Hydroxybutyrate         | Overexpression ribulose-1,5-bisphosphate carboxylase protein    | [31]       |
| Methyl viologen               |          | <i>M. thermoacetica</i>   | CO <sub>2</sub>  | Formate                        | –   | [56]       |
| Methyl viologen               |          | <i>C. formicoaceticum</i> | CO <sub>2</sub>  | Formate                        | –   | [56]       |

“No”: No mediator is required.

“–”: No genetic engineering.

sources of electrons and energy, respectively, enabling direct electron uptake at a potential of +0.1 V [58]. Based on this result, Bai et al. introduced the n-butanol biosynthesis pathway into *R. palustris* TIE-1 and successfully produced biofuel from CO<sub>2</sub> [25].

Owing to its low overpotential requirement, the DET pathway has considerable potential to achieve high current efficiencies between electrodes and EABs [59]. Additionally, EABs can easily form biofilms on electrode surfaces, providing advantages such as direct catalysis and prolonged residence time. However, increasing biofilm thickness may limit the diffusion of both substrates and products. More significantly, although many strains have been confirmed to possess the capability of inward electron transfer, the corresponding molecular mechanism remains obscure. The MtrCBA pathway is one of the few inward electron transfer pathways with a known molecular mechanism that can be utilized for engineering purposes. Introducing the MtrCBA pathway and cytochrome *c* maturation system I separately into *Escherichia coli* was demonstrated to provide engineered strains with the direct ability of extracellular electron uptake, and these engineered strains successfully converted malate to succinate [48]. Furthermore, the efficiency of the DET pathway is also influenced by factors such as the type, specific surface area, and biocompatibility of electrode materials [60], which will be comprehensively discussed in another section of this review.

### 3.1.2. H<sub>2</sub>-mediated indirect electron transfer pathway

H<sub>2</sub> is an excellent electron donor for biocatalysts in the reduction of CO<sub>2</sub> [61–63]. It can be captured and oxidized by biocatalyst-possessing hydrogenase systems to generate the necessary reducing power for NAD(P)H during CO<sub>2</sub> reduction (Fig. 2C). Hydrogenase, an important enzyme in energy metabolism, employs electron bifurcation to drive the thermodynamically uphill reduction of endergonic ferredoxin by cou-

pling it with the energetically downhill reduction of the exergonic NAD<sup>+</sup> [64].

The most widely recognized hydrogenase system is characterized by the presence of four oxygen-tolerant [Ni-Fe] hydrogenases in *R. eutropha* [65–67]. *R. eutropha*, an exemplary autotrophic bacterium, can proficiently harness H<sub>2</sub> from water electrolysis to efficiently channel CO<sub>2</sub> assimilation toward producing the desired target compounds in an MES system. Although *R. eutropha* contains genes encoding four types of hydrogenases, only soluble hydrogenase (SH) and membrane-bound hydrogenase (MBH) play critical roles in H<sub>2</sub> oxidation [68]. The SH in *R. eutropha* primarily supplies reducing power in the form of NADH for CO<sub>2</sub> reduction and other biosynthetic routes [69]. Simultaneously, the MBH releases electrons that feed into the respiratory chain, providing ATP to the bacterial cells [70]. When SH and MBH expression levels are enhanced through plasmid overexpression and chromosomal promoter replacement, the autotrophic growth of *R. eutropha* is enhanced, holding crucial implications for the construction of CO<sub>2</sub>-fixing cellular factories [68].

Theoretically, when the cathodic potential is below the redox potential of H<sup>+</sup>/H<sub>2</sub>, specifically at –0.41 V (vs. the standard hydrogen electrode [SHE], pH 7.0), the cathode can readily undergo electrocatalytic water splitting to produce sufficient H<sub>2</sub> [71]. However, under standard temperature and pressure conditions, the solubility of H<sub>2</sub> in water is only 0.16 mg/100 g H<sub>2</sub>O [72]. Consequently, biocatalysts employing the H<sub>2</sub>-mediated IET pathway for electron transfer are inherently limited to the solubility of H<sub>2</sub>. To address this issue, Bajracharya et al. [52] implemented a solution by reintroducing a headspace gas containing H<sub>2</sub> into the electrolyte of the cathode chamber through a recycling system. This strategy effectively enhanced the H<sub>2</sub> utilization rate by the bacteria in the suspension and enabled efficient acetate production using *S. ovata* as a biocatalyst. Rodrigues et al. [51] proposed another solution using

a biocompatible perfluorocarbon (PFC) nanoemulsion as an H<sub>2</sub> carrier. After being enveloped by PFCs, the solubility of H<sub>2</sub> was increased by an order of magnitude compared to its solubility in water. This optimization ensured an abundant supply of reducing equivalents crucial for the metabolic activity of *S. ovata*. As a result, this modified MES system exhibited significant improvements in CO<sub>2</sub> conversion, mass transfer rates, and Faradaic efficiency. In summary, solubility is a major bottleneck for H<sub>2</sub> as an electron donor. However, the hydrogen evolution catalysts used in practice also affect the total cost and H<sub>2</sub> supply. In addition, the safety problems associated with hydrogen explosion and the negative effects of the high overpotential required for hydrogen evolution on energy loss and Coulomb efficiency should be considered.

### 3.1.3. Formate-mediated indirect electron transfer pathway

Formate is a superior and safer carbon source and electron carrier than H<sub>2</sub>. Due to its high solubility, formate more easily penetrates microbial cells and is captured by formate dehydrogenase (FDH) to provide reducing power (Fig. 2D). Additionally, the non-flammable and non-explosive safety characteristics of formate make it more convenient for storage and transportation than H<sub>2</sub> [53]. Most importantly, formate is involved in simple electrochemical synthesis with a reduction potential as low as -0.42 V (vs. SHE, pH 7.0) [73], enabling the direct reduction of cellular electron carriers [74]. Various catalysts, such as tin, lead, indium, and carbon have been developed for the efficient conversion of CO<sub>2</sub> to formate [34]. Li et al. [53] developed a heterologous pathway for ketoisovalerate supply and 3-methyl-1-butanol synthesis in *R. eutropha* by simultaneously inhibiting polyhydroxybutyrate production and genetic engineering to produce >1 g L<sup>-1</sup> of biofuel using formate as the primary electron donor. Chen et al. [31] designed an FDH-assisted MES system to enhance the efficiency of CO<sub>2</sub> fixation by engineered *R. eutropha*. In this modified system, FDH catalyzes the reduction of CO<sub>2</sub> to formate in the cathode chamber, providing an abundant supply of reducing power and carbon sources for poly-3-hydroxybutyrate biosynthesis.

While remarkable progress has been made in utilizing formate as an electron carrier for biocatalysts, further optimization and improvement are required to industrialize MES technology. For instance, the high solubility of formate not only escalates the separation costs associated with downstream products but also introduces the possibility of anodic decomposition, thereby diminishing the yield of the MES system [53]. Furthermore, the generation of formate typically requires various types of specialized synthetic catalysts, which limits its large-scale application in MES due to its complex preparation, low selectivity, low efficiency, and dependence on precious metals [75–77]. Additionally, increased formate accumulation can cause cytotoxicity to many microorganisms [78]. This heightened cytotoxicity diminishes the proton motive force [79] and inhibits respiratory cytochromes [80], impeding cellular proliferation. Within the concentration range of 0–1.5 g L<sup>-1</sup>, an increase in formate concentration is associated with the gradual decrease of biomass, as exhibited by *R. eutropha*. However, once the formate concentration exceeds 3.0 g L<sup>-1</sup>, the biomass of *R. eutropha* approaches negligible levels. Some research also indicated that the formate-mediated MES system is limited by the transfer of CO<sub>2</sub> or O<sub>2</sub>, which depends on the gas feed composition [73]. The transfer of CO<sub>2</sub> to the electrode surface restricts formate production at high O<sub>2</sub> partial pressures, thereby limiting microbial growth. Conversely, at higher CO<sub>2</sub> partial pressure, the gas/liquid mass transfer limits the rate of oxygen consumption driven by microbial respiration, leading to slower microbial growth and formate accumulation to toxic levels. By separating the CO<sub>2</sub> electrocatalytic reduction and biological conversion of reduced products into two interconnected yet independent systems, this scalable coupling employs highly soluble formate as an electrochemical intermediate to achieve the synthesis of high-value compounds from CO<sub>2</sub>. This approach not only avoids the mutual interference between the electrochemical and biosynthesis processes but also mitigates the challenges of downstream

**Table 2**  
Different RMs used in MES.

| Type           | Name                          | Source    | References |
|----------------|-------------------------------|-----------|------------|
| Endogenous RMs | Riboflavin                    | Microbe   | [82,87,91] |
|                | Phenazine                     | Microbe   | [83,88]    |
|                | Anthraquinone-2,6-disulfonate | Microbe   | [54]       |
|                | 2-Hydroxy-1,4-naphthoquinone  | Microbe   | [89]       |
|                | Hydroquinone                  | Microbe   | [89]       |
| Exogenous RMs  | Humic acid                    | Nature    | [86]       |
|                | Neutral red                   | Synthetic | [31,87]    |
|                | Methyl viologen               | Synthetic | [56,85,87] |

separation and associated costs, which offers possibilities for the industrial scale-up of MES systems [81].

### 3.1.4. Redox mediator-mediated indirect electron transfer pathway

Microorganisms can indirectly receive electrons from the cathode by utilizing endogenously synthesized soluble redox mediators (RMs) (such as flavins [82], phenazines [83], and quinones [84]) or exogenously added electron shuttles (such as methyl viologen and neutral red [31,85]). Details about these molecules are shown in Table 2.

Endogenous RMs are a class of electron shuttles produced by microorganisms, among which flavins and quinones are the most studied ones. Flavin compounds, primarily generated by *Shewanella* bacteria, have been widely applied in MES to facilitate the internal electron transfer of various biocatalysts. This class of mediators specifically interacts with c-type cytochromes on the outer membrane of biocatalysts, thereby enhancing the electron uptake process [90]. Therefore, the heterologous expression of the flavin biosynthesis gene cluster *ribD-ribC-ribBA-ribE* in specific biocatalysts may be a promising way to improve MES yield [91]. Quinone compounds comprise another common type of endogenous RMs. Hydroquinone and 2-hydroxy-1,4-naphthoquinone are quinones that are deeply investigated in MES applications [89]. Compared to 2-hydroxy-1,4-naphthoquinone, hydroquinone has consistently shown negative effects on the yield of MES systems. This could be due to its smaller molecular weight (110.11 g mol<sup>-1</sup>), which allows it to quickly permeate the cell membrane and act as a decoupler of the electron transfer chain to inhibit cellular respiration [89]. Conversely, 2-hydroxy-1,4-naphthoquinone has a performance-promoting effect on the MES system at low concentrations. However, it exhibits significant inhibitory effects at concentrations above 0.5 mM due to its toxicity on microbial metabolism [92,93]. From the perspective of redox potentials, the failure of hydroquinone in promoting acetate accumulation in an MES system is attributed to its significantly higher reduction potential (+0.09 V vs. SHE, pH 7.0) compared to that of CO<sub>2</sub> conversion to acetate (-0.29 V vs. SHE, pH 7.0). Similarly, the failure of flavin to serve as an RM in the reduction of NAD<sup>+</sup> can also be attributed to its slightly higher reduction potential (-0.4 V vs. Ag/AgCl) compared to that of NAD<sup>+</sup>/NADH (-0.52 V vs. Ag/AgCl) [31].

Exogenous RMs are the most abundant electron shuttles and can be divided into two categories: artificial and natural mediators. Neutral red and methyl viologen are artificial RMs widely used in MES systems. Methyl viologen and neutral red were found to be coupled with the electron transfer complex of microorganisms to achieve electron transfer and energy conversion and were conducive to the formation of butyrate [87]. In enzyme-assisted MES systems [31], neutral red facilitates the extracellular regeneration of the co-factor NADH for formate dehydrogenase and acts as an additional electron mediator beyond formate. Without an electron mediator, a cathode potential lower than -1.6 V (vs. Ag/AgCl) is required for the electrochemical reduction of CO<sub>2</sub> to formate [53]. By incorporating neutral red, the MES system can efficiently synthesize poly-3-hydroxybutyrate at a reduced cathode potential of -0.6 V (vs. Ag/AgCl), resulting in considerable electricity savings [31].

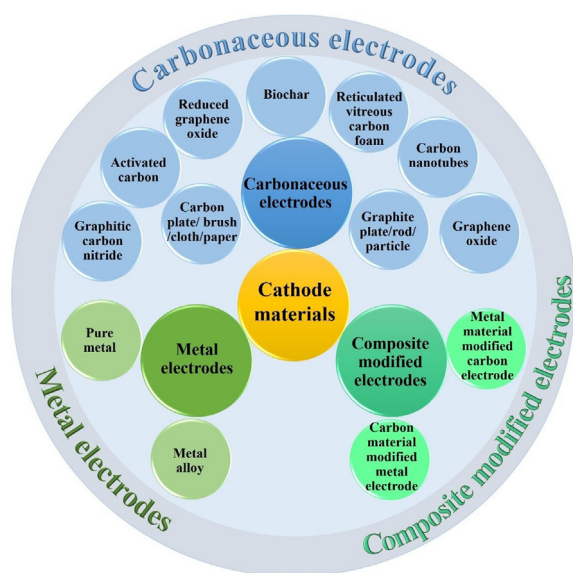


Fig. 3. Classification of cathode materials commonly used in MES systems.

Due to their relatively low reduction potential and excellent redox activity, RMs improve the indirect transmission of reducing force and broaden the selection range of electrode materials. Additionally, the involvement of RMs can significantly enhance the reaction rate and energy efficiency in MES systems, substantially improving energy consumption and production efficiency. Despite the numerous advantages of RMs, they are mostly expensive and toxic compounds, significantly increasing operational costs and complicating product separation in MES applications. Therefore, the optimal solution is to construct engineered strains that adaptively regulate the secretion of RMs.

### 3.2. Cathode materials

The efficiency of electron transfer between biocatalysts and cathodes has a direct impact on the process of CO<sub>2</sub> reduction in an MES system. This process is not only dependent on the inherent electron transfer pathway of biocatalysts but is also influenced by the cathode materials. The MES cathode is the central platform for CO<sub>2</sub> recovery and biochemical production [94]. The ideal cathode material for an MES system possesses excellent characteristics, including conductivity, chemical stability, mechanical strength, biocompatibility, high specific surface area, hydrophilicity, and affordability [95–97]. Other factors, such as the cost of fabrication and the lifespan of the cathode, also need to be considered [98]. The cathode materials used in MES systems can be broadly classified into three main categories: carbonaceous, metal, and carbon-metal composite modified electrodes, as illustrated in Fig. 3.

#### 3.2.1. Carbonaceous electrodes

Carbon is one of the most abundant elements in nature. Its unique electron structure makes it difficult to fully occupy or unoccupy an orbital state during chemical reactions. Meanwhile, carbonaceous materials can be readily modified by incorporating foreign atoms into carbon hybridization compounds [99,100]. These properties confer carbonaceous materials with excellent physicochemical stability, electrical conductivity, and modification potential. Hence, as a cathode candidate, carbonaceous electrodes have inherent advantages and are currently the most extensively employed materials in MES systems (Table 3).

Conventional carbon materials, such as graphite plates, graphite rods, carbon plates, carbon cloth, and carbon paper can be categorized as planar or two-dimensional (2D) materials consisting of carbon atoms arranged within sp<sup>2</sup>-hybridized orbitals along with two additional atoms

[101]. Nevin et al. [43] pioneered direct CO<sub>2</sub> reduction by employing negatively charged solid-state graphite block cathodes as electron sources. In contrast to graphite electrodes, alternative 2D carbon materials such as carbon plates, carbon cloth, and carbon paper exhibit superior attributes, including lightweightness, flexibility, higher porosity, and greater suitability for electrode modification strategies. Although 2D carbon materials possess good performance characteristics, they do not fulfill the requirements of MES systems in terms of specific surface area and porosity availability [97,101].

This shortcoming impedes bacterial contact and internal adhesion, directly affecting biofilm formation and electron transfer efficiency [102]. In contrast, carbon materials with open three-dimensional (3D) macro-porous structures, such as graphite felt [103], carbon felt [104], and carbon fiber brushes [105], are the optimal choices for MES systems. The 3D topology of these carbon materials provides more reaction spaces and contact sites for biomass, significantly reducing mass transfer limitations. To further improve the performance of 3D carbon materials, researchers have developed a wide range of advanced carbon materials for 3D carbon-based electrode modification, including carbon nanotubes [106], graphene, graphene oxide, reduced graphene oxide [107], graphitic carbon nitride, activated carbon [108], reticulated vitreous carbon foam [109], biochar [110], and other related compounds [111]. These advanced carbon materials play a key role in improving mass transfer efficiency between the electrode and its surface microenvironment and are typically utilized on the surface of substrate materials to develop novel electrodes. Aryal et al. [112] relied on these advanced carbon materials to fabricate a 3D graphene-modified carbon felt composite cathode. Compared with the original electrode, their modified cathode had a higher electron transfer rate and the yield of the electrochemical synthesis of acetate was increased 6.8-fold. The amorphous shape of these advanced carbon materials enables the modified 3D carbon-based electrode to possess an open, continuous 3D macro-porous structure [113]. This characteristic offers the possibility of absorbing or entrapping microbial cells within its pores and on the external surface to facilitate biofilm formation. It also confers good conductivity over the entire matrix, providing multiplexed and highly conductive pathways for CO<sub>2</sub> conversion.

#### 3.2.2. Metal electrodes

The unique atomic arrangement of metal materials endows them with exceptional mechanical strength, ductility, conductivity, and electrochemical catalytic activity [120,121]. The metal materials used as cathodes in MES systems can be broadly classified into two categories: pure metals and metal alloys (Table 4).

Metal materials are cathodes with both conductivity and electrochemical catalytic properties. Pure metals such as copper, lead, indium, and tin have been reported as cathodes in MES systems [34]. For instance, Baek et al. [122] have developed an electroless-Cu cathode with high performance and prolonged stability. Wang et al. [123] found that nickel electrodes possess superior hydrogen evolution capabilities compared to copper electrodes based on methane titer analysis. In addition, precious metals such as platinum [124], molybdenum [125], rhodium, and titanium [126] also possess potential applications in MES systems.

Foam metal materials have been developed for MES systems to enhance the limited specific surface area of conventional metal electrodes [127,128]. For example, nanofoam copper displays excellent catalytic performance in CO<sub>2</sub> reduction. Its high surface roughness and hierarchical porosity are key factors in determining the final product and the Faradaic efficiency of MES systems [129]. Nanofoam nickel has also proved to be a superior material for hydrogen evolution [130].

Considering the limitations of pure metal materials in terms of stability and lifespan, metal alloy catalysts have been developed to optimize the performance of the reaction interface and enhance the stability and catalytic activity of the catalyst. Stainless steel is a typical metal alloy that can be employed as a hydrogen evolution catalyst in MES systems to synthesize diverse high-value products [11]. Despite the numerous

**Table 3**  
Applications of common carbonaceous cathodes in MES systems.

| Cathode materials                | Inoculum                               | Applied potential (V vs. SHE) | Current density          | Products        | Titer                        | References |
|----------------------------------|--|-------------------------------|--------------------------|-----------------|------------------------------|------------|
| Graphite plate                   | Acetobacterium-dominated mixed culture | -0.8                          | NR                       | Acetate         | 1.8 g L <sup>-1</sup>        | [32]       |
| Graphite plate                   | <i>C. ljungdahlii</i>                  | -1.0                          | NR                       | Acetate         | 1.1 g L <sup>-1</sup>        | [32]       |
| Graphite granules                | Enriched brewery WW sludge             | -0.59                         | -2.5 A m <sup>-2</sup>   | Acetate         | 175 mM                       | [30]       |
| Graphite granules                | Enriched brewery WW sludge             | -0.59                         | -2.5 A m <sup>-2</sup>   | H <sub>2</sub>  | 1164 mM                      | [30]       |
| Graphite rod                     | <i>M. maripaludis</i>                  | -0.70                         | -0.22 mA m <sup>-2</sup> | CH <sub>4</sub> | 21.85 mM                     | [45]       |
| Graphite felt                    | Activated sludge                       | -0.79                         | -0.5 mA cm <sup>-2</sup> | Acetate         | 157.6 mmol C L <sup>-1</sup> | [114]      |
| Carbon cloth                     | Salt marsh sediment                    | -1.2                          | -1.8 A m <sup>-2</sup>   | CH <sub>4</sub> | 4.9 mM                       | [115]      |
| Carbon cloth                     | Salt marsh sediment                    | -1.2                          | -1.8 A m <sup>-2</sup>   | Acetate         | 1.5 mM                       | [115]      |
| Carbon cloth                     | Mangrove sediment                      | -1.2                          | -1.5 A m <sup>-2</sup>   | CH <sub>4</sub> | 3.8 mM                       | [115]      |
| Carbon cloth                     | Mangrove sediment                      | -1.2                          | -1.5 A m <sup>-2</sup>   | Acetate         | 3.1 mM                       | [115]      |
| Carbon Paper                     | <i>S. ovata</i>                        | -0.69                         | -0.37 A m <sup>-2</sup>  | Acetate         | 0.1 g L <sup>-1</sup>        | [116]      |
| Carbon felt                      | Enriched culture                       | -1.26                         | -5.0 A m <sup>-2</sup>   | Acetate         | 1.29 g L <sup>-1</sup>       | [104]      |
| Carbon felt                      | Anaerobic digestate                    | -0.6                          | -0.74 A m <sup>-2</sup>  | Acetate         | 162 mg L <sup>-1</sup>       | [117]      |
| Carbon brush                     | Anaerobic sludge                       | -0.76                         | NR                       | Acetate         | 630 mg L <sup>-1</sup>       | [118]      |
| Reticulated vitreous Carbon foam | Enriched acetogenic culture            | -1.1--1.3                     | -83.3 A m <sup>-2</sup>  | Acetate         | 3.6 g L <sup>-1</sup>        | [119]      |

“NR”: not reported in the reference.

**Table 4**  
Applications of metal cathodes in MES systems.

| Materials       | Inoculum                  | Potential (V vs. SHE) | Current density              | Product         | Productivity                                | References |
|-----------------|---------------------------|-----------------------|------------------------------|-----------------|---|------------|
| Stainless steel | <i>C. necator</i> C5      | NR                    | -1.6--3.2 mA m <sup>-2</sup> | Lycopene        | 0.43 mg L <sup>-1</sup> d <sup>-1</sup>     | [11]       |
| Stainless steel | Mixed culture             | -0.45                 | -6 A m <sup>-2</sup>         | CH <sub>4</sub> | about 14.06 mL d <sup>-1</sup>              | [123]      |
| Cu              | Mixed culture             | -0.48                 | -5 A m <sup>-2</sup>         | CH <sub>4</sub> | about 16.88 mL d <sup>-1</sup>              | [123]      |
| Ni              | Mixed culture             | -0.48                 | -9 A m <sup>-2</sup>         | CH <sub>4</sub> | about 18.13 mL d <sup>-1</sup>              | [123]      |
| Pt              | <i>C. necator</i> DSM-541 | NR                    | -500 μA cm <sup>-2</sup>     | H <sub>2</sub>  | 0.23 mL h <sup>-1</sup>                     | [124]      |
| Ni-Mo alloy     | <i>M. maripaludis</i>     | NR                    | -1 mA cm <sup>-2</sup>       | CH <sub>4</sub> | about 3 mL d <sup>-1</sup> cm <sup>-2</sup> | [125]      |
| Ti alloy        | Anaerobic sludge          | -0.9                  | -7.26 A cm <sup>-2</sup>     | Acetate         | 2.15 g L <sup>-1</sup> d <sup>-1</sup>      | [126]      |
| Rh              | Anaerobic sludge          | -0.9                  | -6.11 A cm <sup>-2</sup>     | Acetate         | 1.06 g L <sup>-1</sup> d <sup>-1</sup>      | [126]      |

“NR”: not reported in the reference.

enticing advantages of metals, most metal electrodes suffer from poor corrosion resistance due to electrochemical corrosion caused by electrolytic solutions [131], which can potentially have toxic effects on microbial growth through metal leaching [132]. The efficient alloy catalyst NiMoZn, which has excellent hydrogen evolution performance, cannot avoid the production of reactive oxygen species that negatively affect cell growth [133]. Additionally, the leaching of nickel from alloy materials exacerbates the toxicity risks to microorganisms. To address these issues, Liu et al. [134] optimized Co-P alloy electrodes to mitigate the limitations associated with the material defects of metals.

Table 4 reveals a narrower range of metal electrode types used in MES than carbon-based electrodes, mainly due to their relatively limited biocompatibility and specific surface area. Nonetheless, metal materials possess better plasticity, conductivity, and electrocatalytic activity frequently functioning as modifying materials in composite electrode construction to enhance the catalytic activity of electrodes.

### 3.2.3. Composite modified electrodes

Carbonaceous materials naturally possess good biocompatibility and high specific surface areas, while metal materials possess conductivity and electrochemical catalytic activity. Therefore, the mutual modification of these two types of materials can compensate for their respective shortcomings, resulting in composite electrodes with superior performance, as shown in Table 5. Carbonaceous materials like graphite felt, carbon felt, and carbon cloth are inexpensive and highly customizable to accommodate various reactor types [120]. Therefore, these materials are commonly employed as substrate materials for composite electrode construction. Given the good biocompatibility and high specific surface area of carbon materials, modifying them with metals or other materials could enhance their catalytic activity and conductivity. For instance, when carbon felt electrodes modified with cobalt and stainless steel were used as cathodes, the acetate titer of an MES system increased by 2-

and 1.7-fold, respectively, compared to the usage of original carbon felt [135]. These enhancements were mainly attributed to the diverse oxidation states of cobalt, which facilitated electron transfer between the microorganisms and the cathodes [136]. Meanwhile, stainless steel primarily improves the conductivity of carbon felt [137]. Nickel is also an excellent modifying material. As the specific surface area is increased 50-fold, graphite electrodes modified with nickel nanowires can significantly improve microbial electrochemical activity, with a 2.3-fold increase in bioreduction rates [138].

When a metal substrate is modified with a carbon material, its primary purpose is to provide more abundant microbial attachment sites and growth space for the initial metallic material. For instance, a composite electrode integrating porous graphene foam onto the surface of hollow stainless steel could utilize both the developed pore layer structure of graphene and the excellent conductivity of stainless steel [139]. The methane titer of the composite electrode is 3.6 times higher than that of the conventional carbon cloth alone [139]. Although composite electrodes may entail more intricate processing techniques and lead to elevated manufacturing costs, numerous reports have demonstrated the viable and substantial enhancement of MES system performance for pure metals or modified carbonaceous electrodes, which will be a key determinant in overcoming the production bottleneck of MES systems. In addition, the design concept of composite electrodes should be based on the characteristics of biocatalysts rather than simply stacking excellent materials. Moreover, not all modifications or combinations have positive effects on MES.

### 3.3. Cathode applied potentials

To facilitate CO<sub>2</sub> reduction by a bioelectrode, microorganisms must respire and capture energy to produce ATP, which is necessary for sustaining their normal growth [143]. This external power provides energy



**Table 5**  
Applications of representative composite cathodes in MES systems.

| Substrate material | Modified material                | Inoculum                           | Applied potential (V vs. Ag/AgCl) | Current density            | Product         | Productivity   | Fold increase | Coulombic efficiency (%) | References |
|--------------------|----------------------------------|------------------------------------|-----------------------------------|----------------------------|-----------------|--|---------------|--------------------------|------------|
| Carbon felt        | Co-stainless steel               | Enriched anaerobic sludge          | -0.8                              | -1.75 mA cm <sup>-2</sup>  | Acetate         | 622.5 g m <sup>-2</sup> d <sup>-1</sup>                | 2             | 60                       | [135]      |
| Carbon felt        | Stainless steel                  | Enriched anaerobic sludge          | -0.8                              | -1.49 mA cm <sup>-2</sup>  | Acetate         | 556.6 g m <sup>-2</sup> d <sup>-1</sup>                | 1.7           | 52                       | [135]      |
| Graphite           | Nickle nanowire                  | <i>Sporomusa</i>                   | -0.6                              | -0.63 A m <sup>-2</sup>    | Acetate         | 3.38 g m <sup>-2</sup> d <sup>-1</sup>                 | 2.3           | 82.14                    | [138]      |
| Stainless steel    | Graphene foam                    | MES effluent                       | -1.0                              | -3.1 A m <sup>-2</sup>     | CH <sub>4</sub> | 848.0 mM m <sup>-2</sup> d <sup>-1</sup>               | 3.6           | 84.2                     | [139]      |
| Carbon cloth       | Stainless steel                  | Enriched homoacetogenic consortium | -0.4                              | -0.22 mA cm <sup>-2</sup>  | Acetate         | 610 mg L <sup>-1</sup> d <sup>-1</sup>                 | 1.3           | 48                       | [140]      |
| Carbon cloth       | Stainless steel                  | Enriched homoacetogenic bacteria   | -0.8                              | -0.011 mA cm <sup>-2</sup> | Acetate         | 0.070 g L <sup>-1</sup> d <sup>-1</sup>                | 1.20          | 44                       | [141]      |
| Carbon cloth       | Stainless steel-Activated carbon | Enriched homoacetogenic bacteria   | -0.8                              | -0.024 mA cm <sup>-2</sup> | Acetate         | 0.072 g L <sup>-1</sup> d <sup>-1</sup>                | 1.23          | 47                       | [141]      |
| Carbon cloth       | Graphene                         | <i>S. ovata</i>                    | -0.89                             | -2.45 A m <sup>-2</sup>    | Acetate         | 2.28 g L <sup>-1</sup> m <sup>-2</sup> h <sup>-1</sup> | 6.8           | 86.5                     | [112]      |
| Carbon felt        | Mxene                            | Sludge inculum                     | -0.8                              | -174.2 mA m <sup>-2</sup>  | Acetate         | 2.13 mg L <sup>-1</sup> d <sup>-1</sup>                | 1.6           | 41                       | [142]      |
| Carbon felt        | Mxene                            | Sludge inculum                     | -0.8                              | -174.2 mA m <sup>-2</sup>  | Butyrate        | 2.42 mg L <sup>-1</sup> d <sup>-1</sup>                | 1.1           | 41                       | [142]      |
| Carbon felt        | Mxene                            | Sludge inculum                     | -0.8                              | -174.2 mA m <sup>-2</sup>  | Propionate      | 4.36 mg L <sup>-1</sup> d <sup>-1</sup>                | 1.7           | 41                       | [142]      |
| Carbon cloth       | Chitosan                         | <i>S. ovata</i>                    | -0.8                              | -0.47 A m <sup>-2</sup>    | Acetate         | 13.51 g m <sup>-2</sup> d <sup>-1</sup>                | 7.6           | 86                       | [95]       |
| Carbon cloth       | Cyanuric chloride                | <i>S. ovata</i>                    | -0.8                              | -0.45 A m <sup>-2</sup>    | Acetate         | 12.09 g m <sup>-2</sup> d <sup>-1</sup>                | 6.8           | 81                       | [95]       |
| Carbon cloth       | 3-Aminopropyltriethoxysilane     | <i>S. ovata</i>                    | -0.8                              | -0.20 A m <sup>-2</sup>    | Acetate         | 5.6 g m <sup>-2</sup> d <sup>-1</sup>                  | 3.1           | 82                       | [95]       |
| Carbon cloth       | Polyaniline                      | <i>S. ovata</i>                    | -0.8                              | -0.18 A m <sup>-2</sup>    | Acetate         | 5.32 g m <sup>-2</sup> d <sup>-1</sup>                 | 3             | 85                       | [95]       |
| Carbon cloth       | Melamine                         | <i>S. ovata</i>                    | -0.8                              | -0.06 A m <sup>-2</sup>    | Acetate         | 1.8 g m <sup>-2</sup> d <sup>-1</sup>                  |               | 80                       | [95]       |
| Carbon cloth       | Ammonia                          | <i>S. ovata</i>                    | -0.8                              | -0.06 A m <sup>-2</sup>    | Acetate         | 1.65 g m <sup>-2</sup> d <sup>-1</sup>                 | Negative      | 82                       | [95]       |
| Carbon cloth       | Gold                             | <i>S. ovata</i>                    | -0.8                              | -0.38 A m <sup>-2</sup>    | Acetate         | 10.67 g m <sup>-2</sup> d <sup>-1</sup>                | Negative      | 83                       | [95]       |
| Carbon cloth       | Nickle                           | <i>S. ovata</i>                    | -0.8                              | -0.30 A m <sup>-2</sup>    | Acetate         | 8.024 g m <sup>-2</sup> d <sup>-1</sup>                | 4.53          | 80                       | [95]       |
| Carbon cloth       | Palladium                        | <i>S. ovata</i>                    | -0.8                              | -0.32 A m <sup>-2</sup>    | Acetate         | 8.32 g m <sup>-2</sup> d <sup>-1</sup>                 | 4.7           | 79                       | [95]       |
| Carbon cloth       | CNT-Cotton                       | <i>S. ovata</i>                    | -0.8                              | -0.22 A m <sup>-2</sup>    | Acetate         | 6.618 g m <sup>-2</sup> d <sup>-1</sup>                | 3.4           | 83                       | [95]       |
| Carbon cloth       | CNT-Polyester                    | <i>S. ovata</i>                    | -0.8                              | -0.21 A m <sup>-2</sup>    | Acetate         | 5.66 g m <sup>-2</sup> d <sup>-1</sup>                 | 3.2           | 82                       | [95]       |

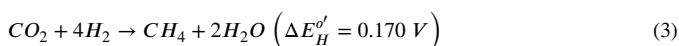
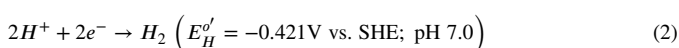
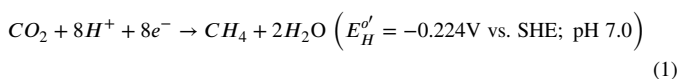
“Negative”: The composite strategy did not achieve positive improvement.



**Table 6**  
Cathode potentials required for synthesizing bioproducts in MES systems.

| Cathode potential (V vs. SHE) | Product                                      | Inoculum  | Cathode materials                               | Configuration  | References |
|-------------------------------|--|---|---|----------------|------------|
| -0.35                         | CH <sub>4</sub>                              | Mixed culture                                     | Carbon cloth                                    | Single-chamber | [148]      |
| -0.4                          | CH <sub>4</sub>                              | <i>Methanobacterium</i> -like archaeon strain IM1 | Graphite rods                                   | Two-chamber    | [149]      |
| -0.5                          | CH <sub>4</sub>                              | Mixed culture                                     | Carbon cloth                                    | Two-chamber    | [46]       |
| -0.6                          | CH <sub>4</sub>                              | Mixed culture                                     | Graphite  | Two-chamber    | [155]      |
| -0.8                          | CH <sub>4</sub>                              | Mixed culture                                     | Granular graphite                               | Two-chamber    | [156]      |
| -0.6                          | Acetate                                      | Mixed culture                                     | Graphite  | Two-chamber    | [157]      |
| -0.66                         | Acetate                                      | Biological sludge                                 | Stainless steel                                 | Two-chamber    | [62]       |
| -0.8                          | Acetate                                      | Mixed culture                                     | Activated carbon                                | Two-chamber    | [158]      |
| -0.85                         | Acetate                                      | Mixed culture                                     | NanoWeb-<br>Reticulated vitreous<br>Carbon foam | Two-chamber    | [159]      |
| -0.7                          | Formate, Acetate                             | Mixed culture                                     | Carbon cloth                                    | Two-chamber    | [143]      |
| -0.7                          | Acetate, Butyrate and Propionate             | Anaerobic sludge                                  | Carbon felt                                     | Two-chamber    | [153]      |
| -0.7—0.9                      | CH <sub>4</sub>                              | Mixed culture                                     | Carbon cloth                                    | Two-chamber    | [143]      |
| -0.9                          | H <sub>2</sub> , CH <sub>4</sub>             | Mixed culture                                     | Stainless steel felt                            | Three-chamber  | [160]      |
| -0.9                          | H <sub>2</sub> , CH <sub>4</sub> and Acetate | Mixed culture                                     | Graphite  | Two-chamber    | [143]      |
| -1.0—1.1                      | H <sub>2</sub> , CH <sub>4</sub>             | Mixed culture                                     | Carbon cloth                                    | Two-chamber    | [146]      |
| -1.0                          | H <sub>2</sub> , CH <sub>4</sub>             | Mixed culture                                     | Carbon cloth                                    | Two-chamber    | [146]      |

for the catalytic conversion of CO<sub>2</sub> in the MES system. The lower potential of the cathode in an MES system increases the electrochemical driving force, accelerates the reaction kinetics, and improves electron availability [144–146], thus ensuring abundant energy supply for microbial growth [143,147]. The cathode potential is usually set below the theoretical potential to account for overpotential and losses associated with MES system design and electrolyte characteristics. Table 6 lists the cathode potentials applied for synthesizing bioproducts in MES systems. Different cathode potentials affect the electron transfer behaviors of microorganisms, leading to the adoption of various reaction pathways [143]. For example, the electrosynthesis of methane can be performed by methanogenic microorganisms through two distinct electron transfer pathways: DET or IET [148]. When biocatalysts produce methane through DET (Eq. (1)), the cathode potential theoretically needs to be as low as -0.244 V (vs. SHE) to facilitate the reaction [46,149]. Conversely, according to Eq. (2) and (3), if methane is produced via IET, the cathode potential must be at least as low as the hydrogen evolution potential of -0.421 V (vs. SHE) [150]. However, due to overpotential, when the cathode potential was set at -0.7 or -0.8 V (vs. SHE), the bioelectrode still produced methane via the DET pathway. When the potential increased to -0.9 to -1.1 V (vs. SHE), the process shifted towards the IET pathway [143]. Therefore, to produce methane, the cathode potential is usually set below -0.6 V, which is much lower than the theoretical potential.



Additionally, the cathode potential also has a significant influence on the type and composition of products in an MES system. At a cathodic potential of -1.0 V, enriched electromethanogenic communities favored the production of H<sub>2</sub> and CH<sub>4</sub>, while only acetate was detected after operating at -0.7 V for a 90-minute period [146]. In another study, the cathode was subjected to two different potentials (-0.36 and -0.66 V vs. SHE) [62]. Although both potentials were thermodynamically favorable for the electroreduction of CO<sub>2</sub> to acetate, the presence of acetate was observed only at a cathode potential of -0.66 V. This may be because H<sub>2</sub> is a necessary substrate for the synthesis of acetate and is only produced when the potential drops below approximately -0.41 V [151,152].

External power supply is a key part of the operating cost of a MES system. Although several reasons account for the increase in cathode overpotential and energy loss in MES systems, estimating the energy requirement (the electrical energy required to produce 1.0 mol of the target product) by calculating the energy consumed per mole to synthesize the target product can effectively reduce operating costs. For instance, although the titer of volatile fatty acids steadily increased with the rising applied potential between -0.6 and -1.0 V (vs. SHE), the catalytic conversion of CO<sub>2</sub> has the lowest energy requirement and the highest economic benefit only when the cathode potential is set to -0.7 V [153]. Therefore, designing an MES system with a high electron supply rate is critical to ensure a high conversion efficiency and low power input [154].

#### 3.4. pH of the cathode chamber

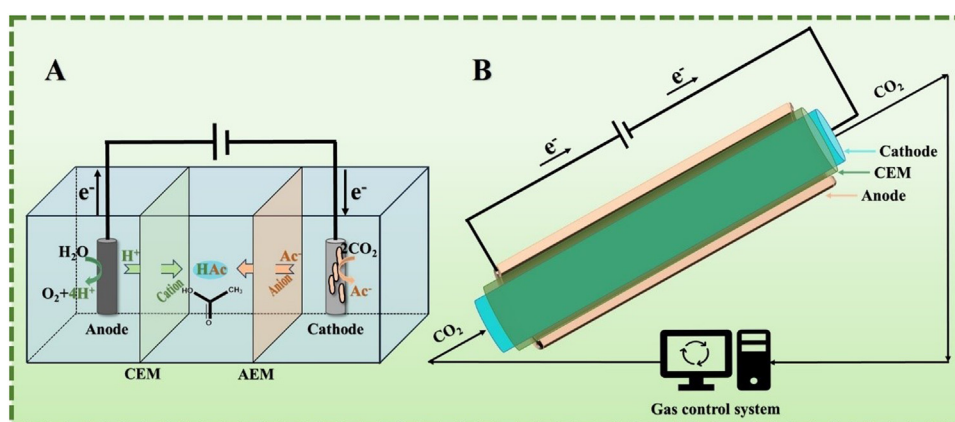
The fluctuation of catholyte pH can change the activity and reactivity of the biocatalysts in the cathode chamber, affecting the performance of the MES system [157]. As shown in Table 7, MES systems operated at different pH levels exhibit significant productivity differences even when synthesizing the same product. Therefore, to increase the titer of high-value products in an MES system, the pH of the cathode chamber must be controlled within the appropriate range according to the specific pH requirements of the chosen biocatalysts.

Acetate is one of the most common products synthesized in MES systems and pH value has an important effect on acetate synthesis. The conversion rate of CO<sub>2</sub> and H<sub>2</sub> to acetate can be increased by moderately reducing the initial pH of the system [161]. This is because stabilizing the pH in a weakly acidic environment provides thermodynamic advantages for converting CO<sub>2</sub> into acetate, enhancing substrate availability for the biocatalyst [162]. Furthermore, maintaining a relatively low pH ensures a reducing environment in the cathode chamber, which favors the synthesis of long-chain compounds [163]. For example, an MES system successfully generated long-chain compounds such as C4 and C6 by regularly injecting gaseous CO<sub>2</sub> to maintain the pH of the catholyte to approximately 5.0 [164]. However, during the electrosynthesis of acetate from CO<sub>2</sub>, when the pH falls below the pK<sub>a</sub> value of acetate (4.75), protonated acetate (CH<sub>3</sub>COOH) exhibits negative effects on the biocatalysts. CH<sub>3</sub>COOH can easily permeate microbial cells through passive diffusion to dissociate in the cytoplasm, posing a direct threat to biocatalysts involved in the MES system [165]. In addition, the excess protons from CH<sub>3</sub>COOH dissociation require additional energy consumption, further reducing the energy utilization of the biocatalysts [166,167]. pH also plays an indispensable role in methane elec-

**Table 7**  
Effects of pH on the synthesis of bioproducts in MES systems.

| Product         | pH       | Productivity                              | Configuration   | Coulombic efficiency | Inoculum                    | References |
|-----------------|----------|---|---|----------------------|-----------------------------|------------|
| Acetate         | 5.2      | 0.81 mM d <sup>-1</sup>                   | Two-chamber   | 68.81%               | Mixed culture               | [174]      |
| Acetate         | 5.5–8.0  | 137.92 mM m <sup>-2</sup> d <sup>-1</sup> | Microbial reverse-electrodialysis electrosynthesis cell | 24.35%               | <i>C. ljungdahlii</i> ERI-2 | [175]      |
| Acetate         | 5.5      | 49.2 mg L <sup>-1</sup> d <sup>-1</sup>   | Two-chamber   | 35%                  | Mixed culture               | [176]      |
| Acetate         | 5.8      | 0.98 mM L <sup>-1</sup> d <sup>-1</sup>   | Two-chamber   | 30%                  | Mixed culture               | [162]      |
| Acetate         | 6.7      | 1330 g m <sup>-2</sup> d <sup>-1</sup>    | Two-chamber   | 99%                  | Mixed culture               | [177]      |
| Butyrate        | 5.25–6.6 | 37.67 mg L <sup>-1</sup> d <sup>-1</sup>  | Two-chamber   | 16.54%               | Mixed culture               | [178]      |
| Butyrate        | 5.5      | 30 mg L <sup>-1</sup> d <sup>-1</sup>     | Two-chamber   | 35%                  | Mixed culture               | [176]      |
| CH <sub>4</sub> | 6.2      | 290 mL L <sup>-1</sup> d <sup>-1</sup>    | Single-chamber  | NR                   | Mixed culture               | [171]      |
| CH <sub>4</sub> | 6.7      | 750 mL L <sup>-1</sup> d <sup>-1</sup>    | Single-chamber  | NR                   | Mixed culture               | [171]      |
| CH <sub>4</sub> | 7.2–7.6  | 0.03 mM h <sup>-1</sup>                   | Single-chamber  | 90%                  | Effluent from MES           | [179]      |
| CH <sub>4</sub> | 7.5      | 213.4 m <sup>-3</sup> d <sup>-1</sup>     | Two-chamber   | above 90%            | Effluent from MES           | [170]      |
| CH <sub>4</sub> | 7        | 22.1 mM L <sup>-1</sup> d <sup>-1</sup>   | Single-chamber  | 98.9%                | Mixed culture               | [180]      |
| Ethanol         | 5.5–8.0  | 130.75 mg L <sup>-1</sup> d <sup>-1</sup> | Microbial reverse-electrodialysis electrosynthesis cell | 66.06%               | <i>C. ljungdahlii</i> ERI-2 | [175]      |
| Isobutyrate     | 5.2      | 0.63 mM d <sup>-1</sup>                   | Two-chamber   | 68.81%               | Mixed culture               | [174]      |
| Propionate      | 5.2      | 0.44 mM d <sup>-1</sup>                   | Two-chamber   | 68.81%               | Mixed culture               | [174]      |
| 2-Piperidone    | 5.2      | 0.53 mM d <sup>-1</sup>                   | Two-chamber   | 68.81%               | Mixed culture               | [174]      |

“NR”: not reported in the reference.



**Fig. 4.** Advanced MES configurations: (A) three-compartment and (B) concentric tube types.

tro-synthesis. When the pH of the cathode chamber exceeds 8.5, the rate of acetate decomposition into CH<sub>4</sub> is reduced, resulting in the formation of volatile fatty acids and alcohols [168]. The reason may be that, to mitigate the concomitant toxicity associated with excessive acetate accumulation, microorganisms use alternative metabolic pathways to convert acetate into alcohol [169]. The maximum methane productivity was observed under neutral conditions with a pH of 7.5 [170]. This phenomenon that a neutral pH is conducive to efficient methane production has been widely recognized [171]. These results demonstrated that increased acidity and alkalinity adversely affect the methane titer, particularly in alkaline environments, where a substantial deposition of inorganic substances on the electrode surface could notably reduce methane production and biofilm growth [172,173].

### 3.5. Reactor configuration

The reactor configuration significantly influences the performance and potential applications of MES systems. Tables 6 and 7 show that a typical MES system is primarily designed as a two-chamber system separated by a proton exchange membrane. This configuration facilitates easy assembly and sterilization, effectively minimizing mutual interference between the two compartments while expanding the range of applicable electrode materials [181]. However, it also faces challenges such as increased internal resistance and reduced mass transfer efficiency [182], and pH changes in the cathode chamber [178].

To overcome the inherent limitations of two-chamber reactors, a membraneless single-chamber MES has been developed. This design significantly reduces internal resistance and energy consumption, offering promising prospects for process scalability. However, the applicability of this configuration is limited as it is only suitable for select aerobic bacterial strains due to the release of O<sub>2</sub> and reactive oxygen species during anodic water electrolysis [53,133]. In addition, many advanced reactors with different functions and purposes have been developed, such as the three-chamber reactor and concentric tube reactor (Fig. 4). These advanced configurations showed excellent product purification, stable reaction environments, increased specific surface area, and reduced internal resistance within the system. Among various MES configurations, special membrane materials such as the cation exchange membrane, anion exchange membrane, and bipolar membrane are commonly employed [183]. These membrane materials can have a substantial impact on MES by maintaining the overall charge balance of the system and impeding oxygen diffusion.

## 4. Conclusions and perspectives

As a novel energy regeneration strategy, MES technology has advantages in CO<sub>2</sub> conversion, including high efficiency, catalyst reusability, mild operating conditions, and a wide product range. Furthermore, the product spectrum of the MES system has been expanded to poly-3-hydroxybutyrate, terpenes, carotenoids, lycopene, and other valuable compounds in addition to methane, short-chain fatty acids,

and their corresponding alcohols. However, the output of MES remains relatively low as the reported productivity of most systems falls far short of practical application requirements. Therefore, many challenges remain in using MES to achieve CO<sub>2</sub> conversion, as outlined below:

(1) Ability of biocatalysts to capture CO<sub>2</sub> needs to be improved

Autotrophic biocatalysts adapted for MES typically employ the Calvin–Benson–Bassham cycle and Wood–Ljungdahl pathway for CO<sub>2</sub> fixation. The efficiency of the Calvin–Benson–Bassham cycle is limited by the subpar catalytic capability of its key enzyme, ribulose-1,5-bisphosphate carboxylase (Rubisco). Therefore, the molecular-level modification of Rubisco is essential to enhance its catalytic activity. The anaerobic Wood–Ljungdahl pathway is the primary carbon fixation pathway for acetogenic bacteria and methanogenic archaea, the most common biocatalysts in MES systems. Enhancing the oxygen tolerance of the Wood–Ljungdahl pathway is crucial due to the presence of oxygen-sensitive enzymes. In addition, only a few autotrophic microorganisms have biological carbon fixation ability. Another breakthrough would be the design and operation of efficient artificial carbon fixation pathways in heterotrophic microorganisms with short routes, low energy consumption, and high atomic economy, reducing the dependence of heterotrophic microorganisms on abiotic CO<sub>2</sub> electroreduction catalysts and further expanding the selection of suitable biocatalysts for MES systems.

(2) CO<sub>2</sub> supply of microorganisms needs to be strengthened

The concentration of extracellular CO<sub>2</sub> into the intracellular space is a critical process in microbial carbon fixation. However, when the CO<sub>2</sub> concentration is limited, the CO<sub>2</sub> demand of intrinsic CO<sub>2</sub>-concentrating autotrophic microorganisms may not be met. Many novel carrier materials with CO<sub>2</sub> adsorption capacity can assist microorganisms in concentrating CO<sub>2</sub>. Among these CO<sub>2</sub> carrier materials, metal-organic frameworks consisting of metal nodes and organic ligands may be promising CO<sub>2</sub> adsorbents, as they can capture and store CO<sub>2</sub> from their ambient environment. These CO<sub>2</sub> carriers can also be combined with CO<sub>2</sub> convertases such as carbonic anhydrase to facilitate efficient CO<sub>2</sub> concentration and ensure an adequate supply of CO<sub>2</sub> for microorganisms.

(3) Development of rational cathode designs based on the properties of biocatalysts

The cathode is the core of an MES production platform and its adaptation with biocatalysts determines the production efficiency of an MES system. However, most cathode designs are simple combinations of different materials and this random combination does not account for the properties of biocatalysts; hence, the efficiency improvement of MES systems is limited. Therefore, rational cathode design based on the physiological and biochemical properties of biocatalysts may be an effective way of improving the efficiency of an MES system. For instance, factors including surface charge characteristics, adhesion capacity, and the cell size of biocatalysts are crucially considered in cathode design. Moreover, 3D printing and electrospinning are two promising techniques for cathode preparation. The products fabricated using these techniques are characterized by significant advantages, including a high specific surface area, high porosity, low density, excellent directionality, and adjustable composition. Additionally, both of these techniques enable precise control at the nanoscale, providing technical support for the rational design of cathodes.

To conclude, as a newly emerging technology, MES offers many opportunities for converting CO<sub>2</sub> into high-value products. This review summarized the application potential of MES in CO<sub>2</sub> conversion and analyzed the key factors for CO<sub>2</sub> conversion via MES, which will help researchers understand the current research progress, challenges, and opportunities of CO<sub>2</sub> conversion via MES.

## 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.

## CRedit authorship contribution statement

**Ting Cai:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation. **Xinyu Gao:** Writing – review & editing, Conceptualization. **Xiaoyan Qi:** Visualization, Methodology. **Xiaolei Wang:** Validation, Investigation. **Ruijun Liu:** Formal analysis, Data curation. **Lei Zhang:** Validation, Data curation. **Xia Wang:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization.

## Acknowledgments

This work was supported by grants from National Natural Science Foundation of China (32070097 and 91951202) and National Key Research and Development Program of China (2019YFA0904800).

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