REVIEW ARTICLE

Bioelectrocatalytic Materials for Green Agriculture and Environmental Remediation

Yuying Jiang[1] **and Denghui Xu**[1,*]

[1] Department of Physics, Beijing Technology and Business University, Beijing 100048, China

Abstract

The advancement of global sustainable agriculture is currently impeded by the dual challenges of energy-intensive industrial nitrogen fixation and the persistent accumulation of agro-environmental pollutants. Bioelectrocatalysis has emerged as a transformative solution to these issues by synergizing the exquisite selectivity of biological catalysts with the controllability of renewable electricity-driven systems. However, the practical deployment of bioelectrocatalytic technologies is fundamentally constrained by kinetic bottlenecks associated with interfacial electron transfer (ET) between biocatalysts and solid electrodes. This review systematically summarizes recent advances in bioelectrocatalytic materials, with a specific focus on interface engineering strategies designed to overcome energy barriers and optimize both Direct Electron Transfer (DET) and Mediated Electron Transfer (MET) pathways. Furthermore, we critically examine the application of these systems in electricity-driven nitrogen fertilizer synthesis, real-time environmental sensing, and pollutant remediation. Finally, future perspectives on integrating synthetic biology and advanced material design are discussed to accelerate the development of next-generation technologies for green agriculture and ecological preservation.

Keywords: bioelectrocatalysis, green agriculture, nitrogen fixation, interface engineering, waste valorization, sustainable energy.

1 Introduction

Global sustainable agriculture and ecological preservation currently face a confluence of deeply entrenched challenges. On one hand, modern agricultural production relies heavily on the energy-intensive Haber-Bosch process for industrial nitrogen fixation [1–3]. The concomitant excessive application of synthetic nitrogen fertilizers has precipitated substantial energy consumption, greenhouse gas emissions, and nutrient losses across the agricultural lifecycle. On the other hand, the mismanagement of agricultural residues, compounded by the persistent accumulation of environmental pollutants ranging from excess nitrogen species to agrochemicals and recalcitrant organic contaminants poses severe, long-term threats to ecosystem stability, soil health, and water quality [4]. These intertwined issues underscore an urgent imperative for innovative technologies capable of simultaneously addressing resource efficiency,

Submitted: 31 January 2026
Accepted: 07 February 2026
Published: 28 February 2026

Vol. 3, **No.** 1, 2026.
10.62762/ASFP.2026.804492

***Corresponding author:**
✉ Denghui Xu
xudh@btbu.edu.cn

Citation
Jiang, Y., & Xu, D. (2026). Bioelectrocatalytic Materials for Green Agriculture and Environmental Remediation. *Agricultural Science and Food Processing*, 3(1), 6–18.

environmental remediation, and climate change mitigation.

Within this landscape, bioelectrocatalysis has emerged as a pivotal technological nexus bridging renewable energy utilization with ecological sustainability. By synergizing the exquisite molecular-level selectivity of biological catalysis with the high thermodynamic efficiency and controllability of electrochemical systems, bioelectrocatalysis provides a unique platform for driving environmentally benign redox transformations [5, 6]. In contrast to conventional inorganic electrocatalysis, bioelectrocatalytic materials comprising redox enzymes and electroactive microorganisms exhibit exceptional substrate specificity. This capability enables precise chemical transformations even within complex, heterogeneous environmental matrices. Furthermore, these reactions typically proceed under mild operating conditions (ambient temperature, atmospheric pressure, and near-neutral pH), significantly reducing energy input and enhancing operational safety, which is particularly advantageous for decentralized or field-deployable applications in agro-environmental settings [7–11].

A distinguishing feature of bioelectrocatalytic systems is their capacity to directly couple renewable electricity derived from intermittent sources such as solar and wind power with biological redox pathways. This direct electrical driving force facilitates the sustainable conversion of electrical energy into chemical energy, establishing novel routes for green synthesis and resource recovery. Representative applications can be broadly categorized into two strategic directions: (1) Electricity-driven green synthesis and remediation, where nitrogenases, oxidoreductases, or microbial catalysts are employed for sustainable nitrogen fertilizer production, CO_2 fixation into value-added chemicals, and pollutant detoxification; and (2) Bioenergy recovery and environmental sensing, exemplified by microbial fuel cells (MFCs) for waste valorization and bioelectrochemical sensors for the real-time monitoring of agro-environmental contaminants.

Despite these compelling advantages, the transition of bioelectrocatalysis from laboratoryscale demonstrations to practical implementation remains fundamentally constrained by kinetic bottlenecks associated with interfacial electron transfer (ET) [12]. In native biological systems, catalytic redox centers are often deeply buried within insulating protein shells, while in electroactive microorganisms, cellular membranes and extracellular structures impose significant barriers to efficient electron exchange with solid electrodes [13–16]. These structural and physicochemical constraints result in sluggish electron-transfer kinetics, limited current densities, and compromised operational stability, thereby impeding overall system performance.

In light of the specific demands of green agriculture and environmental remediation, this review systematically summarizes recent advances in bioelectrocatalytic materials, with a particular focus on oxidoreductase-based and microorganism-based systems. We critically examine emerging interface engineering strategies aimed at overcoming interfacial energy barriers, emphasizing the mechanistic optimization of direct electron transfer (DET) and mediated electron transfer (MET) pathways. Furthermore, we discuss representative and transformative applications of bioelectrocatalysis in sustainable nitrogen fertilizer synthesis, agro-environmental sensing, and bioenergy recovery. Finally, we provide a forward-looking perspective on future research directions, highlighting opportunities in materials innovation, interface design, and synthetic biology-enabled catalyst engineering to accelerate the practical deployment of bioelectrocatalytic technologies.

2 Bioelectrocatalytic Systems in the Context of Green Agriculture

The energy transduction inherent in bioelectrocatalytic systems offers a versatile platform for addressing agricultural and environmental challenges. This process involves converting chemical energy from organic substrates into electricity or, conversely, utilizing electrical energy to drive specific redox transformations. Based on the direction of electron flow and the biocatalyst type, comprising isolated oxidoreductases or electroactive microorganisms, these systems can be tailored into distinct configurations for sustainable agriculture. Specifically, the interconversion of chemical and electrical energy within these systems facilitates three critical functions relevant to green development (Figure 1) [17].

1. **Agro-environmental Monitoring (Biosensing)**: Bioelectrocatalysis serves as a foundational technology for high-specificity electrochemical sensors in agricultural settings. By functioning as precise biorecognition elements, bioelectrocatalysts enable the real-time detection of environmental stressors, including pesticide

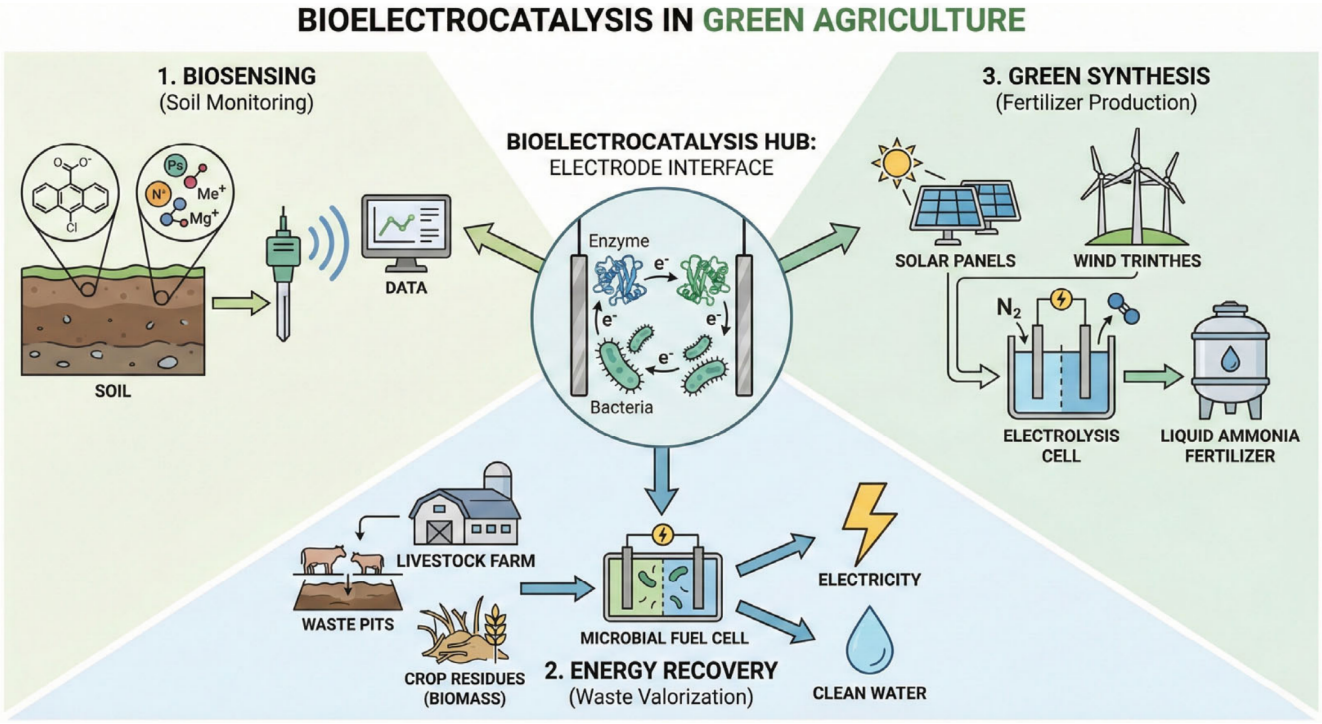

Figure 1. Overview of bioelectrocatalysis applications in sustainable agriculture. The diagram highlights the versatility of the bio-electrode interface in driving three interconnected sectors: biosensing for soil health monitoring, waste valorization for energy and water recovery, and the renewable energy-driven electrosynthesis of nitrogen-based fertilizers. The Bioelectrocatalysis Hub is centered on the electrode–biocatalyst interface, facilitating efficient coupling between renewable energy inputs and target biocatalytic reactions for sustainable agricultural applications.

residues, soil heavy metals, and nutrient levels such as nitrate and nitrite. Notably, these systems can often operate as self-powered devices, eliminating the need for external energy sources.

2. **Waste Valorization & Energy Recovery (Bioelectricity)**: Electroactive microbial cells act as self-regenerating catalysts capable of oxidizing complex organic matter present in agricultural wastewater, ranging from livestock waste to lignocellulosic biomass. This bioelectrochemical process simultaneously remediates pollutants and harvests chemical energy in the form of bioelectricity, thereby transforming agricultural waste into a valuable resource.

3. **Green Chemical Synthesis (Bioelectrosynthesis)**: This field has gained significant traction as a sustainable route for producing value-added agricultural chemicals. By coupling renewable electricity with specific oxidoreductases like nitrogenases, bioelectrocatalytic systems can drive thermodynamically challenging reactions under ambient conditions. Key applications include N_2 fixation for green ammonia fertilizer and CO_2 reduction for carbon-neutral fuels, offering an environmentally benign alternative to energy-intensive industrial processes.

Compared to conventional inorganic electrocatalysts, bioelectrocatalytic materials present unique merits tailored to agro-environmental applications. The hallmark of these systems is their exquisite molecular specificity, which allows for robust catalysis even amidst the interference typical of complex matrices like soil and sludge, environments where inorganic catalysts are prone to deactivation. Furthermore, the ability to function under mild physiological conditions facilitates safe in situ deployment, thereby mitigating the risk of secondary contamination often caused by aggressive chemical processing. Crucially, the capacity to couple these biological transformations with intermittent renewable energy establishes a sustainable paradigm for decentralized chemical synthesis, enabling the on-site production of ammonia fertilizers from off-grid electricity [18, 19].

2.1 Interfacial Barriers Limiting Bioelectrocatalytic Energy Conversion

While bioelectrocatalysis encompasses both analysis-oriented applications and product-oriented systems, the focus of energy conversion lies strictly

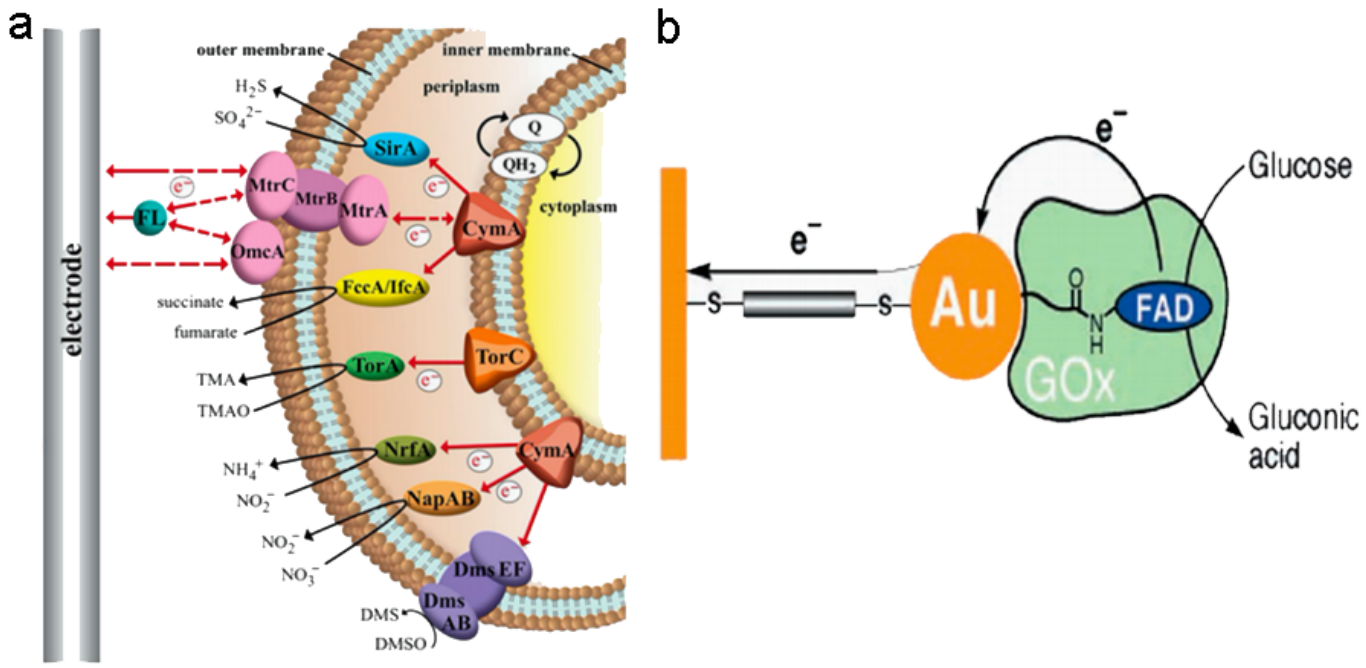

Figure 2. Approaches for direct electron transfer. (a) The electron transfer mechanism and conductive membrane structure of S. oneidensis, showing unique Mtr-pathway and terminal reductases. Quinones (Q) transfer electrons to CymA or TorC, which pass electrons to MtrCAB or terminal reductases. The MtrCAB complex interacts with the electrode surface either via direct contact or flavin molecules. The dashed arrows indicate the theoretical electron flow direction, whereas the solid arrows indicate the experimentally determined electron flow path [18]. (b) Glucose oxidase (GO_x) incorporated with an "electrical nanoplug" (Au nanoparticles) [19].

in the latter. In systems such as biofuel cells and bioelectrosynthesis for nitrogen fixation, the overarching performance metrics of power density and space-time yield are fundamentally governed by the efficiency of interfacial electron transfer (ET). However, establishing efficient electrical communication at the bio-interface remains a formidable challenge for both isolated enzymes and whole cells. In native oxidoreductases such as glucose oxidase (GO_x) or nitrogenase, the redox-active cofactors are typically buried deep within insulating protein shells to prevent non-specific side reactions. This structural sequestration intrinsically hinders direct electrochemical contact with electrodes and often creates electron tunneling distances that exceed the critical threshold of approximately 14 Å for effective transfer. Parallel kinetic limitations exist for electroactive microorganisms used in wastewater treatment. For instance, the rate of extracellular electron transfer (EET) in model exoelectrogens like Shewanella oneidensis and Geobacter sulfurreducens [19] is physically constrained by the non-conductive nature of lipid cell membranes. These organisms must therefore rely on complex transmembrane machinery, such as the outer-membrane cytochromes or conductive pili illustrated in Figure 2(a), to bridge the insulating gap between intracellular metabolism and solid electrodes. The Mtr pathway is predominantly constituted by the outer-membrane cytochrome complex MtrCAB, which mediates extracellular electron transfer (EET) between the microbial cytoplasm and solid electrodes" in manuscript.

Consequently, overcoming these interfacial barriers is the primary objective in designing advanced bioelectrocatalytic materials. Current optimization strategies focus on three synergistic approaches. The first is Biocatalyst Engineering which utilizes protein engineering to physically expose active sites, such as the deglycosylation of enzymes to shorten the electrode distance or the trimming of non-catalytic subunits. The second approach is Electrode Engineering which involves developing nanostructured interfaces, such as using gold nanoparticles as "electrical nanoplugs" to penetrate the enzyme shell as shown in Figure 2(b). Finally, Interface and Media Optimization employ strategies like redox polymers to facilitate mediated electron transfer in systems where direct contact is sterically prohibited. These advancements are critical for unlocking the full potential of bioelectrocatalysis in sustainable nitrogen fixation and environmental

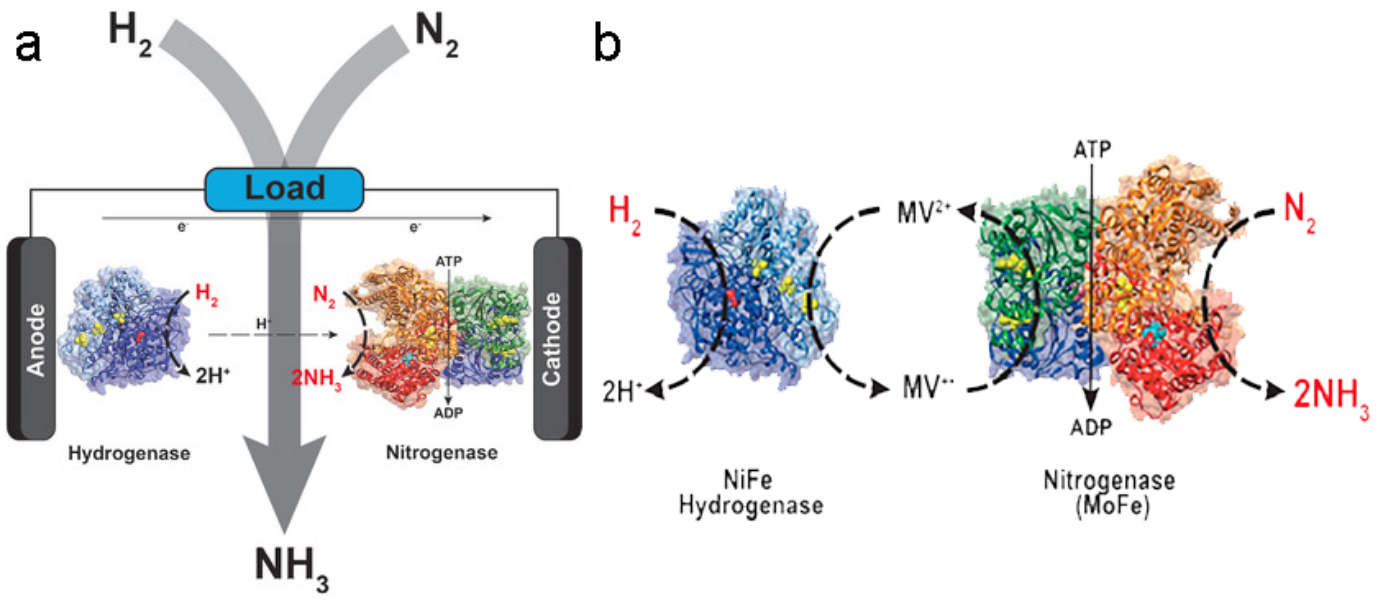

Figure 3. Bioelectrocatalytic N_2 fixation and upgraded nitrogen fixation based on the utilization of nitrogenase. (a) Compartmentalization of hydrogenase and nitrogenase Fe/MoFe proteins by the use of a proton exchange membrane (PEM) leads to an Enzymatic Fuel Cell(EFC) configuration that is able to utilize MV as the electron mediator in both chambers and simultaneously produces NH_3 and electrical energy from H_2 and N_2 at room temperature and ambient pressure. (b) Ammonia production by nitrogenase and hydrogenase using methyl viologen [20].

remediation.

3 Bioelectrocatalytic Materials for Agricultural and Environmental Applications

Bioelectrocatalysts serve as the fundamental functional units bridging biological metabolism and electrochemical interfaces. In the context of green agriculture and environmental remediation, these materials are primarily categorized into oxidoreductases and electroactive microorganisms based on their structural complexity and catalytic functions.

3.1 Enzyme-Based Materials: Green Fertilizer Synthesis and Pollutant Degradation

Oxidoreductases are macromolecular catalysts composed of an insulating protein shell and a conductive redox cofactor. To address agro-environmental challenges, the following enzyme classes are of paramount importance:

Nitrogenases are the premier bioelectrocatalytic materials for agricultural sustainability capable of reducing atmospheric dinitrogen (N_2) into bioavailable ammonia (NH_3). The MoFe-type nitrogenase represents the most pivotal bioelectrocatalytic material for advancing agricultural sustainability, capable of reducing atmospheric dinitrogen (N_2) to bioavailable ammonia (NH_3) under ambient conditions. The MoFe-nitrogenase complex comprises two metalloproteins including the Fe protein containing a [4Fe-4S] cluster and the catalytic MoFe protein. Electrons are transferred from the [4Fe-4S] cluster through the P-cluster ([8Fe-7S]) and finally to the FeMo-cofactor ($[Fe_7MoS_9C]$) where the energy-intensive N_2 reduction occurs. Unlike the Haber-Bosch process which requires high temperature and pressure, nitrogenases operate under ambient conditions. Research has demonstrated that by coupling these enzymes with electrodes in fuel cell configurations, it is feasible to produce ammonia or even upgrade it into higher value chiral amines as illustrated in Figure 3(a). This capability supports the establishment of distributed and on-site green fertilizer production systems directly at agricultural facilities to reduce transportation costs and carbon footprints [20].

Multi-copper Oxidases and Hydrogenases. Multi-copper oxidases such as laccases and bilirubin oxidases contain distinctive copper centers (Type 1, Type 2, and Type 3) that exhibit broad substrate specificity and high redox potentials. They are effective in the oxidative degradation of phenolic pollutants and lignin in agricultural biomass as well as the sensing of heavy metals like arsenic. Hydrogenases containing Fe-S clusters catalyze the reversible oxidation of molecular hydrogen. In systems treating agricultural organic waste, hydrogenases serve as critical electrocatalysts for recovering chemical energy

in the form of clean hydrogen fuel or establishing bioanodes for power generation as seen in Figure 3(b) where hydrogenase is coupled with nitrogenase.

Exoelectrogens for Remediation. Exoelectrogens such as Geobacter sulfurreducens and Shewanella oneidensis are microorganisms capable of extracellular electron transfer (EET) to solid electrodes. Shewanella utilizes a porin-cytochrome complex known as MtrCAB across its outer membrane to interact with electrodes or flavin shuttles. Conversely, Geobacter employs conductive microbial nanowires (e-pili) or cytochrome filaments (OmcS) to facilitate long-range electron transport. These microbes are widely applied in microbial fuel cells (MFCs) where they efficiently oxidize organic matter in agricultural wastewater to remove chemical oxygen demand (COD) while simultaneously generating bioelectricity.

Electrotrophs for Green Synthesis. Electrotrophic microorganisms function as electron acceptors by directly taking electrons from a cathode to synthesize value-added products. For example, Sporomusa ovata can be interfaced with semiconductor nanowires to reduce CO_2 into acetate via microbial electrosynthesis (MES) as depicted in Figure 4(a). Furthermore, nitrogen fixing bacteria such as Xanthobacter autotrophicus [21, 22] can function in hybrid inorganic biological systems to convert atmospheric nitrogen into ammonium soil fertilizer powered by renewable electricity as demonstrated in Figure 4(b).

3.2 Engineering Materials for Enhanced Energy Conversion

To overcome the challenges of complex agricultural environments including temperature fluctuations and non-neutral pH, bioelectrocatalytic materials require engineering modifications. Protein engineering strategies play a critical role in optimizing biocatalysts. For instance, the deglycosylation of enzymes like cellobiose dehydrogenase can strip away the insulating glycan shell to reduce the distance between the enzyme active site and the electrode as shown in Figure 4(c). This modification significantly enhances the rate of direct electron transfer (DET). Additionally, directed evolution allows for the tailoring of enzymes for non-physiological conditions. As exemplified in Figure 4(d), CueO (copper efflux oxidase) variants have been engineered to exhibit positively shifted onset potentials and improved stability. This makes them highly suitable for the treatment of acidic agricultural wastewaters. In microbial systems, synthetic biology tools enable the modification of non-native exoelectrogens. For example, the Mtr pathway from Shewanella has been successfully transplanted into E. coli to create engineered strains capable of efficient metal reduction and electron transfer [23, 24].

4 Interfacial Electron Transfer Mechanisms in Bioelectrocatalysis

The catalytic performance of bioelectrocatalytic materials is fundamentally governed by the efficiency of interfacial electron transfer (ET). In the context of agro-environmental applications, establishing robust electrical communication in complex matrices (e.g., soil, wastewater) is critical. The ET mechanisms are primarily categorized into Direct Electron Transfer (DET) and Mediated Electron Transfer (MET), along with the thermodynamically crucial Proton-Coupled Electron Transfer (PCET). However, realizing these mechanisms requires overcoming significant kinetic barriers at the bio-interface. As illustrated in Figure 5, advanced electrode engineering strategies, such as entrapping enzymes within conductive graphene-chitosan nanocomposites or utilizing phase-inversion polymer coatings, are frequently employed to bridge the insulating protein shell and facilitate efficient electron tunneling.

4.1 Direct Electron Transfer (DET)

Enzymatic DET: For isolated enzymes, this process is highly distance-dependent, typically requiring the active site to be positioned within approximately 14 Å of the electrode surface. Strategies such as site-specific orientation via genetic tags (e.g., His-tags) or the incorporation of gold nanoparticles acting as "electrical nanoplugs" are employed to minimize tunneling distances. For instance, an oriented binding without activity loss is crucial for efficient surface utilization. Lee and co-workers demonstrated that by genetically fusing a gold-binding peptide sequence to the terminus of glucose dehydrogenase, the enzyme achieved oriented immobilization on a gold electrode. Compared with the natural enzyme, this modified counterpart enabled apparent direct electron transfer across the interface, leading to stable current generation.

Microbial DET (Extracellular Electron Transfer): In environmental remediation and waste valorization, electroactive microorganisms (e.g., Geobacter and Shewanella) employ sophisticated extracellular electron transfer (EET) pathways. Shewanella utilizes outer-membrane c-type cytochromes (e.g.,

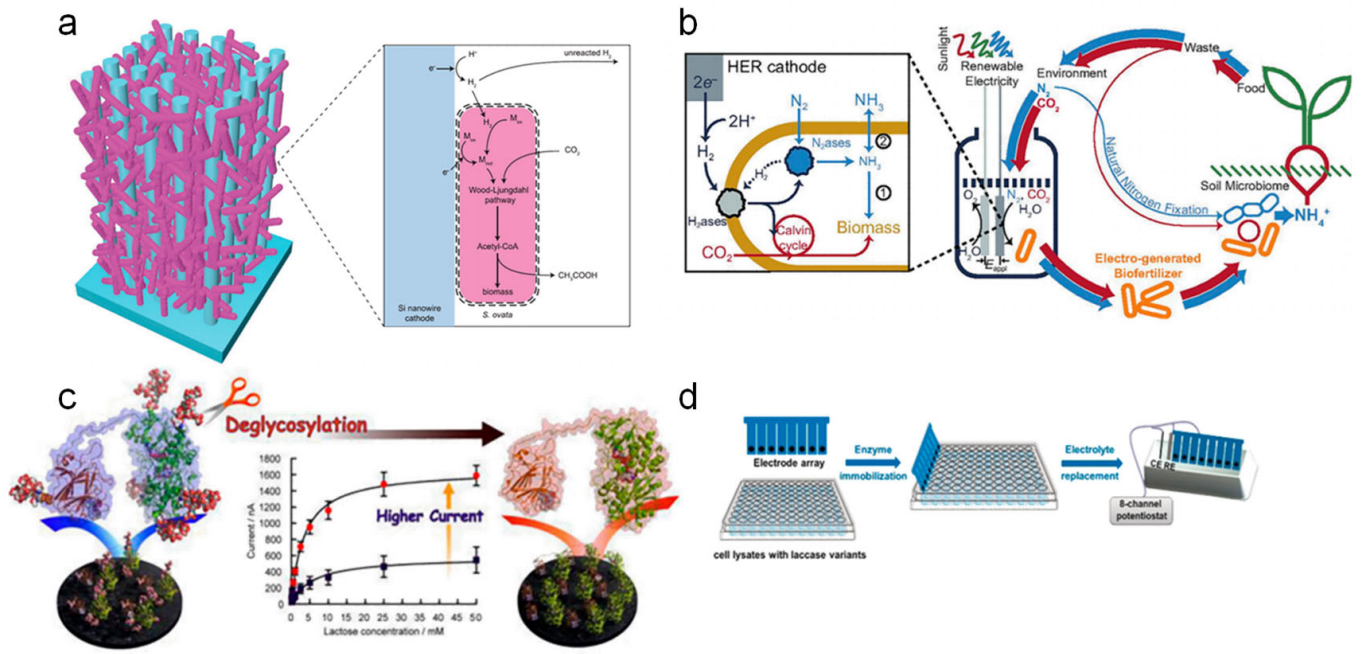

Figure 4. Modification oxidoreductase based on directed evolution. (a) Schematics of the close-packed nanowire-bacteria hybrid system (left) and the reaction pathway (right). The electrons are transferred (via either a direct pathway or a H_2-mediated pathway) from the Si nanowire cathode to S. ovata to generate the intracellular reducing equivalents (Mred). The reducing equivalents are finally passed on to the Wood-Ljungdahl pathway to produce acetate and biomass [21]. (b) Schematic of the electroaugmented nitrogen cycle. A constant voltage (Eappl) is applied between CoPi OER and Co-P HER electrode for water splitting. Hydrogenase of X. autotrophicus oxidizes the H_2, fueling CO_2 reduction in the Calvin cycle and N_2 fixation by nitrogenase. The generated NH_3 is typically incorporated into biomass (pathway 1) but can also diffuse extracellularly by inhibiting biomass formation (pathway 2) [22]. (c) Surface modification. Deglycosylation leads to the downsizing of cellobiose dehydrogenase, decreases the distance between the active site and the electrode, and finally facilitates the directed electron transfer [23]. (d) Schematic illustration of the electrochemical screening platform to get the mutant copper efflux oxidase with higher redox potential [24].

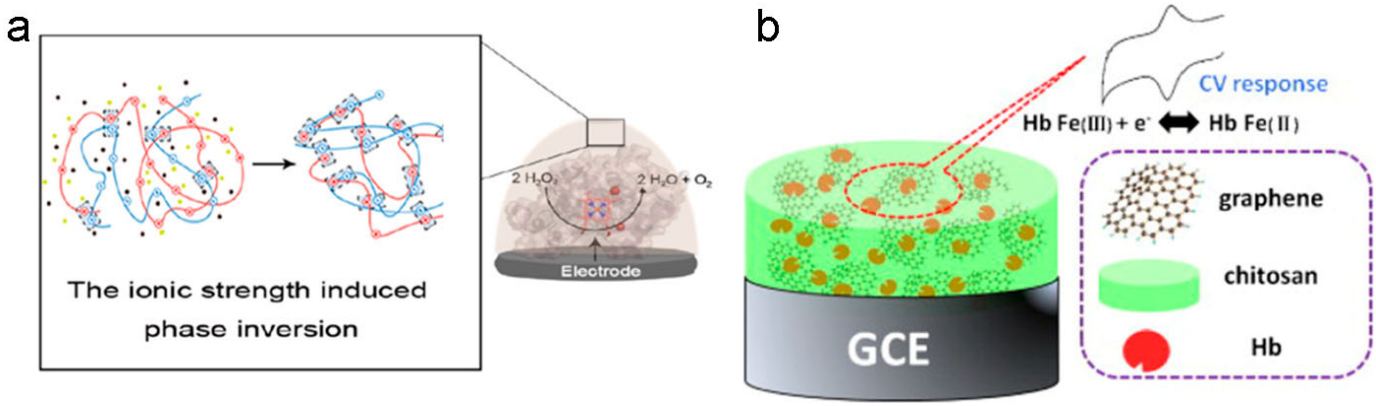

Figure 5. Representative interface engineering strategies to facilitate Direct Electron Transfer (DET) via enzyme entrapment. (a) Enzyme immobilization utilizing ionic strength-induced phase inversion to create a stable polymeric matrix on the electrode surface [25]. (b) Construction of a highly conductive bio-interface using a chitosan-graphene nanocomposite, which entraps redox proteins (e.g., Hemoglobin, Hb) on a glassy carbon electrode (GCE) to enhance electron tunneling efficiency [26].

MtrCAB complex) to transfer electrons across the cell envelope. Crucially for agricultural wastewater treatment, Geobacter species express conductive pili (microbial nanowires) that facilitate long-range electron transport through thick biofilms, enabling high current densities.

4.2 Mediated Electron Transfer (MET)

When DET is kinetically hindered due to deeply buried active sites or steric constraints, MET utilizes

redox-active mediators to shuttle electrons.

Redox Polymers: Advanced MET architectures employ redox-active hydrogels (e.g., pyrene-modified linear polyethylenimine) to "wire" enzymes in a 3D matrix. This is particularly vital for nitrogenase-based biofertilizer synthesis, as the polymer matrix protects oxygen-sensitive catalytic centers from deactivation in aerobic agricultural environments.

Endogenous Mediators: Endogenous mediators are biosynthesized and secreted by electroactive microorganisms endogenously, eliminating the requirement for external supplementation in bioelectrocatalytic systems. In natural agro-ecosystems, bacteria such as Pseudomonas secretion endogenous shuttles like phenazines and flavins. These diffusive small molecules facilitate electron exchange between cells and solid electron acceptors (e.g., soil minerals or electrodes), playing a key role in in situ bioremediation.

4.3 Proton-Coupled Electron Transfer (PCET)

For energy-intensive agricultural reactions, specifically nitrogen fixation ($N_2 \rightarrow NH_3$) and CO_2 reduction, the transfer of electrons must be tightly coupled with proton movement to bypass high-energy intermediates. PCET mechanisms are fundamental to the function of nitrogenases, lowering the thermodynamic barrier for breaking the triple bond of dinitrogen under ambient conditions. Optimizing the electrochemical interface to support efficient PCET is essential for developing sustainable, low-energy processes for green fertilizer production.

5 Bioelectrocatalytic Systems and Interfaces: Engineering for Agro-Environmental Applications

The transition of bioelectrocatalysis from laboratory benchtops to field-deployable agricultural and environmental applications hinges on the robust design of the electrode-bio interface. In complex matrices such as soil extracts, livestock wastewater, or fermentation broths, the interface must not only facilitate rapid electron transfer (ET) but also withstand environmental fluctuations and biofouling.

5.1 Electrode-Bio Interface Design: Stability and Scalability

The selection and modification of electrode materials are critical determinants for the performance of bioelectrocatalytic systems, necessitating a balance between electrical conductivity, biocompatibility, and cost-effectiveness for large-scale agricultural deployment.

Carbon-Based Materials: Carbon-based materials are the most widely used substrates due to their versatility. The core objective of surface modification for carbon-based materials is to enhance their biocompatibility with biocatalysts and improve interfacial electron transfer efficiency, thereby optimizing overall system performance. Forms include carbon paper, carbon cloth, carbon felt, and carbon nanotubes (CNTs). While chemically stable, the innate hydrophobicity of carbon can hinder cell adhesion and electron transfer. Consequently, surface modifications using chemical treatments like acid oxidation or coatings with hydrophilic polymers such as chitosan are essential to introduce N- or O-containing functional groups. These modifications enhance bacterial colonization and biofilm formation efficiency which is critical for wastewater treatment. To further overcome kinetic limitations, composite materials are engineered. For example, carbon electrodes modified with metal oxide nanocomposites (e.g., TiO_2, SnO_2) or conductive polymers (e.g., polyaniline) are employed to boost ET rates and environmental robustness. For microbial systems specifically, stainless steel remains a promising candidate for large-scale reactors due to its corrosion resistance and cost-effectiveness.

Hierarchical Porosity and Immobilization Strategies. To maximize the loading of enzymes or electroactive biofilms, 3D porous architectures such as carbon fiber brushes or reticulated vitreous carbon are employed. These structures provide a high surface-area-to-volume ratio which is essential for achieving high current densities in waste-to-energy systems. Furthermore, maintaining the stability of biocatalysts on these surfaces is paramount. As illustrated in Figure 6(a), distinct immobilization strategies ranging from adsorption to entrapment within polymeric matrices are utilized. Entrapment methods are particularly valuable in agricultural settings as they protect enzymes from leaching and denaturation in harsh wastewater environments while still allowing substrate diffusion [27].

5.2 Reaction Media and Operating Conditions

Unlike controlled laboratory buffers, agricultural environments present fluctuations in pH, temperature, and substrate solubility. Engineering the reaction medium is pivotal for maintaining catalytic turnover.

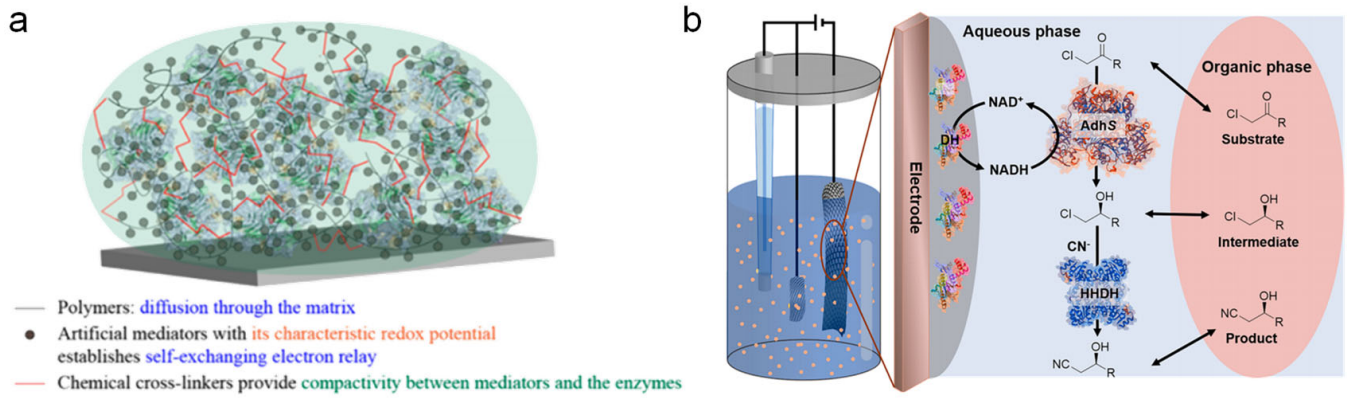

Figure 6. (a) scheme of enzyme immobilization techniques used in enzymatic bioelectrocatalysis systems (EBS). (b) Schematic representation of the biphasic bioelectrocatalytic system for the preparation of chiral β-hydroxy nitrile [27].

pH and Buffer Regulation. The pH of the reaction medium significantly influences enzymatic activity and stability. To address the acidity often found in agricultural effluents, protein engineering strategies such as directed evolution have generated enzyme variants capable of stable operation at acidic pH. For instance, modified 6-phosphogluconate dehydrogenase can operate efficiently at pH 5.4, enabling the direct treatment of acidic fluids without costly neutralization steps. Alternatively, immobilization matrices using proton-conducting hydrogels can create a localized pH microenvironment on the electrode surface to protect the biocatalyst from the bulk solution's harsh conditions.

Biphasic Reaction Media for Product Extraction. Many high-value agricultural chemicals and pollutants are hydrophobic, leading to solubility issues in aqueous media. To address this, biphasic reaction media composed of immiscible organic and aqueous phases are employed. As depicted in Figure 6(b), this configuration is transformative for bioelectrosynthesis. In this system, the organic phase acts as a reservoir for substrates and continuously extracts products (such as chiral β-hydroxy nitriles) from the aqueous phase. This in situ extraction shifts thermodynamic equilibria and mitigates product inhibition. Consequently, it simplifies downstream processing and makes the synthesis of complex agrochemicals economically viable.

This configuration is particularly transformative for green chemical synthesis (e.g., converting CO_2 to alcohols) and pollutant degradation, as it continuously extracts products from the aqueous phase. This in situ extraction shifts thermodynamic equilibria, mitigates product inhibition, and simplifies downstream processing, making the synthesis of complex agrochemicals economically viable.

6 Applications in Green Agriculture and Environmental Sustainability

6.1 Biofuel Cells and Bioenergy Conversion

Bioelectrocatalysis provides a transformative technological platform for addressing the dual challenges of resource efficiency and environmental protection. By harnessing the specificity of biological catalysts, these systems facilitate the valorization of agricultural waste, the precise monitoring of environmental pollutants, and the sustainable synthesis of nitrogen-based fertilizers.

6.2 Waste Valorization and Bioenergy Recovery

The microbial conversion of organic waste into electrical energy represents a paradigm shift from simple waste disposal to resource recovery. This approach transforms agricultural effluents into valuable assets.

Microbial Fuel Cells (MFCs) for Agricultural Wastewater Treatment: MFCs utilize electroactive microorganisms (e.g., Geobacter, Shewanella) to oxidize complex organic substrates found in agricultural effluents, such as swine wastewater and winery wastewater. In these systems, the anode acts as an inexhaustible electron acceptor for bacterial respiration, achieving significant Chemical Oxygen Demand (COD) removal while simultaneously recovering energy as bioelectricity. This "waste-to-energy" approach not only mitigates environmental pollution but also provides power for remote agricultural sensors or low-power devices.

Bio-hydrogen Production: Beyond electricity, microbial electrolysis cells (MECs) can upgrade

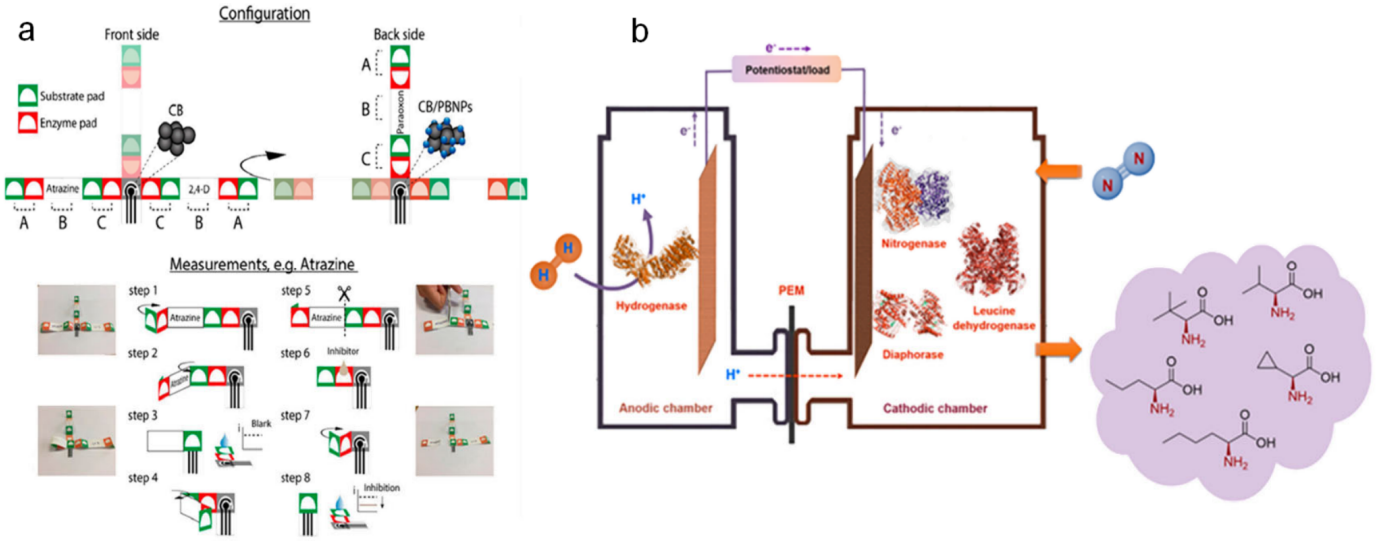

Figure 7. Adopted and modified schemes of electrochemical enzymatic biosensors for the chemical sensing of water samples. The 3D-origami setup (a) was used to detect numerous pesticides by immobilizing different enzymes on the electrode surface. This setup was tested with wastewater samples, showing a promising selective detection [28]. (b) Schematic representation of bioelectrocatalytic conversion from N_2 to chiral amino acids in a H_2/α-keto acid enzymatic fuel cell [29].

organic waste (e.g., fermentation effluents) into hydrogen gas (H_2), a clean fuel. By applying a small external voltage, electroactive bacteria at the anode degrade organic matter, while protons are reduced to H_2 at the cathode, offering a sustainable route for agricultural biomass energy conversion.

6.3 Agro-Environmental Sensing and Monitoring

The exquisite selectivity of enzymes and microbes enables the development of high-performance biosensors for precision agriculture and environmental safety.

Self-Powered Biosensors for Pollutant Detection: Bioelectrocatalysis plays a pivotal role in self-powered sensing, where the analyte itself serves as the fuel, eliminating the need for external batteries. A key advantage of self-powered biosensors lies in their elimination of reliance on external power supplies, rendering them highly suitable for on-site, decentralized monitoring of agro-environmental pollutants. This principle is applied to detect toxic agricultural pollutants that inhibit biocatalytic activity. For instance, laccase-based biocathodes have been engineered to detect arsenic (As^{3+}/As^{5+}) and phenolic compounds in groundwater, where the decrease in power output correlates with pollutant concentration.

Pesticide and Herbicide Monitoring: Enzymatic inhibition mechanisms are widely exploited for detecting organophosphate pesticides and herbicides. To facilitate rapid on-site screening, these systems are increasingly integrated into portable devices. As illustrated in Figure 7(a), researchers have developed 3D paper-based origami biosensors that integrate screen-printed electrodes with specific enzymes. In this configuration, the inhibition of alkaline phosphatase or tyrosinase allows for the sensitive detection of agricultural herbicides like 2,4-dichlorophenoxyacetic acid (2,4-D) and atrazine in surface water samples. This low-cost design enables rapid field deployment to safeguard agricultural ecosystems [28–32].

6.4 Reshaping the Nitrogen Cycle: Green Fertilizer Synthesis

Bioelectrosynthesis offers a sustainable alternative to the energy-intensive Haber-Bosch process for nitrogen fixation, enabling decentralized production of green fertilizers directly from air and renewable electricity.

Green Ammonia Production. Utilizing nitrogenase enzymes or nitrogen-fixing bacteria (e.g., Xanthobacter) at the electrode interface allows for the reduction of atmospheric N_2 to ammonia (NH_3) under ambient temperature and pressure. This process bypasses the thermodynamic extremes of industrial synthesis. Recent advances using redox polymers (e.g., pyrene-LPEI) to immobilize nitrogenase have achieved ATP-independent electrosynthesis of ammonia, significantly reducing the energy cost for fertilizer production [33–36].

Upgrading to High-Value Agricultural Chemicals. Beyond simple ammonia synthesis, bioelectrocatalytic cascades can upgrade fixed nitrogen into higher-value organic nitrogen compounds. By coupling upstream N_2 reduction with downstream enzymatic transformations, it is possible to synthesize complex agricultural biostimulants [37–41]. As depicted in Figure 7(b), a self-powered H_2/α-keto acid enzymatic fuel cell has been developed to produce chiral amino acids. In this system, electrons from anodic H_2 oxidation drive the cathodic reduction of N_2 to ammonia, which is then immediately incorporated into α-keto acids by leucine dehydrogenase to form chiral amino acids such as L-norleucine or L-valine [42–47]. This "electro-augmented nitrogen cycle" provides a green pathway for producing premium agricultural feed additives directly from renewable resources [48, 49].

7 Conclusion and Outlook

In summary, this review has elucidated the transformative potential of bioelectrocatalytic materials, ranging from redox enzymes to electroactive microorganisms, as a technological cornerstone for advancing sustainable agriculture and environmental remediation. By bridging the critical gap between biological selectivity and electrochemical efficiency, these systems offer a paradigm shift from linear resource consumption to a circular bioeconomy. This transition is particularly evident in enabling decentralized green fertilizer production via nitrogenase-based N_2 fixation and achieving simultaneous waste valorization and energy recovery. We emphasized that the fundamental bottleneck restricting these applications remains the kinetic barriers of interfacial electron transfer (ET). Consequently, overcoming these barriers through advanced electrode engineering, such as nanostructuring and redox polymer wiring, alongside mechanistic optimization of DET and MET pathways is a prerequisite for high-performance systems. Looking forward, to propel bioelectrocatalysis from laboratory benchtops to field-deployable agricultural technologies, future research must prioritize three critical areas. First, enhancing the environmental robustness of bio-interfaces against biofouling and fluctuations in complex matrices is essential for long-term operation. Second, integrating synthetic biology tools to engineer "super-catalysts" with superior electron transfer capabilities will drive system efficiency. Bridging the engineering gap toward low-cost and scalable system integration is vital for realizing the practical deployment of these green technologies. Finally, cost control, such as the replacement of noble metal components with low-cost carbon-based materials, constitutes a critical prerequisite for the scalable deployment of bioelectrocatalytic technologies in agricultural and environmental remediation contexts.

Data Availability Statement

Data will be made available on request.

Funding

This work was supported without any funding.

Conflicts of Interest

The authors declare no conflicts of interest.

AI Use Statement

The authors declare that no generative AI was used in the preparation of this manuscript.

Ethical Approval and Consent to Participate

Not applicable.

References

[1] Hill, H. A. O., & Higgins, I. J. (1981). Bioelectrocatalysis. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences, 302*(1468), 267-273. [CrossRef]

[2] Schmid, A., Dordick, J. S., Hauer, B., Kiener, A., Wubbolts, M., & Witholt, B. (2001). Industrial biocatalysis today and tomorrow. *nature, 409*(6817), 258-268. [CrossRef]

[3] De Carvalho, C. C. (2011). Enzymatic and whole cell catalysis: finding new strategies for old processes. *Biotechnology advances, 29*(1), 75-83. [CrossRef]

[4] Chen, H., Dong, F., & Minteer, S. D. (2020). The progress and outlook of bioelectrocatalysis for the production of chemicals, fuels and materials. *Nature Catalysis, 3*(3), 225-244. [CrossRef]

[5] Cadoux, C., & Milton, R. D. (2020). Recent enzymatic electrochemistry for reductive reactions. *ChemElectroChem, 7*(9), 1974-1986. [CrossRef]

[6] Wong, T. S., & Schwaneberg, U. (2003). Protein engineering in bioelectrocatalysis. *Current Opinion in Biotechnology, 14*(6), 590-596. [CrossRef]

[7] Milton, R. D., Wang, T., Knoche, K. L., & Minteer, S. D. (2016). Tailoring biointerfaces for electrocatalysis. *Langmuir, 32*(10), 2291-2301. [CrossRef]

[8] Arechederra, R., & Minteer, S. D. (2008). Organelle-based biofuel cells: Immobilized mitochondria on carbon paper electrodes. *Electrochimica Acta, 53*(23), 6698-6703. [CrossRef]

[9] Takeuchi, R., Suzuki, A., Sakai, K., Kitazumi, Y., Shirai, O., & Kano, K. (2018). Construction of photo-driven bioanodes using thylakoid membranes and multi-walled carbon nanotubes. *Bioelectrochemistry, 122*, 158-163. [CrossRef]

[10] Adachi, T., Kataoka, K., Kitazumi, Y., Shirai, O., & Kano, K. (2019). A bio-solar cell with thylakoid membranes and bilirubin oxidase. *Chemistry Letters, 48*(7), 686-689. [CrossRef]

[11] Rasmussen, M., Shrier, A., & Minteer, S. D. (2013). High performance thylakoid bio-solar cell using laccase enzymatic biocathodes. *Physical Chemistry Chemical Physics, 15*(23), 9062-9065. [CrossRef]

[12] Lovley, D. R., & Walker, D. J. F. (2019). Geobacter protein nanowires. *Frontiers in Microbiology, 10*, 2078. [CrossRef]

[13] Ueki, T., Walker, D. J., Tremblay, P. L., Nevin, K. P., Ward, J. E., Woodard, T. L., ... & Lovley, D. R. (2019). Decorating the outer surface of microbially produced protein nanowires with peptides. *ACS synthetic biology, 8*(8), 1809-1817. [CrossRef]

[14] Tan, Y., Adhikari, R. Y., Malvankar, N. S., Ward, J. E., Nevin, K. P., Woodard, T. L., ... & Lovley, D. R. (2016). The low conductivity of Geobacter uraniireducens pili suggests a diversity of extracellular electron transfer mechanisms in the genus Geobacter. *Frontiers in microbiology, 7*, 980. [CrossRef]

[15] Hartshorne, R. S., Reardon, C. L., Ross, D., Nuester, J., Clarke, T. A., Gates, A. J., ... & Richardson, D. J. (2009). Characterization of an electron conduit between bacteria and the extracellular environment. *Proceedings of the National Academy of Sciences, 106*(52), 22169-22174. [CrossRef]

[16] Ross, D. E., Flynn, J. M., Baron, D. B., Gralnick, J. A., & Bond, D. R. (2011). Towards electrosynthesis in Shewanella: Energetics of reversing the Mtr pathway for reductive metabolism. *PLoS ONE, 6*(2), e16649. [CrossRef]

[17] Wu, R., Ma, C., & Zhu, Z. (2020). Enzymatic electrosynthesis as an emerging electrochemical synthesis platform. *Current Opinion in Electrochemistry, 19*, 1-7. [CrossRef]

[18] Kracke, F., Vassilev, I., & Krömer, J. O. (2015). Microbial electron transport and energy conservation–the foundation for optimizing bioelectrochemical systems. *Frontiers in microbiology, 6*, 575. [CrossRef]

[19] Xiao, Y., Patolsky, F., Katz, E., Hainfeld, J. F., & Willner, I. (2003). " Plugging into enzymes": Nanowiring of redox enzymes by a gold nanoparticle. *Science, 299*(5614), 1877-1881. [CrossRef]

[20] Milton, R. D., Cai, R., Abdellaoui, S., Leech, D., De Lacey, A. L., Pita, M., & Minteer, S. D. (2017). Bioelectrochemical Haber–Bosch process: an ammonia-producing H2/N2 fuel cell. *Angewandte Chemie International Edition, 56*(10), 2680-2683. [CrossRef]

[21] Su, Y., Cestellos-Blanco, S., Kim, J. M., Shen, Y. X., Kong, Q., Lu, D., ... & Yang, P. (2020). Close-packed nanowire-bacteria hybrids for efficient solar-driven CO2 fixation. *Joule, 4*(4), 800-811. [CrossRef]

[22] Liu, C., Sakimoto, K. K., Colon, B. C., Silver, P. A., & Nocera, D. G. (2017). Ambient nitrogen reduction cycle using a hybrid inorganic biological system. *Proceedings of the National Academy of Sciences of the United States of America, 114*(25), 6450-6455. [CrossRef]

[23] Ortiz, R., Matsumura, H., Tasca, F., Zahma, K., Samejima, M., Igarashi, K., Ludwig, R., & Gorton, L. (2012). Effect of deglycosylation of cellobiose dehydrogenases on the enhancement of direct electron transfer with electrodes. *Analytical Chemistry, 84*(23), 10315-10323. [CrossRef]

[24] Zhang, L., Cui, H., Zou, Z., Garakani, T. M., Novoa Henriquez, C., Jooyeh, B., & Schwaneberg, U. (2019). Directed evolution of a bacterial laccase (CueO) for enzymatic biofuel cells. *Angewandte Chemie International Edition, 58*(14), 4610-4613. [CrossRef]

[25] Lim, K., Sima, M., Stewart, R. J., & Minteer, S. D. (2020). Direct bioelectrocatalysis by redox enzymes immobilized in electrostatically condensed oppositely charged polyelectrolyte electrode coatings. *Analyst, 145*(4), 1250-1257. [CrossRef]

[26] Xu, H., Dai, H., & Chen, G. (2010). Direct electrochemistry and electrocatalysis of hemoglobin protein entrapped in graphene and chitosan composite film. *Talanta, 81*(1-2), 334-338. [CrossRef]

[27] Dong, F., Chen, H., Malapit, C. A., Prater, M. B., Li, M., Yuan, M., ... & Minteer, S. D. (2020). Biphasic bioelectrocatalytic synthesis of chiral β-hydroxy nitriles. *Journal of the American Chemical Society, 142*(18), 8374-8382. [CrossRef]

[28] Arduini, F., Cinti, S., Caratelli, V., Amendola, L., Palleschi, G., & Moscone, D. (2019). Origami multiple paper-based electrochemical biosensors for pesticide detection. *Biosensors and Bioelectronics, 126*, 346-354. [CrossRef]

[29] Chen, H., Prater, M. B., Cai, R., Dong, F., Chen, H., & Minteer, S. D. (2020). Bioelectrocatalytic conversion from N2 to chiral amino acids in a H2/α-keto acid enzymatic fuel cell. *Journal of the American Chemical Society, 142*(8), 4028-4036. [CrossRef]

[30] Blackford, J. C., & Gilbert, F. J. (2007). pH variability and CO2 induced acidification in the North Sea. *Journal of Marine Systems, 64*(1-4), 229-241. [CrossRef]

[31] Finn, C., Schnittger, S., Yellowlees, L. J., & Love, J. B. (2012). Molecular approaches to the electrochemical reduction of carbon dioxide. *Chemical Communications, 48*(10), 1392-1399. [CrossRef]

[32] Delecouls-Servat, K., Basseguy, R., & Bergel, A. (2002). Designing membrane electrochemical reactors for oxidoreductase-catalysed synthesis. *Bioelectrochemistry, 55*(1-2), 93-95. [CrossRef]

[33] Steckhan, E. (2005). Electroenzymatic synthesis. In *Electrochemistry V* (pp. 83-111). Berlin, Heidelberg: Springer Berlin Heidelberg. [CrossRef]

[34] Simon, H., Gunther, H., Bader, J., & Tischer, W. (1981). Electro-enzymatic and electro-microbial stereospecific reductions. *Angewandte Chemie International Edition in English, 20*(10), 861-863. [CrossRef]

[35] Son, E. J., Lee, S. H., Kuk, S. K., Pesic, M., Choi, D. S., Ko, J. W., ... & Park, C. B. (2018). Carbon nanotube–graphitic carbon nitride hybrid films for flavoenzyme-catalyzed photoelectrochemical cells. *Advanced Functional Materials, 28*(24), 1705232. [CrossRef]

[36] Montpart, N., Rago, L., Baeza, J. A., & Guisasola, A. (2015). Hydrogen production in single chamber microbial electrolysis cells with different complex substrates. *Water Research, 68*, 601-615. [CrossRef]

[37] Lovley, D. R. (2011). Powering microbes with electricity: direct electron transfer from electrodes to microbes. *Environmental microbiology reports, 3*(1), 27-35. [CrossRef]

[38] Jiang, Y., May, H. D., Lu, L., Liang, P., Huang, X., & Ren, Z. J. (2019). Carbon dioxide and organic waste valorization by microbial electrosynthesis and electro-fermentation. *Water research, 149*, 42-55. [CrossRef]

[39] Mateo, C., Palomo, J. M., Fernandez-Lorente, G., Guisan, J. M., & Fernandez-Lafuente, R. (2007). Improvement of enzyme activity, stability and selectivity via immobilization techniques. *Enzyme and microbial technology, 40*(6), 1451-1463. [CrossRef]

[40] Li, J., Ma, H., Ma, H., Lei, F., He, D., Huang, X., ... & Fan, G. (2023). Comprehensive effects of N reduction combined with biostimulants on N use efficiency and yield of the winter wheat–summer maize rotation system. *Agronomy, 13*(9), 2319. [CrossRef]

[41] Babanova, S., Jones, J., Phadke, S., Lu, M., Angulo, C., Garcia, J., ... & Bretschger, O. (2020). Continuous flow, large-scale, microbial fuel cell system for the sustained treatment of swine waste. *Water Environment Research, 92*(1), 60-72. [CrossRef]

[42] Ieropoulos, I. A., Stinchcombe, A., Gajda, I., Forbes, S., Merino-Jimenez, I., Pasternak, G., Sanchez-Herranz, D., & Greenman, J. (2016). Pee power urinal - Microbial fuel cell technology field trials in the context of sanitation. *Environmental Science: Water Research & Technology, 2*(2), 336-343. [CrossRef]

[43] Schievano, A., Colombo, A., Grattieri, M., Trasatti, S. P., Liberale, A., Tremolada, P., Pino, C., & Cristiani, P. (2017). Floating microbial fuel cells as energy harvesters for signal transmission from natural water bodies. *Journal of Power Sources, 340*, 80-88. [CrossRef]

[44] Walter, X. A., Stinchcombe, A., Greenman, J., & Ieropoulos, I. (2017). Urine transduction to usable energy: A modular MFC approach for smartphone and remote system charging. *Applied Energy, 192*, 575-581. [CrossRef]

[45] Logan, B. E., & Rabaey, K. (2012). Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. *science, 337*(6095), 686-690. [CrossRef]

[46] Santoro, C., Talarposhti, M. R., Kodali, M., Gokhale, R., Serov, A., Merino-Jimenez, I., Ieropoulos, I., & Atanassov, P. (2017). Microbial desalination cells with efficient platinum-group-metal-free cathode catalysts. *ChemElectroChem, 4*(12), 3322-3330. [CrossRef]

[47] Alkotaini, B., Tinucci, S. L., Robertson, S. J., Hasan, K., Minteer, S. D., & Grattieri, M. (2018). Alginate-encapsulated bacteria for the treatment of hypersaline solutions in microbial fuel cells. *ChemBioChem, 19*(11), 1162-1169. [CrossRef]

[48] Grattieri, M., & Minteer, S. D. (2018). Microbial fuel cells in saline and hypersaline environments: Advancements, challenges and future perspectives. *Bioelectrochemistry, 120*, 127-137. [CrossRef]

[49] Lazzarini Behrmann, I. C., Grattieri, M., Minteer, S. D., Ramirez, S. A., & Vullo, D. L. (2020). Online self-powered Cr(VI) monitoring with autochthonous Pseudomonas and a bio-inspired redox polymer. *Analytical and Bioanalytical Chemistry, 412*(24), 6449-6457. [CrossRef]

Yuying Jiang is a Ph.D. candidate majoring in Systems Science at Beijing Technology and Business University. Her research focuses on the intersection of systems science and electrocatalysis. She is dedicated to introducing system modeling, complex system analysis, and data-driven methods into the study of electrocatalytic materials and reaction processes. Her work revolves around catalytic performance evaluation, mechanism analysis, and multi-scale optimization, aiming to provide systematic ideas and methodological support for the design and application of efficient electrocatalytic systems. (Email: fightingjyy@163.com)

Denghui Xu , Ph.D. in Science, is a Professor and Doctoral Supervisor who has long been engaged in the research of photoelectric materials and devices. He has extensive experience in interface control for novel light-emitting and photovoltaic devices, as well as new perovskite light-emitting devices. By regulating carrier injection and exciton recombination processes through interface engineering, he creatively achieved electroluminescence in liquid semiconductor materials and has made outstanding achievements in the mechanisms of novel light-emitting materials and devices. He has presided over and completed projects for the National Natural Science Foundation of China, the Military Science and Technology Commission, and the Beijing Outstanding Talent Program. He has published over 70 SCI papers as first or corresponding author and has applied for more than 10 invention patents and 3 international patents. (Email: xudh@btbu.edu.cn)