Integration of electroactive bacteria into electrodes combines strengths of intracellular biochemistry with electrochemistry for energy conversion and chemical synthesis. However, such biohybrid systems are often plagued with suboptimal electrodes, which limits the incorporation and productivity of the bacterial colony. Here, we show that an inverse opal-indium tin oxide electrode hosts a large population of current-producing Geobacter and attains a current density of 3 mA cm\(^{-2}\) stemming from bacterial respiration. Differential gene expression analysis revealed Geobacter's transcriptional regulations to express more electron-relaying proteins when interfaced with electrodes. The electrode also allows coculturing with Shewanella for syntrophic electrogenesis, which grants the system additional flexibility in converting electron donors. The biohybrid electrode containing Geobacter can also catalyze the reduction of soluble fumarate and heterogeneous biosynthesis. Geobacter sulfurreducens is its current-producing capability in microbial fuel cells (6). Its ability to metabolize organic pollutants and precipitate soluble heavy metals renders it also potentially applicable in bioremediation (15). Moreover, its complete genome sequence primes transcriptome analysis to probe its regulation strategies to maintain cellular homeostasis under various conditions (16).

Here we employ an inverse opal-indium tin oxide (IO-ITO) electrode as a platform for microbial electrogenesis and electrosynthesis using G. sulfurreducens (Fig. 1 A and B). ITO is hydrophilic and the porous electrode architecture provides easy access for bacteria penetration and colonization (Fig. 1C). When positive potentials are applied, planktonic G. sulfurreducens from the medium solution attaches on the electrode surface. The electrical interaction with hydrophilic bacteria (13). Therefore, sessile bacteria on such electrodes tend to form compact biofilms with sluggish electron transfer and inefficient mass transport, which engender adverse stresses limiting their proliferation and productivity (14).

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sessile bacteria metabolize acetate to support its growth through the tricarboxylic acid (TCA) cycle, while discharging excess electrons to the electrode via OMCs, which is registered as a continuous anodic current (Fig. 1 D and E). Transcriptome analysis by RNA sequencing revealed that G. sulfurreducens regulates gene expression in order to respire on electrodes. Furthermore, Shewanella loihica PV-4 was introduced together with G. sulfurreducens on the IO-ITO electrode to achieve syntrophic electrogenesis by linking their metabolic pathways (Fig. 1F), which will grant the system additional flexibility in using different electron donors. Electrosynthesis was carried out by poising negative potentials on the resulting IO-ITO/G. sulfurreducens electrode. Under such conditions, G. sulfurreducens accepts electrons from the electrode to sustain its metabolism and disposes respiratory electrons by reducing soluble fumarate or heterogeneous graphite oxide (GO) (Fig. 1G). Lastly, to outsource the electron supply to a renewable source, the biohybrid electrode was coupled with a photoanode to achieve photoelectrosynthesis without applying an external electrochemical bias.

Results and Discussion

Microbial Electrogenesis. IO-ITO electrodes were prepared by a coassembly method using 10-μm polystyrene beads as the structural template and ITO nanoparticles (average size: 50 nm) as the electrode material to suit the dimension of G. sulfurreducens (length: 1.5 to 2 μm; diameter: 400 to 500 nm) (SI Appendix, Fig. S1 and Fig. 1B) (17, 18). The resulting electrode features interconnected macropores (8 to 10 μm) accessible to bacteria and a mesoporous skeleton permeable to both nutrients and products (Fig. 2 and Movies S1 and S2). The IO-ITO electrode had a geometrical area of 0.25 cm² and a film thickness of ~60 μm (Fig. 2 A and E). G. sulfurreducens was integrated on an IO-ITO scaffold from the electrolyte solution by applying a potential of 0.1 V vs. standard hydrogen electrode (SHE). During this process, planktonic G. sulfurreducens penetrated into the electrode scaffold and metabolized acetate into CO₂ while discharging electrons to the electrode (Fig. 1 C and D). Bacteria then proliferated and progressively colonized the entire electrode, producing an increasing anodic current that plateaued at 3 mA cm⁻² after 80 h (Fig. 34), which corresponds to a volumetric current density of 500 mA cm⁻³. This volumetric current density represents a benchmark performance in microbial electrogensist and approaches the volumetric current limit (1,000 mA cm⁻³) of a single bacterium (SI Appendix, Table S1) (19). Control experiments show that the recorded current was exclusively derived from bacterial metabolism (SI Appendix, Figs. S2 and S3), making it a good proxy for the bacteria’s metabolic activity. Quantification of the proteins inside the hybrid electrode supported that the growth of bacteria aligned with the increase of current density (Fig. 3B). The high current density is attributed to the IO-ITO electrode
architecture, which compartmentalized bacteria colonies with a conductive and permeable scaffold, and thus allowed a large population of bacteria to actively metabolize therein. In contrast, \textit{G. sulfurreducens} on a flat ITO-coated glass and a flat gold electrode produced substantially less current (~0.2 mA cm\(^{-2}\)) and therefore yielded a much thinner biofilm (<5 μm) (\textit{SI Appendix}, Fig. S4) (14). The current started decaying in the wake of acetate depletion, which can be partially restored by supplementing acetate into the current medium or replenishing with a fresh medium. Depletion, which can be partially restored by supplementing acetate into the current medium or replenishing with a fresh medium.

The resulting IO-ITO/\textit{G. sulfurreducens} electrode displayed a typical reddish color stemming from the redox-active multihem c-type cytochrome (Cyt \(c\)) (Fig. 3C, \textit{Inset}). Focused ion beam-scanning electron microscopy (FIB-SEM) imaging shows that the bacteria penetrated through the entire IO-ITO electrode and were in close contact with the mesoporous scaffold (Fig. 3C and D, \textit{SI Appendix}, Fig. S5, and Movie S3). Confocal laser scanning microscopy (CLSM) images manifest the respiratory activity of living bacteria and indicate that bacterial viability was well-retained in the electrode scaffold (Fig. 3E and \textit{SI Appendix}, Fig. S6).

Under turnover conditions, the IO-ITO/\textit{G. sulfurreducens} electrode exhibited a characteristic sigmoidal cyclic voltammetry (CV) trace with an onset potential of ~0.25 V vs. SHE (Fig. 3F, \(E_{CO_2/acetate} = -0.29\) V vs. SHE, pH 7.0) (20). The CV profile points to a typical catalytic response of a biofilm, where the catalytic current is limited by the extracellular electron transport via OMCs (21). This is further evidenced by a control experiment that suppressed Cyt \(c\) production in bacteria by limiting the iron availability during growth, without affecting the bacterial viability (\textit{SI Appendix}, Fig. S7 A–C) (22). The iron-depleted (ΔFe) \textit{G. sulfurreducens} produced negligible current (0.5 μA cm\(^{-2}\)) and a nonturnover CV wave (\textit{SI Appendix}, Fig. 7D–F), which confirms the necessity of Cyt \(c\) for microbial electrogenesis. Electrons delivered from the bacterium were transferred through the conducting IO-ITO scaffold. A control experiment with an insulating IO-ZrO\(_2\) scaffold on an ITO-coated glass produced negligible current and no bacterial colony was formed (\textit{SI Appendix}, Fig. S8), which demonstrates that the conductivity of the electrode scaffold is essential for the bacterium’s outward electron transfer and biofilm formation.

\textbf{Potential-Dependent Electrogenesis.} The plateau anodic current varies with the applied electrochemical potential (Fig. 3G and \textit{SI Appendix}, Fig. S9). The highest current density was attained at 0.1 V vs. SHE (2.9 ± 0.1 mA cm\(^{-2}\), \(n = 10\)), whereas it reduced to 1.1 ± 0.1 mA cm\(^{-2}\) (\(n = 10\)) at 0.4 V vs. SHE (Fig. 3G). Colormetric protein quantification revealed that the biohybrid electrode at 0.1 V vs. SHE contained more proteins than at 0.4 V vs. SHE (Fig. 3H). We thus infer that bacteria can overcome the thermodynamic challenge arising from a lower electrochemical potential to discharge electrons outward by adopting a different set of pathways (23). This would allow them to maintain competitive advantages in habitats where redox states of electron acceptors are frequently varying due to environmental and meteorological perturbations. It is common practice in the field to apply high potentials (e.g., 0.4 V vs. SHE) to establish an electron sink for microbial respiration (\textit{SI Appendix}, Table S1), but our results suggest that such positive potentials might not be optimal for microbial electrogenesis.

RNA sequencing was then employed to understand whether the culturing in electrodes and potential difference can induce transcriptional responses. \textit{G. sulfurreducens} for RNA extraction was collected after the bacteria ceased proliferation in the electrodes at different potentials (after the current plateau) and in a planktonic solution with fumarate (in the stationary phase) (\textit{SI Appendix}, Figs. S3B and S10). Differential gene expression analysis shows a substantial down-regulation of gene expression when bacteria are grown on electrodes, compared with those cultured in...
a medium solution with fumarate as the electron acceptor (Fig. 3 I and J and SI Appendix, Supplementary Text). This observation agrees with a previous study using graphite as the electrode and Fe(III) citrate as the soluble electron acceptor (24). It suggests that G. sulfurreducens deployed a different metabolic strategy that consumes less energy when interfaced with an electrode (24, 25). The transcriptional regulation is likely to occur during the initial lag phase (Fig. 3A), during which electron transfer pathways are shifted to favor an insoluble electron acceptor (electrode) (24). Nevertheless, there was no significant change in gene expression at different potentials (0.1 V and 0.4 V vs. SHE) (Fig. 3K), despite large differences in current density (Fig. 3G). These findings imply that G. sulfurreducens adjusted its gene expression to keep intracellular metabolism in tune with physiological needs with different electron acceptors, whereas electrode potentials cannot induce tangible responses at a transcriptional level. The question of how cellular metabolism in tune with physiological needs with different electron acceptors, whereas electrode potentials cannot induce tangible responses at a transcriptional level. The question of how
**G. sulfurreducens** can sense electrode potentials and respond to potential variations, remaining unclear and requires further investigations (26, 27).

**Syntrophic Electrogenesis.** In nature, different bacteria form symbiotic partnerships via interspecies mass transport or electron transfer to overcome environmental disadvantages (28). This inspires a syntrophic strategy for electrogenesis, which employs the syntrophy between mixed cultures of electroactive bacteria, and thus grants the system additional resilience to environmental perturbations such as limited electron donors. **S. loihica** is an electrogenic bacterium ubiquitously thriving in aquatic and sedimentary environments. It has evolved robust sensing and regulatory systems that confer its metabolic versatility (29). **S. loihica** and **G. sulfurreducens** have similar morphology and dimensions (SI Appendix, Fig. S11), but differ in metabolic pathways: **S. loihica** utilizes lactate as the carbon and energy resource instead of acetate and it engages with extracellular electron acceptors mainly through self-secreted flavins (30). By coculturing **S. loihica** and **G. sulfurreducens** in an IO-ITO electrode, lactate can be used as the sole electron donor to support the electrogenesis of both strains. In this case, **S. loihica** metabolizes lactate into acetate that can be further utilized by **G. sulfurreducens**, while both bacteria release electrons to the electrode (Fig. 1F). Such a syntrophic pathway can

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![Fig. 4. Microbial electrosynthesis and photoelectrosynthesis with IO-ITO/G. sulfurreducens electrodes.](image-url)

(A) Representative cathodic current of an IO-ITO/G. sulfurreducens electrode catalyzing fumarate (10 mM, pH 7.4) reduction at −0.45 V vs. SHE. A bare IO-ITO electrode was used as a control. (B) 1 H NMR spectra of the electrolyte solution aliquoted during the course of reaction. TMSP-d4 (1 mM) was used as the reference (0 ppm) and internal standard for quantification. 1H NMR peaks of fumarate (singlet, 6.52 ppm) and succinate (singlet, 2.41 ppm) are indicated. (C) Quantification of reactants and products and Faraday efficiency during the course of reaction. (D) Cathodic current of an IO-ITO/G. sulfurreducens electrode reducing GO (0.1 mg mL−1) at −0.3 V vs. SHE. A bare IO-ITO electrode was used as a control. The inset shows photographs of GO solutions before (labeled “GO”) and after reduction by a bare IO-ITO electrode labeled “Control”). (E) A two-electrode system at zero bias. A bare IO-ITO electrode without bacteria was used as the cathode for a control experiment (gray trace). (F) Schematic representation of a PEC cell consisting of a BiVO4-CoOx anode and an IO-ITO/G. sulfurreducens cathode. Under irradiation, the excited RuP+ dye injects an electron into the conduction band of the TiO2 electrode, which is further directed to the cathode via an external circuit. The RuP+ dye is regenerated by extracting an electron from TEOA. (F) SEM image of an IO-TiO2 electrode. The inset shows the top view of the electrode (Scale bar: 10 μm.) The IO-TiO2 electrode has a thickness of 40 μm and macropore size of 10 μm. (G) Photocurrent from chronoamperometry of the IO-TiO2/RuP (0.25 cm2) and BiVO4-CoOx (1.0 cm2) photoanodes (plotted at different applied potentials) and cyclic voltammogram of the IO-ITO/G. sulfurreducens electrode in fumarate (10 mM, pH 7.2) solution. Three-electrode configuration, scan rate: 5 mV s−1. (H) Light-driven fumarate reduction with an IO-TiO2/RuP/G. sulfurreducens two-electrode system at zero bias. A bare IO-ITO electrode without bacteria was used as the cathode for a control experiment (gray trace). TEOA (25 mM, in 50 mM KCl) was used as the electron donor for the photoanode. (I) Schematic representation of a PEC cell consisting of a BiVO4-CoOx anode and an IO-ITO/G. sulfurreducens cathode. BiVO4 absorbs light and donates excited electrons to the external circuit while oxidizing water with the aid of the CoOx cocatalyst. (J) Top-view (Top) and cross-sectional (Bottom) SEM images of a BiVO4-CoOx electrode. The thickness of BiVO4 film was 500 nm and CoOx cocatalysts were deposited on top. (K) Light-driven fumarate reduction with a BiVO4-CoOx/O. IO-ITO/G. sulfurreducens two-electrode system at zero bias. A hybrid electrode with dead bacteria ( deactivated by 0.1% glutaraldehyde) was used as the cathode for a control experiment (gray trace). A PBS solution (20 mM Na2HPO4, pH 7.3) was used for the photoanode compartment. The insets in H and K are 1 H NMR spectra of the solution extracted from the cathode compartment after 24 h of irradiation. TMSP-d4 (1 mM) was used as the reference (0 ppm) and internal standards for quantification. The NMR peak of succinate (singlet, 2.41 ppm) is highlighted and the doublet peak at 2.7 ppm is assigned to malate. Conditions: 20 mM fumarate, pH 7.2, U = 0 V, I = 100 mW cm−2, AM 1.5G, in a N2:CO2 atmosphere at 25 °C. The photocurrent was normalized to the geometrical area of the cathode (0.25 cm2).
increase the stoichiometric production of electrons and further attest that the IO-ITO electrode is a robust and versatile host for various microbial communities.

As G. sulfurreducens poorly utilizes lactate for metabolism (31), the current output at 0.4 V vs. SHE (0.13 mA cm⁻²) with lactate was far below that with acetate as the electron donor (1.07 mA cm⁻²) (Fig. 3L). This is also evidenced by a reduced G. sulfurreducens population on the electrode (SI Appendix, Fig. S12A). The current density produced by S. loihica (0.30 mA cm⁻²) with lactate was smaller than that of G. sulfurreducens with acetate at 0.4 V vs. SHE, despite a large population of S. loihica on the electrode (Fig. 3L and SI Appendix, Fig. S12B). This results from a diffusion-governed extracellular electron transfer by S. loihica (32), which is kinetically less efficient compared with direct electron transfer via OMCs in G. sulfurreducens. Inoculation of both S. loihica and G. sulfurreducens attained a higher current of 0.68 mA cm⁻², and yielded more acetate (~2.9 mM) than S. loihica alone (~1.6 mM) (Fig. 3 L and M). These together point to a syntrophy between G. sulfurreducens and S. loihica: the presence of G. sulfurreducens perhaps assisted S. loihica in discharging more electrons via interspecies electron transfer (33), which produced more acetate and facilitated the growth of both strains (SI Appendix, Fig. S12C).

Microbial Electrolysis. Electrosynthesis was carried out by poised a negative potential on the biohybrid electrode that was cultured at 0.1 V vs. SHE for 80 to 100 h, until the current stabilized. In this case, G. sulfurreducens receives electrons to sustain its metabolism and disposes excess reducing equivalents to reduce chemicals (20). We employed a prototypical reaction, fumarate reduction, to exemplify the potential of leveraging intracellular metabolism for chemical synthesis. Fumarate reduction to succinate with a Faraday efficiency of 93 ± 1.1% (Fig. 4F). The presence of additional metabolites indicates that the bacteria retained their metabolic activity with electrons supplied by the photoanode and thus reduced fumarate via intracellular biosynthetic sequences.

The IO-TiO₂-RuP photoanode employs a sacrificial reagent (TEOA) as the electron donor and is prone to photodegradation (38). To overcome these drawbacks, we resorted to monoclinic BiVO₄ as the light-absorbing material in light of its well-suited band structure for water oxidation to O₂ (band gap: 2.4 eV; conduction band potential: ~0.4 V vs. SHE, pH 7.0) (40). We employed BiVO₄ deposited with a CoO₇ cocatalyst as the photoanode to directly extract electrons from water (in a phosphate buffer solution, pH 7.3) (Fig. 4 J and J) (41). The BiVO₄-CoO₇ photoanode displayed a photocurrent onset potential at ~0.35 V vs. SHE (Fig. 4G and SI Appendix, Fig. S14C) and the BiVO₄-CoO₇ photoanode therefore generated a smaller current at zero bias in a two-electrode configuration with 0.5 ± 0.20 mM succinate being detected after 24 h of irradiation (I = 100 mW cm⁻², AM 1.5G) (Fig. 4K and SI Appendix, Fig. S14D). Inactivation of the bacteria by biocide on the cathode resulted in no succinate and other metabolites, confirming fumarate reduction was performed through bacterial metabolism (Fig. 4K).

Light-driven fumarate reduction has been previously carried out using isolated flavoenzymes as the biocatalyst, but the system performance was highly limited by the fragility of isolated enzymes and susceptible to enzyme orientations that dictate the electron transfer at biointerfaces (42, 43). The microbial system here enabled higher catalytic capacity and improved stability, thanks to the large number of robust bacteria integrated inside the IO-ITO scaffold. Moreover, the proteinaceous electron conduits on bacterial membranes allow for omnidirectional electron transfer toward electrodes, regardless of the orientation of the bacteria. This photosynthetic system decouples light harvesting on the photoanode from chemical transformation at the cathode, rendering the system optimization flexible.

Conclusion

We present a semibiological system employing electroactive bacteria integrated inside a porous and hydrophilic IO-ITO electrode architecture. The resulting biohybrid electrodes provide a platform to wire the bacteria’s intrinsic physiological functionalities with artificial electronics and allow a high degree of control over system configuration and operation. The biohybrid electrode attained a current density of 3 mA cm⁻² at 0.1 V vs. SHE arising from microbial metabolism and represents a benchmark performance for microbial electrosynthesis. Differential gene expression analysis revealed regulation of gene expression by G. sulfurreducens in response to changes in electron acceptors. The IO-ITO electrode also allowed S. loihica and G. sulfurreducens to metabolize in tandem and hence formed a syntrophic pathway for electrogensis, which grants the system additional flexibility in using different electron donors to increase the stoichiometric electron production. Moreover, the resulting IO-ITO(G. sulfurreducens) photoanode can serve as a “living” cathode to reduce fumarate and GO with electrons supplied by an external electrochemical bias or by an irradiated photoanode. Coupling of microbial electro-synthesis with photoanodic water oxidation establishes the possibility of sustainable synthesis driven by sunlight. This biohybrid system synergizes metabolism with extracellular redox transformations via the electrical interplay at biointerfaces.
and can further be empowered with emerging methodologies in the realm of synthetic biology. With advancing genetic technologies, new biosynthetic pathways can be created and extended beyond the scope of naturally occurring metabolism. These will pave new avenues toward sustainable energy conversion and chemical synthesis.

Data Availability. Materials and methods, supplementary details, SI Appendix, Figs. S1–S14 and Table S1 and Movies S1–S3 are available at the University of Cambridge data repository (https://doi.org/10.17863/CAM.48465).

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