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Red-light-driven biophotochemical diode based on microorganism-silicon nanowire interface for stable and efficient bias-free CO₂ reduction

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ABSTRACT: Artificial photosynthesis offers a promising route for sustainable liquid fuel and feedstock production, yet integrating efficient CO₂ reduction catalysts with light-harvesting systems remains challenging. Here, we present a biophotochemical diode that couples microorganism-driven CO₂ reduction with glycerol oxidation, enabled by silicon nanowire photoelectrodes under varying red-light intensities. Tuning the biotic-abiotic interface—by increasing biocatalyst loading and adjusting catholyte pH to mitigate local alkalization—significantly improves performance and stability. The enhanced-loading biocathode maintains high faradaic efficiency across a wide potential range, even under elevated light intensities. At 60 mW/cm², the system achieves a bias-free current density of 3.5 mA/cm². Long-term stability testing at 40 mW/cm² demonstrates stable operation for over 100 hours. The photoanode generates valuable C₃ products, primarily glycerate and lactate, enhancing economic viability. This work showcases the importance of microenvironmental control at the biotic-abiotic interface and establishes a scalable platform for light-driven CO₂ reduction using earth-abundant silicon.

Artificial photosynthesis, which aims to mimic nature's conversion of sunlight, water, and carbon dioxide into energy-rich compounds, faces a critical challenge: the development of effective CO₂ reduction reaction (CO₂RR) catalysts and their seamless integration with efficient light-harvesting systems^{1–3}. Inorganic CO₂RR catalysts exhibit relatively high overpotential compared to the hydrogen evolution reaction (HER), and the products are often limited to low-

carbon products, predominantly C₁ species such as formate and CO^{4,5}. In contrast, natural microorganisms like acetogenic bacteria have evolved highly selective pathways for CO₂ fixation into energy-dense multi-carbon products at low overpotentials, yet they inherently lack an efficient light-absorbing system⁶⁻⁸. To bridge this gap, photochemical diodes, first conceptualized by Nozik, offer a compelling solution by integrating a photocathode and photoanode via a back ohmic contact, and drive coupled reduction and oxidation reactions under light illumination⁹. Merging whole-cell CO₂-reducing biocatalysts with a semiconductor photocathode, which serves as an efficient light absorber, represents a promising strategy to store light energy in chemical bonds for liquid fuel and feedstock production.

Semiconductor nanowires have emerged as strong candidates for photochemical diodes¹⁰⁻¹⁵, due to their high surface area for catalyst loading and active sites, as well as their enhanced charge separation¹⁶⁻¹⁹. Liu et al. demonstrated a silicon nanowire (SiNW) loaded with *Sporomusa ovata*, a highly efficient CO₂-reducing biocatalyst that operates with less than 200 mV overpotential²⁰. When coupled with a titanium dioxide (TiO₂) oxygen evolution reaction (OER) photoanode, the system achieved a bias-free current density of 0.3 mA/cm². However, several key challenges remain for improving biophotochemical diode systems: 1) low current density primarily due to high oxidative potential requirement of OER, 1.23 V *versus* the reversible hydrogen electrode (RHE), 2) variability in real-world sunlight intensity due to diurnal irradiation and fluctuating environmental effects²¹⁻²³, which leads to inconsistent electron supply to biocatalysts, and 3) the presence of ultraviolet (UV) light in solar spectrum which can potentially damage microorganisms during long-term operation^{24,25}.

One effective strategy to increase bias-free current density is to replace OER with an alternative oxidation reaction that has a lower thermodynamic potential with faster kinetics. For

instance, the glycerol oxidation reaction (GOR) has a relatively low thermodynamic potential of ~ 0.08 V vs. RHE for major product like glycerate^{26–28} and has been successfully implemented in photoelectrochemical systems to convert glycerol into value-added products^{13,15,29,30}. To overcome the limitations imposed by the solar spectrum, Kim et al. coupled bio-CO₂RR with GOR and powered the photochemical diodes using low-intensity (20 mW/cm²) red-light resulting in current density of 1 mA/cm² for 5 hours¹⁵. Among various LED wavelengths, far-red is a particularly suitable choice for operating a Si photochemical diode. At similar external quantum efficiencies, far-red LEDs offer much higher photon efficacy than blue or green LEDs, resulting in a lower electrical cost per delivered photon^{31,32}. Because the excess energy above the band gap is lost through thermalization^{33,34}, far-red light represents the most economical option for driving a Si photochemical diode. The utilization of far-red LEDs is further rationalized by their high photon utilization efficiency, as prior studies on crystalline Si photocathodes and photoanodes have consistently reported maximum IPCE values in the red to far-red wavelengths (>600 nm)^{35–37}. Moreover, the stable light intensity of LEDs enables continuous 24/7 operation, as showcased for vertical farming of plants^{38–40}. Acetogens utilize Wood-Ljungdahl pathway, a more ATP-efficient carbon-fixation route compared to aerobic carbon fixation route including Calvin Cycle^{41,42}, making red-light-driven biohybrid PEC a sustainable alternative strategy for converting CO₂ to highly selective C₂ fuels. Nevertheless, further improvements in biocatalyst loading, bias-free current density and achieving a long-term stable biotic-abiotic interface under high light intensity comparable to solar are required to advance this system toward practical CO₂-to-fuel bioconversion.

In this work, we demonstrate a stable and efficient bias-free bio-CO₂RR coupled with GOR, enabled by varying red-light intensities and tuning the local biotic-abiotic interface near the

cathode. As shown in Fig. 1a, the overlap of half-cell current-voltage curves indicates the feasibility of bias-free operation for the integrated photoelectrochemical (PEC) bio-CO₂RR and GOR under 740 nm far-red illumination. *Sporomusa ovata* biocatalysts directly take electron or H₂ mediator from the cathode and reduce CO₂ into acetate, while a Pt₁Au₅ co-sputtered photoanode catalyzes GOR to mainly C₃ products- glycerate and lactate. Building on previous work by Su et al., which reported close-packed *S. ovata* interfaced with Si nanowire¹⁴, we further report that an extended two-week start-up period, during which the applied negative potential was gradually increased to enhance current delivery, enabled enhanced biocatalyst loading and the formation of a mature biotic-abiotic interface. An enhanced biocatalyst loading allows high faradic efficiencies across a wide range of potentials by efficiently absorbing parasitic H₂. Increasing the red-light intensity from 20 mW/cm² to 60 mW/cm² raises the overlap current density and thus the acetate production rate. Lowering the catholyte pH effectively mitigates local alkalinity buildup in the enhanced-loading biocathode, enabling stable CO₂RR at even higher light intensity. The schematic of a novel Si nanowire bio-photochemical diode is shown in Fig 1b. As shown in Figure 1c, vertically stacked biohybrid PEC cells continuously operated under red LEDs further increase production rates when land area is limited. By tuning the local cathode environment, the system achieves a maximum bias-free current density of 3.5 mA/cm² at 60 mW/cm² illumination. For long-term stability test, we demonstrate 100 hours of bias-free CO₂RR and GOR under intermediate light intensity of 40 mW/cm², achieving current density of 2.5 mA/cm² and faradaic efficiencies exceeding 80% at both electrodes. The continuous CO₂ reduction with simultaneous glycerol valorization without biocatalyst deactivation provides a model system for long-term artificial photosynthesis of CO₂-to-multicarbon fuel conversion.

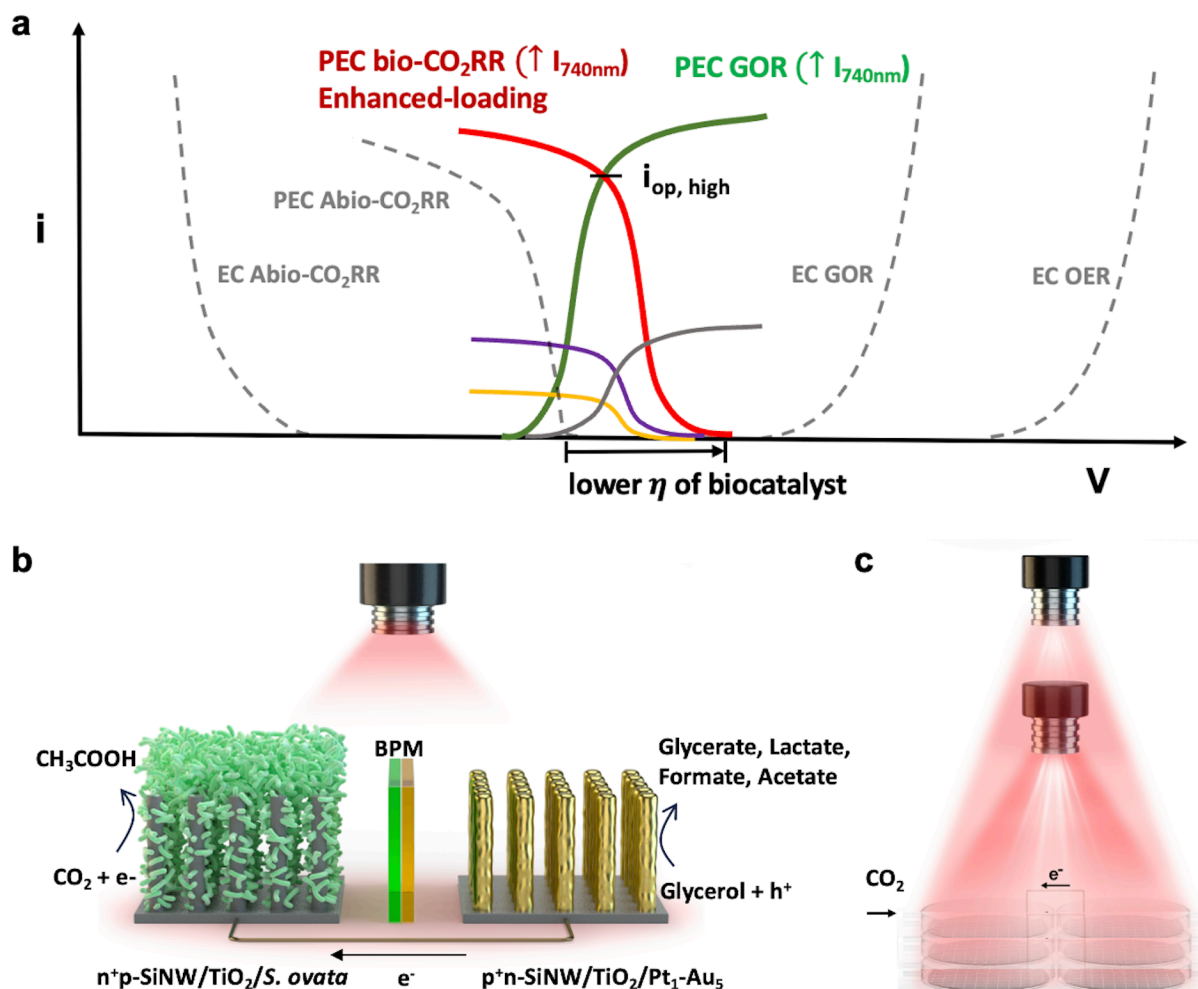


Figure 1. Schematic illustration of a biophotochemical diodes operating under red light (740 nm) illumination at varying light intensities and tuned microorganism-nanowire interface. (a) Schematic illustration of half-cell current–voltage curves; PEC biotic CO₂RR with enhanced loading of biocatalyst under high/low light intensity (red and purple, respectively), PEC biotic CO₂RR without loading enhancement under low light intensity (yellow), PEC GOR under high/low light intensity (green and grey, respectively). GOR serves as an alternative oxidation reaction, replacing OER to enable bias-free operation. The overlap of the currents indicates the feasibility of bias-free operation. EC abiotic CO₂RR, EC OER, EC GOR, and PEC abiotic CO₂RR are shown in dashed lines for reference. (b) Si nanowire PEC system operating under red

light, with performance dependent on light intensity. The system consists of a coupled biophotocathode (n^+p -SiNW/TiO₂/*S. ovata*) and photoanode (p^+n -SiNW/TiO₂/Pt₁-Au₅), separated by a bipolar membrane. Two weeks of start-up period with gradually increasing negative potential bias leads to increased biocatalyst loading and a stable biotic-abiotic interface. Stable and efficient bias-free operation under elevated light intensities is enabled by optimizing biocatalyst loading and further lowering the catholyte pH to mitigate local alkalinity near the cathode. (c) Schematic illustration of vertically stacked PEC cells operating under red-light illumination. Higher red-light intensity is represented by the reduced working distance between the LED and the cells.

Tuning the local microorganism-SiNW interface

Achieving efficient electron transfer from the cathode to biocatalysts is a key challenge in an inorganic biohybrid system^{8,43}. Su et al. and Kim et al. demonstrated that tuning the catholyte pH and supplying electrons only from Si nanowire, enabled close packing of *S. ovata* within the nanowire structures, resulting in significantly enhanced current densities compared to a system with low biocatalyst loading^{14,15}. The well-defined bacteria-nanowire interface enables estimation of bacteria density of ~13 cells per nanowire. We hypothesize that the close-packed system approaches the maximum electron uptake rate achievable by the biocatalyst at the operating current density of 1 mA/cm². The electron uptake rate at this current density is calculated to be approximately 100 $\mu\text{mol electrons s}^{-1} \text{gDCW}^{-1}$, using a dry cell weight (DCW) of 330 fg per cell (See Methods for DCW measurement). This value is close to the highest electron uptake rate reported for acetogenic bacteria⁴⁴⁻⁴⁶.

In this context, we report a further enhancement of current density achieved by increasing biocatalyst loading through an extended start-up period of two weeks of bio-interface maturation. During maturation, the cathodic potential was negatively adjusted to increase the current density by approximately 0.1 mA/cm² per day. Concurrently, the catholyte was refreshed every 24 hours to remove unattached planktonic cells and maintain pH. Scanning electron microscopy (SEM) confirms the formation of a dense, tens-of-micrometers-thick biofilm on top of close-packed nanowire structures (Supplementary Fig. 1). The resulting enhanced-loading photocathode exhibited an enhanced photocurrent density-potential (j-V) curve as measured by linear sweep voltammetry (LSV) (Fig. 2a). No visible turbidity was observed after continuous electrolyte exchange, indicating that the attached cells are primarily responsible for the observed current density. To confirm that a thicker biocatalyst layer exhibits negligible red-light absorbance, a ~10 µm artificial biofilm was deposited on top of glass slides (See Methods and Supplementary Fig. 2a for SEM image). UV-Vis spectrophotometry at 740 nm showed <1% light attenuation by a 10 µm biofilm (Supplementary Fig. 2b), supporting the feasibility of using higher biocatalyst loadings in the red-light-driven PEC biohybrid system.

Figure 2b presents the average current density and acetate faradaic efficiency (FE) for the close-packed biocathode, following two hours of half-cell chronoamperometry under continuous illumination (40 mW/cm²). Although average current density increased at more negative potentials, acetate FE declined sharply, falling below 40% at 0.05 V *vs.* RHE, indicative of increased parasitic HER over bio-CO₂ reduction. In contrast, the enhanced-loading cathode maintained high faradaic efficiencies (> 80%) across a wide potential range, while also exhibiting higher average current densities (Fig. 2c). H₂ generated via abiotic HER from the Pt co-catalyst is likely rapidly consumed by the biofilm without escaping, subsequently transferring

electrons to redox couples through H_2 -mediated electron transfer pathways, thereby contributing to high FE.

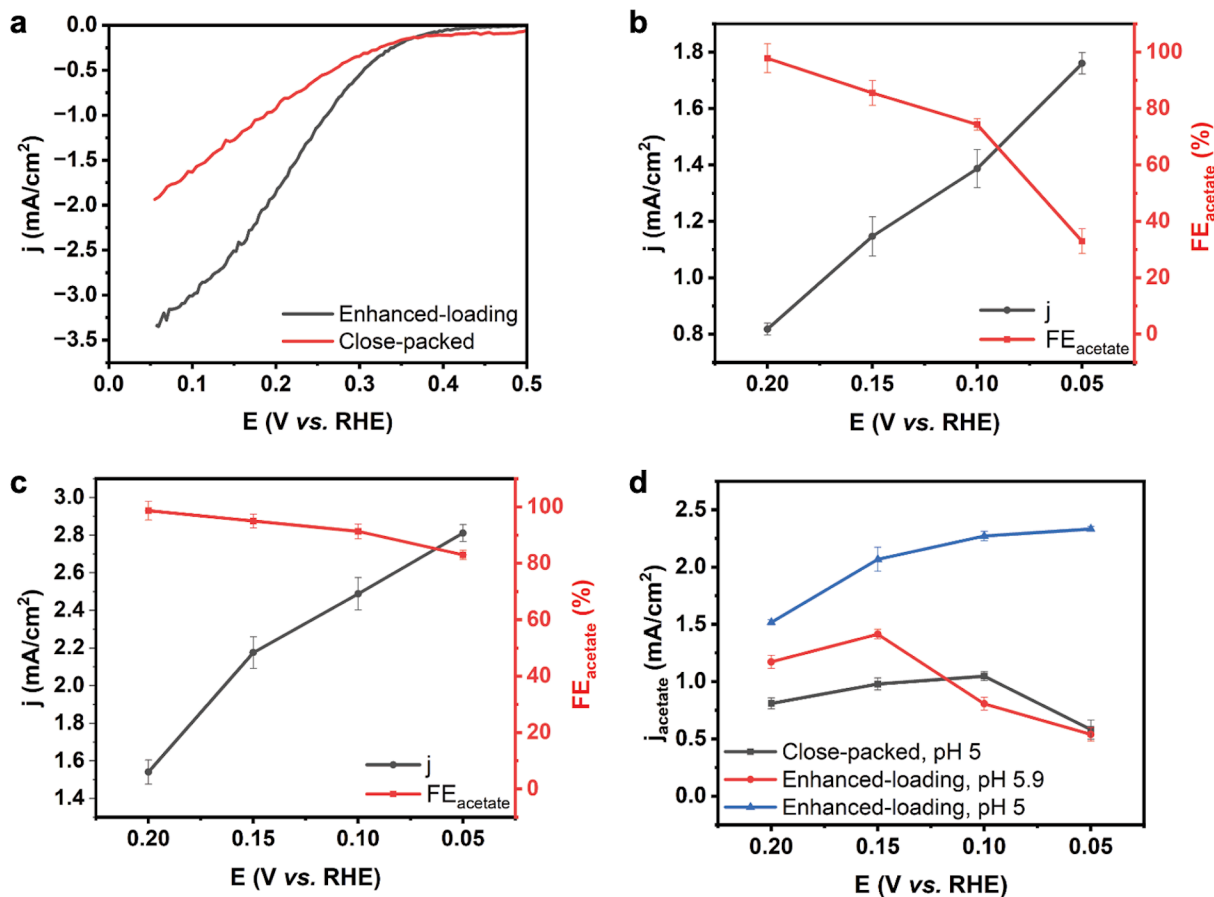


Figure 2. Silicon nanowire biophotocathode n^+p -SiNW/TiO₂/*S. ovata* photoelectrochemical performance with tuned biotic-abiotic interface. (a) Photocurrent density–potential (j -V) curves for two different biocathodes: close-packed (5 days of start-up) and close-packed with enhanced biocatalyst loading (14 days of start-up). 100 mM MES biocatholyte tuned to pH 5 was used. (b) Average photocurrent density and faradaic efficiency (FE) from two hours of chronoamperometry at each potential for the close-packed cathode with catholyte pH tuned to 5. (c) Average photocurrent density and FE from two hours of chronoamperometry at each potential for the enhanced-loading cathode with catholyte pH tuned to 5. (d) Average acetate

faradaic current density at each potential for three cathode configurations: close-packed with pH tuned to 5, enhanced-loading with as-prepared pH 5.9, and enhanced-loading with pH tuned to 5. 1N HCl was added to adjust the pH. All PEC characterizations were performed under 740 nm red light with an intensity of 40 mW/cm². Absolute values of cathodic current densities were used except for Figure 2a. Error bars represent standard deviations of three independent replicates.

A significant concern in biohybrid cathodes-particularly those employing surface-attached cells rather than planktonic cells-is the development of local alkalinity near the cathode surface^{14,47}. In earlier studies, where current densities were relatively low, the impact of local pH shifts on biocatalyst performance was often underappreciated. However, *S. ovata* shows optimal acetate production in the pH range of 6-7⁴⁸, making it critical to maintain the local (rather than bulk) pH near this optimal range during operation. Our data confirm that bacterial growth and metabolism are significantly inhibited above pH 10 (Supplementary Fig. 3) and maximum acetate production is achieved by maintaining pH between 6-7 under anaerobic culture conditions (Supplementary Fig. 4). Accordingly, for the experiments shown in Figure 2b and Figure 2c, we employed 100 mM 2-(N-morpholino)ethanesulfonic acid (MES) buffer. We adjusted the pH to 5 using 1N HCl to ensure a favorable local environment. In contrast, when the as-prepared MES 100mM catholyte at pH 5.9 was used without pH adjustment, the enhanced-loading photocathode's faradaic efficiency dropped below 30% at 0.05 V *vs.* RHE (Supplementary Fig. 5). Even after reversing to more positive potential (0.2 V *vs.* RHE), the FE remained below 50%, indicating irreversible biocatalyst deactivation. Figure 2d compares the average faradaic current density for acetate production of three different cathodes: enhanced-

loading with lowered pH, enhanced-loading without pH adjustment, and close-packed with lowered pH. Only when biocatalyst loading is increased and catholyte pH is properly lowered does the system achieve consistently high faradaic efficiencies and current densities across the wide potential range, thereby maximizing acetate production. Notably although *S. ovata* growth and acetate production are limited at pH 5 in static anaerobic culture (Supplementary Fig. 4), under dynamic bio-PEC operation, a bulk pH of 5 is expected to result in a sufficiently elevated local pH near the electrode and enable over 80% FE.

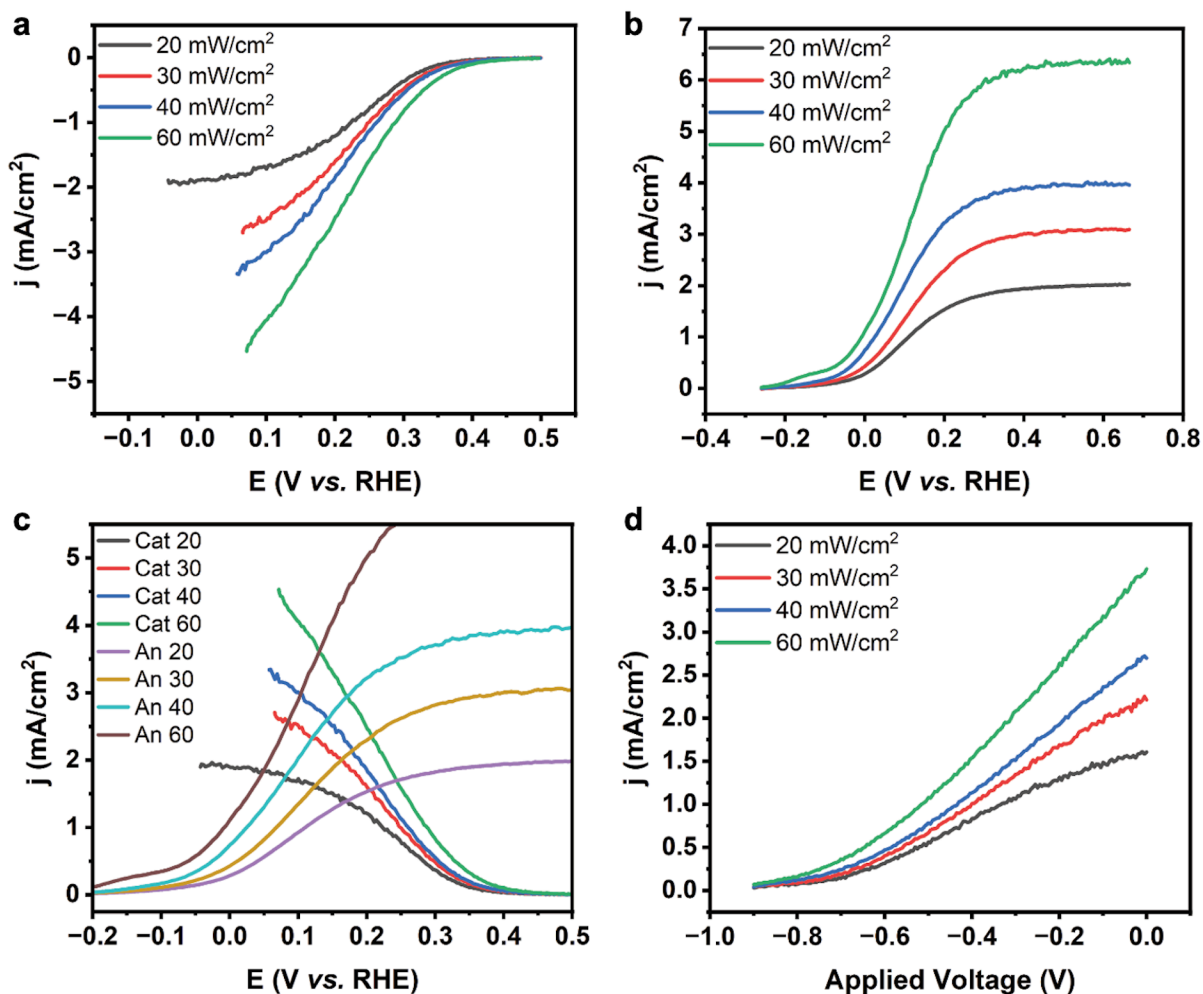


Figure 3. Photoelectrochemical characterizations of the n^+p -SiNW/TiO₂/*S. ovata* enhanced-loading photocathode and p^+n -SiNW/TiO₂/Pt₁-Au₅ photoanode under varying red-light intensities. (a) Half-cell photocurrent density–potential (j-V) curves of the biocathode at varying intensities of 20, 30, 40 and 60 mW/cm². (b) Half-cell j-V curves of the Pt and Au co-sputtered anode at under same varying light intensities. (c) Overlap of the half-cell j-V curves for the biocathode and anode, highlighting the operating potential window and overlapping current densities. (d) Full-cell j-V curves of the integrated photoelectrochemical system in a two-electrode configuration. The catholyte consisted of bacteria growth medium buffered with 100 mM MES buffer and pH was tuned to 5. The anolyte was a solution of 1M glycerol and 1M KOH. All linear sweep voltammetry measurements were conducted at a scan rate of 10 mV/s.

Half-cell red-light power-dependent photoelectrochemical characterizations of bio-CO₂RR and GOR

Following a two-week start-up for *S. ovata* hybridization on n^+p -SiNW photocathode, photocurrent density-potential (j-V) characterizations were performed under varying light intensities of 20, 30, 40, and 60 mW/cm² (Fig. 3a). LSV scans were intentionally stopped before reaching saturation current densities for higher light intensities to avoid damage to biocatalysts. Based on the Air Mass 1.5 spectrum (ASTM G-173), the average red-light (620-750 nm) intensity is ~17 mW/cm². For 740 nm monochromatic light illumination, a light intensity of 73.5 mW/cm² generates the same above-bandgap photon flux for Si as 100 mW/cm² simulated sunlight. (See Methods for calculation). Thus, the 20-60 mW/cm² range used in this study corresponds to a near-ambient red-light spectrum to slightly sub-solar photon flux for Si. At 20 mW/cm², the n^+p -SiNW/TiO₂/*S. ovata* photocathode generates a photovoltage of ~370 mV,

measured by the open-circuit potential (OCP) shift under illumination versus dark. Both OCP measurement and the positive shift in onset potentials indicate that the photovoltage increases logarithmically with light intensities, consistent with previous reports for semiconductor junctions^{49,50} (Supplementary Fig. 6). At 60 mW/cm², the photovoltage increases by ~50 mV. The fill factor (FF) under 20 mW/cm² is 0.28 for biocatholyte system, compared to 0.48 and 0.6 for the abiotic control in 0.5 M H₂SO₄ under 20 and 60 mW/cm², respectively (Supplementary Fig. 7). This reduction in FF is attributed to the low light intensity, which increases the relative contribution of fixed parasitic resistances^{51,52}, as well as the low ionic strength and complexity of biocatholyte species (Supplementary Table 1), which lead to greater concentration overpotentials and uncompensated resistance⁵⁰.

To couple with the bio-CO₂RR, the glycerol oxidation reaction was selected as the counter anodic reaction. A p⁺n-SiNW, protected with TiO₂ and co-sputtered with Pt-Au (1:1) catalysts had previously been shown to be effective for GOR^{13,15}. In this study, the Pt: Au ratio was tuned to 1:5 to improve long-term operational stability, as evidenced by sustained current density in chronoamperometry measurements (Supplementary Fig. 8). X-ray photoelectron spectroscopy (XPS) analysis of the Pt 4f and Au 4f regions confirmed the intended 1:5 ratio (Supplementary Fig. 9). Figure 3b shows j-V curves of p⁺n-SiNW/TiO₂/Pt₁-Au₅ photoanode under the same varying red-light intensities in 1 M KOH with 1 M glycerol. Similar to the photocathode, the photoanode photovoltage increases slightly from 440 to 490 mV as the light intensity increases. The saturated photocurrent density scales nearly linearly with light intensity. Figure 3c overlays the cathode and anode LSVs, confirming the feasibility of bias-free operation across all light intensities. The overlap potential remains around 0.1 - 0.15 V *vs.* RHE, and the overlap current density increases from 1.4 mA/cm² (at 20 mW/cm²) to 3.5 mA/cm² (at 60 mW/cm²). These

values align closely with full-cell LSV current density at zero applied voltage (bias-free), as shown in Figure 3d, and further discussed in the following section.

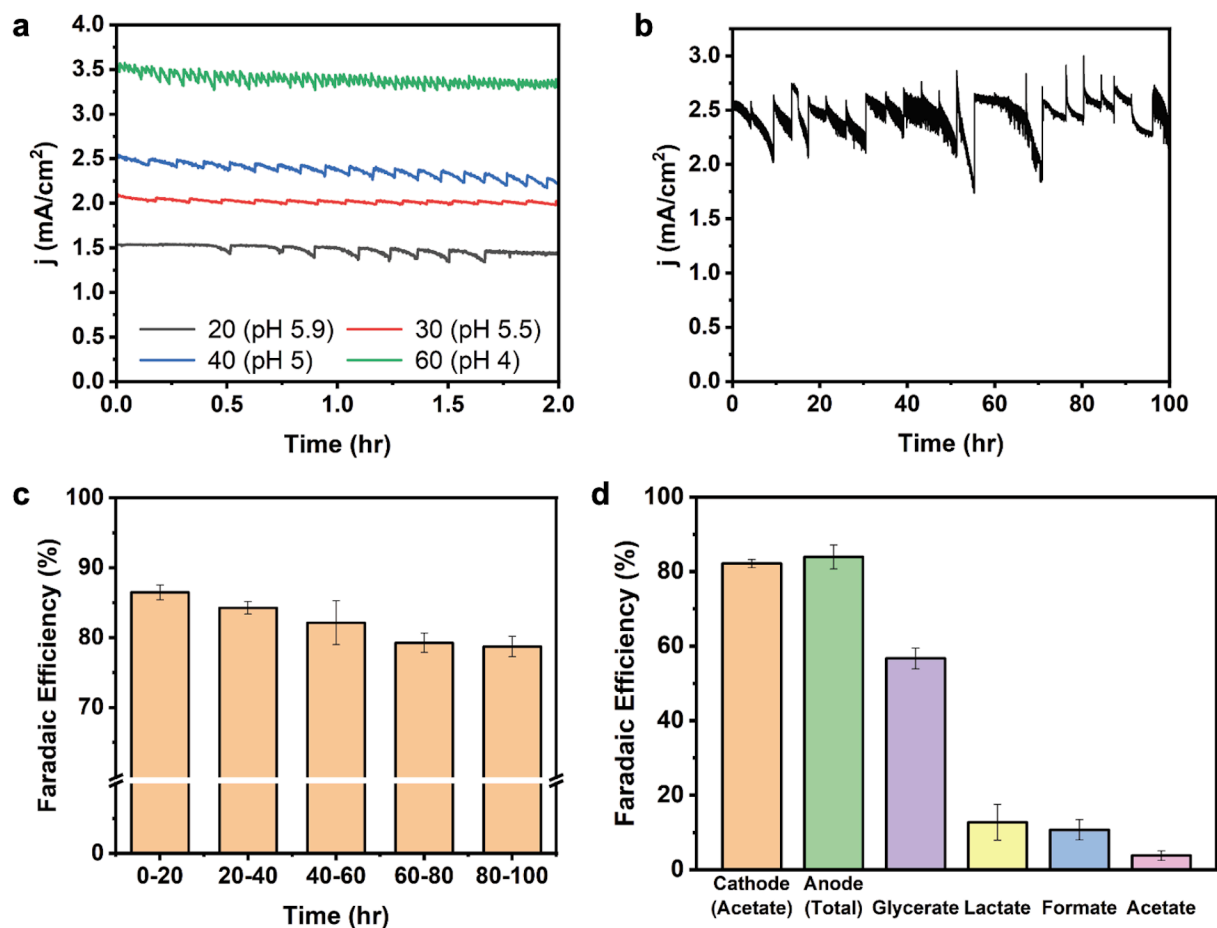


Figure 4. Stable bias-free performance of simultaneous CO₂RR and GOR by the integrated n⁺p-SiNW/TiO₂/*S. ovata* enhanced-loading photocathode and p⁺n-SiNW/TiO₂/Pt₁-Au₅ photoanode under varying light intensities and catholyte pH. (a) Chronoamperometry (CA) measurements showing current densities over time under red-light intensities of 20, 30, 40 and 60 mW/cm² with corresponding catholyte pH adjusted to 5.9, 5.5, 5.0 and 4.0, respectively. (b) Long-term stability CA test conducted over 100 hours under 40 mW/cm² illumination, with the catholyte exchanged every 4 hours. (c) Faradaic efficiencies of acetate production at the biocathode, calculated for

each 20-hour interval of the 100-hour CA test. (d) Average faradaic efficiencies over the full 100-hour CA test for both cathodic product (acetate) and anodic products (glycerate, lactate, formate and acetate). The catholyte consisted of bacterial growth medium buffered with 100 mM MES (initial pH 5.9), adjusted to the desired pH using 1 N HCl. The anolyte was a solution of 1 M glycerol and 1 M KOH. The catholyte was continuously purged with pure CO₂ gas. Error bars represent standard deviations of three independent replicates.

Long-term stable and efficient bias-free bio-CO₂RR coupled with GOR

For the bias-free operation of bio-CO₂RR and GOR, n⁺p-SiNW/TiO₂/*S. ovata* enhanced-loading photocathode and p⁺n-SiNW/TiO₂/Pt₁-Au₅ photoanode were integrated in a two-electrode configuration. Both electrodes are illuminated with red light, and the cathode and anode chambers were separated by a bipolar membrane (Fig. 1b). The bipolar membrane enables the decoupling of the chemical environments at each electrode, maintaining different pH conditions appropriate for each half-reaction⁵³. Specifically, GOR operates optimally under basic condition for both Pt and Au^{54–56}, while bio-CO₂RR requires mildly acidic to neutral condition. The full-cell LSVs of the integrated system showed onset potential of - 0.8 V (at 20 mW/cm²) to - 0.9 V (at 60 mW/cm²), reflecting a photovoltage increase of 50 mV as light intensity increased for both photoelectrodes. Figure 4a presents time-dependent current densities measured over two hours of bias-free chronoamperometry at varying light intensities. The catholyte pH was further lowered to 4, when higher light intensity was used in order to mitigate the increase of local alkalinity as discussed earlier. To minimize biocatalyst exposure to unfavorable low bulk pH, 1N HCl was added during bias-free operation under low light intensity to adjust the bulk pH in real time. Once the bulk pH reached 4, the light intensity was subsequently increased to 60 mW/cm².

At 20 mW/cm², the system achieved a bias-free current density of 1.4 mA/cm², surpassing the previously reported bias-free current density of 1.2 mA/cm² under the same light intensity¹⁵. At 40 mW/cm² and 60 mW/cm², the current density further increased to 2.5 and 3.5 mA/cm², respectively, with corresponding faradaic efficiencies of 87% and 69% (Supplementary Fig. 10). The slight decline in FE at 60 mW/cm² is likely due to partial biocatalysts deactivation, attributed to nutrient and pH gradients caused by mass-transport limitations within the biofilm or nanowire structure⁵⁷.

A long-term stability chronoamperometry test was conducted under intermediate light intensity of 40 mW/cm² for 100 hours (Figure 4b). To maintain catholyte pH and prevent FE degradation, the catholyte was exchanged every 4 hours. Additionally, due to the slow etching of the Si nanowire photoanode under KOH, the GOR anode was replaced every 12 to 24 hours, depending on the decay of current density. The average current density remained 2.4 mA/cm², with the best-performing photoanode results up to 3 mA/cm². The cathode faradaic efficiencies, measured at 20-hour intervals (Figure 4c), showed only a minor decrease from 87% to 79% over 100 hours of continuous operation and reached a stable plateau after approximately 60 hours, indicating a stable biotic-abiotic interface. The post-operation SEM image of the biocathode (Supplementary Fig. 3c) further confirms that the biocatalysts remain well attached to the nanowire array without noticeable detachment or structural damage, supporting the sustained interfacial stability and suggesting the potential for even longer-term operation beyond 100 hours. Figure 4d summarizes the 100-hour average faradaic efficiencies for both cathodic and anodic products. At the cathode, acetate was the dominant product, with an FE of 82% and negligible (<3%) production of 2-oxobutyrate or ethanol byproducts (Supplementary Fig. 11). At the anode, total FE for GOR products that are detectable from ¹H-NMR was 84%, C₃ compounds glycerate (GLA) and

Lactate (LA) being the major products. While the total FE from Pt₁-Au₅ SINW photoanode is comparable to that of previously reported Pt₁-Au₁ SiNW photoanode¹⁵, the increased Au content led to a higher GLA selectivity (~ 57% vs. ~ 40%) enhancing economic viability due to the high-value of C₃ products²⁷. This improvement is likely attributed to more Au sites facilitating the adsorption of reactive oxygen species (e.g., *OH), which promotes further deprotonation of chemisorbed intermediate species instead of C-C bond cleavage⁵⁴. The negligible formation of glycolate (<3%) is likely due to the low oxidation potential of the bias-free point, which inhibits further oxidation of GLA²⁸.

Conclusions

In comparison to previously reported bias-free PEC CO₂ reduction systems, our integrated system-n⁺p-SiNW/TiO₂/*S. ovata* enhanced—loading cathode and p⁺n-SiNW/TiO₂/Pt₁-Au₅ photoanode—exhibits significantly enhanced operating current densities and exceptional selectivity toward C₂ product, acetate (Supplementary Table 2). By tuning the local microbial and chemical environment at the cathode, we achieved stable and efficient simultaneous bio-CO₂RR and GOR for 100 hours, with added economic values from the GOR C₃ products. This result highlights the potential of red-light-driven, continuous acetate production photoelectrodes composed of earth-abundant, low-cost Si as a scalable platform. In this work, we achieved a bias-free current density of 3.5 mA/cm² under 60 mW/cm² red-light illumination corresponding to an acetate current density of 2.4 mA/cm²—approximately two-fold of previously reported record-high bias-free acetate current density¹⁵. The results presented in this study highlight the critical importance of optimized biocatalyst loading and favorable local pH at the biocatalyst-

electrode interface, which is a key for stable operation at higher current densities in photosynthetic biohybrid systems.

ASSOCIATED CONTENT

The following files are available free of charge.

Experimental Methods; Supplementary Tables 1–3, including medium composition, acetate production rate comparison with previous literature, and glycerol oxidation reactions for FE calculation; Supplementary Figures 1–11, including SEM images of biohybrids, characterization of light attenuation, bacterial growth characterization, acetate production rate under autotrophic anaerobic culture, photoelectrochemical characterization of enhanced-loading cathode without pH adjustment, photovoltages of cathodes and anodes, cathode LSV in 0.5 M sulfuric acid, CA comparison of PtAu co-sputtered anodes, XPS spectrum of anodes, FE of two-hour CA under varying light intensities, and the ^1H NMR spectrum of catholyte (PDF).

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Author Contributions

† These authors contributed equally. W. L. and P. Y. designed the project. W. L., A. L. and J. -A. L. fabricated the silicon electrodes. W. L., A. L., Jinhyun Kim, Jimin Kim, and T. L. conducted the PEC experiments. W. L., Jinhyun Kim, T. L., and N. G. cultured the bacteria. Y. S. performed the XPS measurements, and L. J. carried out the UV-Vis measurements. W. L. and P. Y. co-wrote the paper. All authors discussed the results and revised the manuscript.

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Notes

The authors declare no competing financial interest.

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