

1 **Title: A Red light Powered Silicon Nanowire Biophotochemical Diode for Simultaneous**
2 **CO₂ Reduction and Glycerol Valorization**

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16

17 **Abstract:**

18 **A bias-free photochemical diode, connecting a p-type photocathode and an n-type**
19 **photoanode to harness light for driving photoelectrochemical reduction and oxidation**
20 **pairs, serves as a platform for realizing light-driven fuel generation from CO₂. However,**
21 **the conventional design, coupling cathodic CO₂ reduction with anodic oxygen evolution**
22 **(OER), requires substantial energy input. Here, we present a photochemical diode device**
23 **that harnesses red (740 nm) light to simultaneously drive biophotocathodic CO₂-to-**
24 **multicarbon conversion and photoanodic glycerol oxidation as an alternative to OER to**
25 **overcome the thermodynamic limitation. The device consists of an efficient CO₂-fixing**
26 **microorganism, *Sporomusa ovata*, interfaced with a silicon nanowire (SiNW)**
27 **photocathode and a Pt-Au loaded SiNW photoanode. This photochemical diode operated**
28 **bias-free under low-intensity (20 mW/cm²) red light irradiation with ~80% faradaic**
29 **efficiency for both cathodic and anodic products. This work provides an alternative**
30 **photosynthetic route to mitigate excessive CO₂ emissions and efficiently generate value-**
31 **added chemicals from CO₂ and glycerol.**

32 **Main text:**

33 **Introduction**

34 The intermittent nature of sunlight poses a challenge in powering our society on a practical
35 scale^{1,2}. An appropriate technology to store renewable energy for use when the sun is not
36 shining is necessary. One possible solution is to utilize the photon energy to drive uphill
37 chemical reactions to produce chemical fuels that can be stored and transported for later
38 use. Photoelectrochemical (PEC) CO₂ reduction is a promising route to store light energy in
39 chemical bonds and to promote carbon neutrality³⁻⁶. In a photochemical diode first proposed
40 by Nozik, a p-type semiconductor photocathode and an n-type semiconductor photoanode are
41 wired together to drive reduction and oxidation reactions with a p/n-PEC device
42 configuration^{7,8}. The photoexcited charge carriers within a solid-state semiconductor electrode
43 are transferred to reactants, for instance, CO₂ molecules dissolved in a cathodic electrolyte, at
44 the solid-liquid junction to drive redox reactions.

45

46 The working principle of such a device is that the total harvested light energy from both
47 photoelectrodes should be larger than the thermodynamic energy requirement plus kinetic
48 overpotentials for oxidation and reduction reactions⁹. While the photochemical diode approach
49 has been showcased for a thermodynamically and kinetically more accessible hydrogen
50 evolution reaction (HER), limited success has been achieved for a CO₂ reduction reaction
51 (CO₂RR) due to the higher catalytic overpotentials of currently reported abiotic CO₂ catalysts
52 ^{8,10-12}. For example, an Au-loaded amorphous Si photocathode combined with a bismuth
53 vanadate photoanode was recently shown to enable a bias-free PEC system for CO₂RR. Still,
54 the reduction products were CO, a simple 2-electron reduced product, and parasitic H₂ with a
55 low operating photocurrent density (J_{op}) of 0.24 mA cm⁻² ¹³. Incorporating photovoltaic

56 components, such as embedded perovskite photovoltaics, into PEC systems helps to increase
57 the total photovoltage and has been shown to produce C_2 and C_3 ^{14,15} with Cu electrocatalysts,
58 though it still operated at very limited bias-free J_{op} . It also complicates the device structure and
59 increases the system costs. A bias-free PEC device to reduce CO_2 to more reduced products
60 beyond CO has yet to be achieved for the abiotic version of the photochemical diode.

61

62 The challenge posed by the excessive overpotentials associated with inorganic catalysts can be
63 effectively mitigated by utilizing CO_2 -reducing biocatalysts that operate with minimal
64 overpotentials near the standard thermodynamic potentials of given reactions. By capitalizing
65 on an overpotential of less than 200 mV exhibited by the acetogenic bacterium *Sporomusa*
66 *ovata* (*S. ovata*)^{16,17}, a Si – TiO_2 nanowire biophotochemical diode was employed to achieve
67 bias-free CO_2 -to-acetate synthesis with a J_{op} of ~ 0.3 mA/cm² and a solar-to-chemical efficiency
68 of 0.38%¹⁷. This acetate, derived from CO_2 , functioned as a readily available substrate for the
69 synthesis of high-value chemicals, including n-butanol, polyhydroxybutyrate (PHB), and N_2
70 fixation, using various strains of microorganisms, such as *Escherichia coli*¹⁷, *C. Basilenisis*¹⁸,
71 and *R. Pal*¹⁹.

72

73 However, further enhancements in the bias-free photocurrent density of the system are
74 necessary for its widespread application. Notably, two limiting factors contributing to the low
75 J_{op} can be pointed out: the overly oxidative thermodynamic potential of OER ($E_{H_2O/O_2} = 1.23$
76 V vs. RHE) and the sluggish CO_2 -reducing kinetic rates, originating from the slow CO_2
77 turnover rates of wild-type *S. ovata*. These limitations are illustrated by the resulting low
78 crosspoint (J_{op} under the bias-free condition) of two reactions in Fig. 1A. An expanded concept
79 of the photochemical diode can encompass alternative oxidation reactions with faster kinetics

80 and lower overpotential requirements. For instance, glycerol oxidation exhibits standard
81 thermodynamic potentials between 0.14 – 0.41 V vs. RHE, depending on the products²⁰, and it
82 shows a low overpotential of 200 mV when suitable catalysts are employed²¹. Thus, this
83 approach could induce a negative shift in the oxidation curve, improving the overlapping
84 current density between the photocathode and photoanode, thereby reducing the overall
85 photovoltage demand and enhancing J_{op} . To address the second challenge on the biocathodic
86 side, enhancing the CO₂ turnover rates through metabolic engineering, such as adaptive
87 laboratory evolution of biocatalysts, can be readily employed²². By increasing the turnover rate
88 of *S. ovata*, an enhancement in J_{op} towards C₂₊ products and overall solar-to-chemical
89 conversion efficiency can be achieved under bias-free operation. These two strategies lead to
90 the high J_{op} of the two reactions in Fig. 1B.

91

92 With this proposed alternative concept of artificial photosynthesis, here, we developed a
93 biophotochemical device combining a p-type SiNW photocathode integrated with *S. ovata* and
94 a Pt-Au loaded n-type SiNW photoanode. The schematics of the device structure are shown in
95 Fig. 1C and 1D. The nanofabricated silicon wafers served as efficient and inexpensive
96 photoelectrodes (Fig. 1E). The electroactive bacterium, *S. ovata*, is directly interfaced with the
97 SiNW photocathode to uptake photogenerated reducing equivalents, e.g., hydrogen molecules
98 and electrons, and utilize them to reduce CO₂ into acetate by the Wood–Ljungdahl pathway
99 (WLP). The whole-cell catalysts were operated at more positive potentials than the
100 thermodynamic potential of CO₂-to-acetate reduction (0.123 V vs. RHE) with the aid of
101 photovoltage generated by SiNW under red light irradiation. With the bacteria-SiNW
102 photocathode, a Pt-Au loaded n-type SiNW photoanode was wired in parallel for glycerol
103 oxidation reaction (GOR), producing economically valuable oxidation products from glycerol,
104 which is a main byproduct of biodiesel production²³. 0.85 V of photovoltage was generated by

the PEC device under a low-intensity (20 mW/cm²) of 740 nm LED and was sufficient to simultaneously drive biological CO₂ reduction reaction (CO₂RR) and GOR (Fig. 1C). This silicon p/n configuration photochemical diode achieved a maximum J_{op} of ~1.2 mA/cm² — where we report an appreciable bias-free PEC CO₂-to-C₂ reducing photocurrent density—with high faradaic efficiency, ~80% from both cathodic and anodic reactions.

Results

Fundamentals of photoelectrochemistry of SiNW in neutral pH

The PEC performance of the photocathode was first abiotically investigated under red light irradiation and biocompatible operating conditions of neutral pH in brackish bacterial medium for efficient hydrogen evolution (Fig. 2A - D). The hydrogen produced from the photocathode, which is a key reducing equivalent of WLP²⁴, attracts a floating *S. ovata* in the electrolyte to the electrode surface, facilitates their growth on the electrode, and leads to forming a robust bacteria-nanowire hybrid for CO₂ conversion. The wavelength of the red light used here, 740 nm, is well below that of the bandgap of silicon, 1100 nm, to efficiently excite the charge carriers while minimizing the thermalization loss and avoiding the antimicrobial activity associated with high-energy photons^{25–28}. For the fabrication of a stable high-photovoltage SiNW photocathode, an n⁺ shell was formed on a p-type SiNW array to increase the photovoltage, and 30 nm of crystalline titanium dioxide (TiO₂) was deposited by atomic layer deposition (ALD) to protect the substrate from corrosion (Supplementary Fig. 1)^{29–32}. Then, a 3 nm Pt was sputtered on the top surface as a co-catalyst to facilitate the charge transfer to the electrolyte. Nickel was also tested as a co-catalyst due to its good biocompatibility^{33,34} and facile connection to membrane-bound proteins³⁵. However, the photocathodes with sputtered Pt exhibited noticeably higher PEC performances, 200 mV more positive onset potential and four times higher photocurrent density, 1.4 mA/cm² and 0.36 mA/cm² at 0.1 V vs. RHE (Supplementary Fig. 2). Thus, Pt was used as a co-catalyst for the following experiments.

130

131 The fabricated Pt/TiO₂/n⁺p-SiNW photocathode shows an onset potential of ~0.4 V vs. RHE
132 under 20 mW/cm² red light irradiation (Fig. 2A). The dark and chopped scan corroborates that
133 the photocurrents were generated under light irradiation. The control experiments revealed that
134 the n⁺ radial shell adds 200 mV of photovoltage, and the device exhibits a total photovoltage
135 of ~400 mV under irradiation relative to dark Pt electrodes (Supplementary Fig. 3A and 3B).
136 The influence of light intensity ranging from 20 mW/cm² to 7 mW/cm² on the photocurrents
137 is shown in Fig. 2b. The lower light intensity yielded decreased photocurrent and photovoltage,
138 as previously reported for the similar array-type Si photocathode³¹. The light intensity of 20
139 mW/cm² was selected for the following experiments because this intensity matches the daily
140 average intensity of the infrared A (IR-A) radiation (760 nm – 1400 nm) of the solar spectrum
141 so that the condition could closely simulate ambient irradiation conditions³⁶. The intensity also
142 offers the onset voltage of ~0.4 V vs. RHE, which sufficiently overlaps with the onset of GOR
143 Si photoanode, ~0 V vs. RHE, for later integration into a combined system²¹.

144

145 The effect of electrolyte bulk pH was also investigated (Fig. 2C). Su *et al.* previously
146 demonstrated that lowering an initial bulk pH from 7.2 to 6.4 facilitates the formation of a
147 close-packed bacteria-nanowire cathode³⁷. The bulk pH of 7.2 could create a local
148 microenvironment around SiNW with a highly basic pH exceeding 9, which is an inhospitable
149 pH for the microorganism³⁷. Thus, 50 mM of a zwitterionic MES (2-(N-
150 morpholino)ethanesulfonic acid) buffer was added to the bacterial medium to enhance
151 buffering capacity in the lower pH range (see methods for detailed composition). This buffering
152 agent has a pK_a of 6.27, providing enhanced buffering capacity at the pH near its pK_a compared
153 to the conventional phosphate buffer, which has a pK_a of 7.21³⁸. The presence of the buffer had
154 no discernible effect on the metabolism of *S. ovata*, as demonstrated by comparing their growth

155 in cultures with and without MES buffer (Supplementary Fig. 4). Fig. 2C clearly shows pH
156 dependency of the photocurrent from 6.2 to 7.2. This is presumably because the catalytic rate
157 of HER on Pt and the resulting consumption of proton is high relative to the supply of protons
158 from the local environment in the neutral pH. Consequently, a lower bulk pH, creating a lower
159 local pH and facilitating faster proton supply, increases the overall reaction rate. To establish
160 a hospitable microenvironment and provide a faster flux of reducing equivalents to the
161 microorganisms, pH 6.2 of the MES-containing bacterial medium was used for subsequent
162 experiments. Since a pH lower than 6.0 could decrease the buffering capacity of MES buffer
163 and the optimal pH for *S. ovata* is 6.3³⁹, the pH was not further lowered. Fig. 2D shows a stable
164 photocurrent of the abiotic photocathode in the MES buffer for over 12 hours at 0.15 V vs.
165 RHE, which is close to the expected working potential of the bioCO₂RR-GOR bias-free system.
166 The bulk pH increased slightly after the PEC operations of ~12 hours due to proton
167 consumption from HER but was well mitigated at around 6.57 ± 0.13 (n = 3). Additionally,
168 there was no production of acetates observed at these abiotic PEC conditions due to the
169 excellent HER activity of platinum, despite continuous CO₂ gas feeding into the PEC device
170 (Supplementary Fig. 5).

171 Lastly, Fig. 2E shows the linear sweep voltammetry (LSV) scans of a standard 0.5 M sulfuric
172 acid and the biocompatible buffer electrolyte without iR-correction. Biocompatible buffers
173 typically have an ionic concentration below 0.1 M to avoid osmotic stress which can diminish
174 the productivity of bacteria⁴⁰. Consequently, the bacterial medium used in this study exhibited
175 a relatively higher ohmic drop than standard sulfuric acid due to its higher solution resistance,
176 as shown in the electrochemical impedance spectroscopy (EIS) results in the inset of Fig. 2E.
177 Although an additional electrolyte engineering for biocatalysts might reduce the ohmic drop
178 and enhance the electrochemical performances as suggested by the microbial electrosynthesis

research community^{41,42}, the voltage drop remained modest around the expected operating current density of the bias-free system, e.g., ~0.2 V of drop at 1 mA/cm².

PEC half-reactions of biological CO₂RR and GOR

Next, the microbial catalysts were incorporated onto this abiotic photocathode to form a nanowire-bacteria hybrid and upgrade the chemistry from HER to CO₂RR. Two strains of *S. ovata* were tested under the photocathodic condition: wild-type and a methanol-adapted strain. Tremblay et al. reported that the methanol adaptation yields strain met-T18-2 with a faster autotrophic metabolism⁴³, and the strain was successfully hybridized with a silicon nanowire cathode by Kim et al²². From chronoamperometry experiments over 60 hours, the adapted strain exhibited a ~5-fold increase in photocurrent density compared to the initial and that of the wild-type strain (Fig. 3A). Fig. 3B and 3C show scanning electron microscopy (SEM) images of the nanowire-bacteria hybrid after the PEC operations for the two strains. This enhanced performance of adapted *S. ovata* over wild-type *S. ovata* is attributed to its faster ability to uptake electrons and hydrogen²². Even though both strains started from the same bacterial loading density (OD₅₄₅ ~0.04 in the electrolyte), the adapted strain's faster metabolism resulted in quicker reproduction, as clearly shown in the two SEM images after 60 hours of operation. The more direct attachment of biocatalysts creates more charge transfer channels at the abio-bio interface and increases the photocurrent density at the same potential^{37,44}. Also, it must be noted that the increased biocatalyst loading on the photocathode, which fully covered the surface of the photocathode, did not negatively affect the photocurrent generation; instead, it increased it. This shows that the rate of PEC CO₂ reaction is limited by the biocatalysts and stresses the importance of introducing efficient catalysts at the interface. With superior metabolic activity on photocathodes, adapted *S. ovata* was used for the following experiments. Fig. 3D shows the LSV of the biotic and abiotic photocathodes. Both exhibit a

204 similar cathodic onset potential of ~ 0.4 V vs. RHE, and the biophotocathode shows a slightly
205 higher kinetic rate. This can be attributed to the simultaneous consumption of reaction products
206 by microorganisms, which can enhance the reaction rate. Also, the acetates produced from CO_2
207 reduction and present in the electrolyte could enhance the overall buffering capacity of the
208 electrolyte. The LSV scans of the biophotocathode under dark and chopped irradiation in Fig.
209 3E confirm a photo-induced electron transfer. The biophotocathodes with close-packed
210 adapted *S. ovata* exhibit over 80% ($n=3$) of faradaic efficiency toward acetate (Supplementary
211 Figs. 5, 6, and Supplementary Table 1). In addition, we confirmed no change in elemental
212 components of the photocathode for the biotic and abiotic conditions after photoelectrolysis
213 using low-energy energy-dispersive X-ray (EDX) analysis (Supplementary Fig. 7).

214

215 As a counter anodic reaction to CO_2RR , GOR was investigated on an n-type SiNW photoanode.
216 GOR has recently gained attention as an efficient photoanodic reaction for PEC devices^{45,46}. It
217 has been reported that Pt-Au is a suitable GOR catalyst because it combines the advantages of
218 the low overpotential of Pt and the high steady state current of Au synergistically²⁴.
219 Photoelectrochemically, co-sputtering Pt and Au on n-type planar Si could yield a very low
220 onset potential of -0.05 V vs. RHE²¹. Also, GOR enables the production of high-value
221 oxidation compounds, such as glyceric acid (GLA), providing an economic benefit⁴⁷. We
222 adopted a nanowire array structure, replacing the planar Si, and a p^+ shell was formed on a
223 fabricated n-type SiNW and protected by 10 nm of ALD TiO_2 . Then, we optimized the loading
224 amount of the Pt-Au catalyst, considering the high surface area of the SiNW array
225 (Supplementary Fig. 8). Fig. 3F shows the LSV scans of Pt-Au/ $\text{TiO}_2/\text{p}^+\text{n-SiNW}$ photoanode
226 for GOR in 1 M KOH and 0.1 M glycerol under red light irradiation. Notably, the photoanode
227 shows a ~ 0.45 V photovoltage shift relative to a dark Pt-Au on a glassy carbon electrode
228 (Supplementary Fig. 9). Furthermore, the high-surface-area photoelectrode enhanced the

229 photocurrent near the onset potential (around 0 V vs. RHE) and offered a better fill factor
230 compared to the planar counterpart (Supplementary Fig. 9). This enhancement could be
231 attributed to the increased loading of Pt-Au catalysts, which improves the photocurrent density
232 in the lower potential region (around 0 V to 0.3 V vs. RHE) where the catalyst amount limits
233 the overall performance. Fig. 3G shows the overlap of the LSV scans between the photocathode
234 and photoanode, revealing an expected bias-free photocurrent density of $\sim 1.2 \text{ mA/cm}^2$.

235

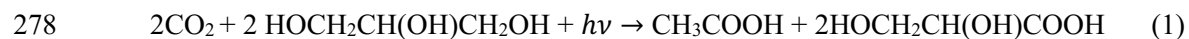
236 **Bias-free operation of SiNW photochemical diodes**

237 For the bias-free PEC setup, the photocathode and photoanode were placed into a two-chamber
238 cell separated by a bipolar membrane (BPM) (Fig. 1D). A utilization of BPM allows to separate
239 two different electrolytes with a significant pH difference⁴⁸. This separation is crucial because
240 GOR is optimal in an alkaline environment with 1 M KOH, whereas microbial CO₂RR operates
241 at a neutral pH of 6.2 in the bacterial medium. The LSV scan of a two-electrode configuration
242 of photocathode and photoanode confirms the bias-free photocurrent density near 1.20 mA/cm^2
243 and the onset potential of -0.8 V (Fig. 4A). The long-term operation and the product analysis
244 of bias-free bioCO₂RR-GOR system are shown in Fig 4B and 4C. The integrated system was
245 able to maintain a photocurrent density of 1.2 mA/cm^2 after 1 hour. The main cathodic product
246 is acetate with a faradaic efficiency (FE) of $86.8 \pm 14.0 \%$. The main anodic product is GLA,
247 with an FE of $38.8 \pm 8.0\%$, and the total anodic product reaches an FE of $79.3 \pm 9.1\%$. The rest
248 likely comes from products that are not analyzable through ¹H NMR, such as tartronic acid
249 and carbonate. The production of glyceraldehyde and dihydroxyacetone was not detected
250 because both of them rearranged into lactic acid (LA) in alkaline conditions, making it hard to
251 differentiate them from the production of LA. The product distribution is similar to previously
252 reported PEC GOR results using the Pt-Au catalyst under similar conditions²¹. The acetate
253 production rate of the system was $44.8 \pm 11.6 \text{ g/m}^2\cdot\text{day}$ and $0.1 \text{ g/L}\cdot\text{day}$, which aligns with

values reported in microbial electrosynthesis (Supplementary Table 2). The bias-free photocurrent density of Pt-Au planar Si photoanode and SiNW biophotocathode was 0.12 ± 0.06 mA/cm², 7.2 times lower than that of SiNW photoanodes and SiNW biophotocathode, which highlights the effectiveness of such nanostructures in the PEC operation (Supplementary Fig. 10). Control experiments under dark indicate almost no photocurrent, less than 0.014 mA/cm², and consequently, negligible product formation, indicating that the products were mainly produced from photosynthesis (Supplementary Fig. 11). The pH changes of the cathodic chamber were analyzed from 6.17 ± 0.03 to 6.75 ± 0.05 . The higher light intensity, e.g., 40 mW/cm² of irradiation, helped to increase the overall operating bias-free photocurrent to 1.6 mA/cm² (Supplementary Fig. 12). However, Su et al. found experimentally and computationally that the higher cathodic current (e.g., 1.5 mA/cm²) kinetically forms a basic pH both in the bulk electrolyte and around the SiNW microenvironment (pH 8.4 and \geq pH 9.3, respectively)³⁷. Similarly, the bulk catholyte was increased to ~ 8.0 after an 8-hour reaction. To further improve the production rate of the system, this local microenvironment issue could potentially be circumvented by adopting a flow system design or electrolyte engineering (see Supplementary Discussion 1 for more details).

Discussion

The bias-free photochemical device simultaneously driving biological CO₂ reduction and glycerol valorization under low-intensity red light was developed. The key to making this device work is using nature's efficient metabolic pathway for CO₂-to-C₂ reduction and replacing oxygen evolution with glycerol oxidation. The artificial photosynthetic reaction follows the overall formula with glyceric acid as an oxygenate product below:



279

280 It is noteworthy that this extended interpretation of biophotochemical diodes, replacing OER
 281 with GOR half-reaction, resembles the fundamental energy conversion principles exhibited by
 282 microorganisms. They can harness chemical energy by oxidizing inorganic sources
 283 (chemoautotrophs) and organic sources (heterotrophs), using these sources as electron donors.
 284 It not only facilitates the efficient conversion of CO_2 into C_{2+} products at high operating current
 285 densities but also enables the simultaneous transformation of organics into value-added
 286 chemicals, all under bias-free irradiated conditions. Supplementary Discussion 2 outlines the
 287 outlook of biophotochemical diodes.

288

289 The meticulously nanofabricated SiNW photoelectrodes can harvest 0.85 V from low-intensity
 290 red light irradiation. The integrated bias-free device coupling CO_2RR and GOR achieves a
 291 maximum of 1.2 mA/cm^2 of photocurrent density with over 80% faradaic efficiencies of C_2
 292 product. The system achieved a high photocurrent density for PEC CO_2 -to- C_2 reduction even
 293 under low light irradiance (Supplementary Table 3). Altogether, the photochemical diode
 294 device presented here provides a promising platform to utilize light energy to simultaneously
 295 convert CO_2 into valuable chemical bonds and upgrade glycerol through the synergistic
 296 combination of the efficient CO_2 -fixing microorganism and the nanomaterials built from earth-
 297 abundant and inexpensive silicon.

298

299

300 **Methods**

301 **Fabrication of p-SiNW and n-SiNW substrates**

302 P-type boron-doped 6" Si wafers (Addison Semiconductor Materials, <100> oriented, 1-30
303 Ohm-cm, prime, double sided-polished) and n-type phosphorus-doped 6" Si wafers (Addison
304 Semiconductor Materials, <100> oriented, 1-10 Ohm-cm, prime, single sided-polished) were
305 used for the fabrication of SiNW array. The wafers were etched in a 4.9% HF bath for 3 minutes,
306 thoroughly washed with DI water, and dried before fabrication processes. Afterward,
307 hexamethyldisilazane was applied on the wafer for 2 minutes, and MiR 701 photoresist was
308 spin-coated to have a thickness of 1 μm . 5x i-line photolithography stepper (GCA 8500) with
309 a mask that is patterned with a square lattice of 3.75 μm circles and 10 μm pitches was used to
310 pattern the wafer with a final photoresist pattern of 0.75 μm circles and 2 μm pitches. The
311 wafer with the patterned photoresist was then developed using MF-26A for 60 seconds,
312 descummed with oxygen plasma at 50 W for 60 seconds, and hard baked at 140 °C using UV
313 light. A low-frequency inductive-coupled plasma deep reaction-ion etch (DRIE) process was
314 employed (Surface Technology Systems Advanced Silicon Etch) to etch the wafer with O₂ and
315 SF₆ as an etch gas and C₄F₈ as a passivation gas and a typical DRIE smooth-wall recipe was
316 used. The etching process was stopped upon nanowire lengths of 21 μm were achieved.
317 Afterward, any remaining photoresist was removed with O₂ plasma at 250 W for 7.5
318 minutes. For details on the nanowire fabrication, see ref. ^{29,30,49}

319 **Fabrication of n⁺p-SiNW and p⁺n-SiNW substrates**

320 A 6" Si wafer was used as a dopant carrier wafer for the doping of the fabricated p-SiNW or
321 n-SiNW substrates. All the wafers were etched in a 4.9% HF bath for 3 minutes to remove
322 native silicon oxides and were thoroughly washed with DI water and dried. The carrier wafer
323 was spin-coated with either an arsenic silicate spin-on-dopant solution (Filmtronics, for n⁺p-

SiNW fabrication) or a gallium silicate spin-on-dopant solution (Filmtronics, for p⁺n-SiNW fabrication) at 2200 rpm for 30 seconds and baked on a hotplate at 150 °C for 30 minutes. Afterward, p-SiNW or n-SiNW array substrates, cleaned with HF, water, and acetone just before this process, were placed onto the carrier wafer upside down such that the nanowire surface is interfaced with the dopant layer. The two were placed into a rapid thermal annealing (RTA) chamber at 900 °C for either 180 seconds (for n⁺p-SiNW fabrication) or 100 seconds (for p⁺n-SiNW fabrication) under N₂. A spin-on-dopant thin film containing a high concentration of arsenic (for n⁺ doping) or gallium (for p⁺ doping) in SiO₂ networks was proximately contacted with SiNW substrates at a high temperature of 900 °C for the diffusion of the dopants. The photovoltage increase was tested on a planar substrate first to exclude the complexity of coherent doping on the nanostructured surfaces of SiNW, and the doping shell gave ~200 mV additional photovoltage for n⁺p photocathode (Supplementary Fig. 3A). The silicon substrate surface should be free of native oxides and vapor molecules to prevent dopant rejections in SiO₂, where the dopants' solubility is much lower than that in silicon. A junction depth, x_j, where the concentrations of shell dopant and substrate dopant, e.g., arsenic and boron for n⁺/p-Si, are equal, can be calculated based on the theoretical Gaussian distribution of dopants:

$$X_j = 2\sqrt{Dt} \operatorname{erfc}^{-1}\left(\frac{N_B}{N_0}\right) \quad (2)$$

where D is a diffusivity of dopant, and t is a diffusion time, N_B is a background concentration, and N₀ is a dopant concentration at the surface. N₀ can be extracted from a theoretical solubility of dopant in silicon at the temperature set for the RTA process. For instance, N₀ of arsenic, an n-type dopant, is 2×10²⁰ at 900 °C, and x_j for the n⁺ layer on p-Si is ~7 nm for 3 minutes at 900 °C of the RTA process.

TiO₂ protection layer deposition

348 The n^+p -SiNW and p^+n -SiNW substrates were cleaned in a 4.9% HF bath for 3 minutes,
349 thoroughly washed with DI water and acetone, and then dried. Afterward, a 30 nm TiO_2 layer
350 was deposited at 250 °C using atomic layer deposition (ALD) and titanium isopropoxide as the
351 precursor (Picosun Atomic Layer Deposition system) for n^+p -SiNW, and a 10 nm ALD TiO_2
352 thin film was deposited at the deposition temperature of 200 °C and
353 tetrakis(dimethylamido)titanium (TDMAT) as a precursor (Cambridge Fiji 200 Plasma ALD
354 system) for p^+n -SiNW in order to maintain a stable device performance for extended operation
355 time. It has been reported that this thin TiO_2 film on Si does not impede the charge transfer
356 from Si to electrolyte and improves the stability of photoelectrodes^{50,51}. Supplementary Fig. 13
357 shows the PEC performance of photoelectrodes with and without ALD TiO_2 . After cooling,
358 these substrates were stored in ambient air until use.

359 **Deposition of Pt-Au and Pt catalyst**

360 Pt-Au and Pt catalyst were deposited on the fabricated TiO_2 /SiNW photoanode on a multi-
361 target co-sputtering system (built in-house) with 3x3" sputter guns (TORUS Mag Keeper)
362 supplied by two 2 kW pulsed DC power supplies and a 1.5 kW DC power supply, as previously
363 reported²¹. After the deposition of the TiO_2 protection layer, around 3 nm of Pt catalyst was
364 sputtered onto n^+p -SiNW substrates with 30 seconds of 50 W power applied on a Pt target. Pt-
365 Au catalyst with a thickness of ~11 nm was co-sputtered onto p^+n -SiNW substrates with 45
366 seconds of 50 W power on a Pt target and 28 W power on a Au target²¹. Both Pt/ n^+p -SiNW
367 and Pt-Au/ p^+n -SiNW substrates were stored in ambient air until use.

368 **Electrode Preparation**

369 For the photoelectrochemical (PEC) experiments, the nanofabricated Pt/ TiO_2 / n^+p -SiNW and
370 Pt-Au/ TiO_2 / p^+n -SiNW substrates were utilized as photoanode and photocathode, respectively,
371 and electrically conductive contacts to a titanium foil were formed. To do this, a Ga-In eutectic

372 was applied and then scratched on the back of the Si substrate. Later on, a quick-drying silver
373 paste was applied on the top of the scratched Si substrate and fixed on the titanium foil using
374 double-sided conductive carbon tapes as previously reported^{17,22}. The electrodes were left to
375 dry for 30 minutes in ambient conditions before being assembled on the cell for PEC
376 chracterization.

377 **PEC characterization**

378 All experiments were performed within a set of custom-built PEC cells. The setup is a two-
379 chamber PEC cell, a cathodic chamber with a working electrode and a reference electrode (CH
380 instruments, Ag/AgCl, 1M KCl) and a Pt wire counter electrode in an anodic chamber. The
381 working electrode is sealed with an X-ring with a contact area of 0.321 cm². A gas inlet and an
382 outlet are embedded to flow CO₂-containing gas for the photocathodic experiments. The two
383 chambers were separated by a bipolar membrane. Each chamber contains a quartz window for
384 PEC experiments. A 740 nm uniform irradiation LED (Mightex Systems) with a power of 20
385 mW/cm² was used for the PEC experiments and calibrated with a certified silicon photodiode.
386 The absorbance spectra of SiNW photocathode, photoanode, and bacteria are shown in
387 Supplementary Fig. 14. The chopped scan group in linear sweep voltammetry was conducted
388 by periodically blocking the optical path of light with a metal plate. During biophotocathodic
389 experiments, the setup was left at the optimal growth temperature of *S. ovata*, which fluctuated
390 between 28 and 30 °C. All the PEC experiments were performed with Gamry Interface
391 1000/600 potentiostats (Gamry Instrument). FE and J were both characterized vs. RHE defined
392 as follows:

$$393 \quad V \text{ vs. RHE (V)} = V \text{ vs. Ag/AgCl} + 0.237 + 0.059 \cdot \text{pH} \quad (3)$$

394

395 The pH of a used electrolyte for an extended operation was often remeasured to get a precise
396 value. For the bias-free operation, the silicon photocathode and photoanode were assembled in
397 the same two-chamber PEC cell with the X-rings. The photocathode was used as a working
398 electrode, the photoanode was used as a counter electrode, and the voltage of the working
399 electrode was set to 0 V versus the counter electrode.

400 **Bacterial strains and growth protocols**

401 Wild-type *S. ovata* (DSM 2662), purchased from the American Type Culture Collection
402 (ATCC), and the methanol-adapted *S. ovata* strain, prepared as detailed in ref.²² and stored in
403 a -80 °C freezer, were used in the experiments. The strains were stored as aliquots with 10%
404 DMSO as a cryoprotectant. ATCC 1425 medium (resazurin omitted; yeast extract added) was
405 used as a standard bacterial growth medium. Anaerobically prepared media, boiled under N₂
406 gas, was stored under ≈80% N₂/20% CO₂ in anaerobic hungate culture tubes (CLS-4208,
407 Chemglass) with flange style butyl rubber stoppers and screw thread caps for heterotrophic
408 cultures, or 18 × 150 mm Balch-type anaerobic culture tubes (CLS-4209, Chemglass) with
409 chlorobutyl rubber stoppers and crimped aluminum seals for autotrophic cultures. To prepare
410 a bacterial cell for experiments, the frozen cells were first revived in betaine medium
411 (Supplementary Table 4) and cultured for two cycles in the betaine medium. *S. ovata* was
412 incubated at 34 °C with a starting pH of 7, measured by a pH strip. The growth of *S. ovata* was
413 monitored by measuring optical absorbance at 545 nm by a Spectrovis Plus Spectrophotometer
414 (Venier). The growth of *S. ovata* typically reaches ~0.4 OD₅₄₅ within two days of cultures in
415 the betaine medium.

416 **Formation of *S. ovata*-nanowire hybrids**

417 The preparation of nanowire-bacteria hybrids were slightly modified from the previous reports
418 using dark electrochemical conditions^{22,37}. The nanowire-bacteria hybrids were prepared on

the SiNW photocathodes with the inorganic medium with 50 mM of MES as an electrolyte and 740 nm irradiation as a photon source. The pH value of the electrolyte was adjusted if needed by adding a corresponding amount of hydrochloric acid or 1M sodium hydroxide into buffer and a digital pH meter (Mettler Toledo) was used to measure the pH by taking out 5 ml of pH-adjusted buffer after 30-minute of equilibration time. The pH-adjusted electrolyte were added to the acid sterilized cathodic (15 ml) and anodic (30ml) chambers, respectively. Abiotic chronoamperometry experiments were conducted typically at ~ 0.3 V vs. RHE for a day with purging 80% N₂/10% H₂/10% CO₂ gas to make anaerobic environment. In parallel, the revived cells in the betaine medium were autotrophically cultured twice in yeast medium (Supplementary Table 4) with 80% H₂/20% CO₂ to adapt them to autotrophic metabolisms. The methanol-adapted *S.ovata* was cultured in the yeast media containing 2% methanol as a sole electron donor before the two hydrogen cycles to upregulate the methanol oxidizing pathways.

The hydrogen-grown *S. ovata* cells were inoculated into the prepared anaerobic cathodic chamber with a final OD₅₄₅ of ~ 0.08 . After the inoculation, the applied electrochemical bias was set at ~ 0.3 V vs. RHE or a potential which gives ~ 100 $\mu\text{A}/\text{cm}^2$. and the inoculated cells were cultured for another day. The purging gas was changed to 80% N₂/20% CO₂ (without H₂), and the applied bias was increased at 0.2 V vs. RHE. The SiNW photocathode served as the sole electron donor after this point. After one-day incubation on the photoelectrode, half of the catholyte was exchanged with a fresh anaerobic electrolyte. This procedure was repeated in one day, and the catholyte became clear (< 0.04 OD₅₄₅) as most of bacterial cells were attached on the SiNWs array or removed during exchange. Then, the stable bacteria-nanowire hybrids were ready for a cathodic half-reaction or bias-free operation.

Cathodic product analysis

Liquid products for CO₂ reduction from the cathode were quantified after electrolysis by proton nuclear magnetic resonance (¹H-NMR) spectroscopy (Bruker Avance I) with 3-(Trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (TMSP-d₄) as an internal standard for quantification. Acetate was the sole detectable product of the CO₂-reducing metabolism of *S. ovata* owing to its highly selective metabolic pathway. 20 vol.% of a D₂O-TMSP standard was added to all the catholyte solutions. The standard solution was prepared by adding 20 mg TMSP to 25 g of D₂O. $FE_{acetate}$ and the incremental mole of acetic acid is calculated based on the following equation:

$$FE_{acetate} = \frac{96485 \times 8 \times \text{incremental mole of acetic acid}}{\int Idt} \quad (3)$$

$$\Delta n_{acetic\ acid} = \alpha \frac{A_{acetate,end}}{A_{TMSP}} \times V_{electrolyte} - \alpha \frac{A_{acetate,start}}{A_{TMSP}} \times (V_{electrolyte} - V_{NMR}) \quad (4)$$

α represents the conversion factor between acetate concentration and the ratio of the NMR peak area of acetate (1.8 ppm) to the NMR peak area of TMSP (0 ppm). The NMR spectrum of catholyte is shown in Supplementary Fig. S5. The factor is determined by the slope of a six-point calibration curve between 0 to 10 mM. $V_{electrolyte}$ is the volume of electrolyte, typically around 15 ml and V_{NMR} is the sampling volume for NMR measurement, typically 0.7 ml. Before starting the reaction, 0.7 ml of electrolyte was sampled, and the fresh electrolyte was subsequently added back to the electrochemical cell to maintain the total volume of electrolyte.

Anodic product analysis

Liquid products for glycerol oxidation from the anode were quantified after electrolysis by ¹H-qNMR spectroscopy (Bruker Avance 600) with water suppression using dimethyl sulfoxide (DMSO) as an internal reference. FE was reported as it is without normalization. A relaxation delay of 42 seconds was used. A standard D₂O-DMSO solution was prepared by adding 400 μ l of DMSO to 100 g of D₂O. A 10 vol.% of D₂O-DMSO standard was added to the analyte solutions. The equation (3) and (4) same as cathodic product analysis were used for anodic

467 product analysis, and the number of electrons used for an electrochemical reaction (e.g., 8 for
468 acetate) was modified depending on the oxidation products.

469 **SEM and EDX characterization.**

470 After the PEC characterizations were complete, the SiNW photoelectrodes were subjected to
471 SEM characterization. For the biophotocathodes, an bacteria fixation was conducted by adding
472 2.5% glutaraldehyde to the catholyte. After ~18 hours, the glutaraldehyde solution was
473 removed and the PEC cell was washed with DI water two times and the PEC cell was
474 disassembled. The prepared biocathode was followed by dehydration process by gradually
475 increasing ethanol concentrations in water (12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5%,
476 100%, for 10 minutes each). For the abiotic photocathodes, the electrolyte was replaced with
477 ethanol to prevent the fingering of nanowires due to a high surface tension of water. Prior to
478 electron imaging, the center of Si electrode was cleaved with a diamond scribe and then
479 sputtered with ~3 nm of Au (Denton Vacuum). Benchtop SEM (JEOL, JCM-7000) was used
480 for visualization of the bacteria-nanowire interface, and field emission SEM (Thermo Fisher
481 Scientific, Scios 2 FIB/SEM) was used for SEM/EDX analysis.

482 **XRD and XPS characterization**

483 Powder X-ray diffraction data were collected using a Bruker D8 laboratory diffractometer with
484 a Cu K α ($\lambda_{K\alpha1} = 1.5406 \text{ \AA}$, $\lambda_{K\alpha2} = 1.54439 \text{ \AA}$) radiation source under ambient conditions. Data
485 were collected at $2\theta = 20\text{--}60^\circ$ with a step size of $0.0158399^\circ \text{ s}^{-1}$.

486 XPS (Thermo Scientific K-Alpha) was used for the characterization of elemental states of ALD
487 TiO₂ film. For XPS measurements, monochromatic Al K α was used with a spot size of 400 μ
488 m and pass energy of 50 eV. Three different spots on a sample were chosen to get a
489 representative measurement of the sample.

490 **EIS characterization**

491 EIS was used to measure the solution resistance of 0.5 M sulfuric acid and the bacterial medium.
492 The EIS measurements were conducted at the open circuit potential (OCP) of the cathodes, and
493 the OCP was measured for 1 minute right before the EIS measurements. The measurements
494 were conducted from 1 kHz to 10 Hz with a 10 mV AC voltage and 10 points per decade. The
495 data analysis was performed with the Gamry Echem Analyst software.

496 **Data availability**

497 The data that support the findings of this study are available within the Article and
498 Supplementary Information or from the corresponding author upon reasonable request.

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509 **Author contributions**

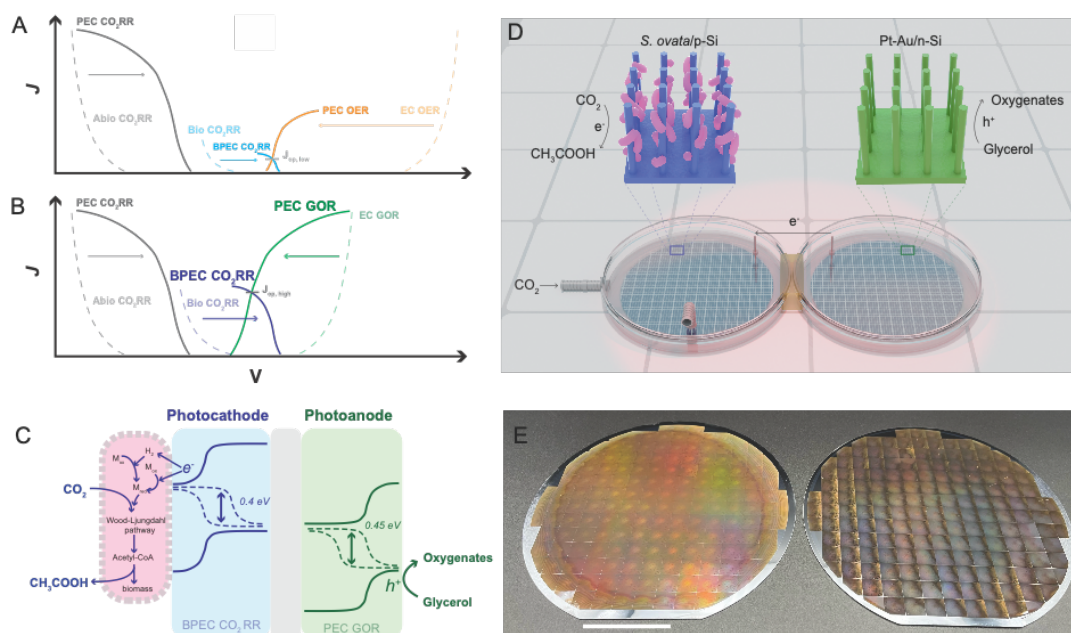
510 Jimin K. and P. Y. designed the experiments. J.-A. L., and I. R. fabricated the silicon nanowire
511 electrodes. Jimin K., and Jinhyun K. performed the bacteria culturing and incubation. Jimin
512 K., J. -A. L, and Jinhyun K. did the electrochemical and light-driven experiments. Jimin K., J

513 -A. L., and P. Y. co-wrote the paper. All authors discussed the results and revised the
514 manuscript.

515 Competing interests

516 Authors declare that they have no competing interests.

517 Figure legends

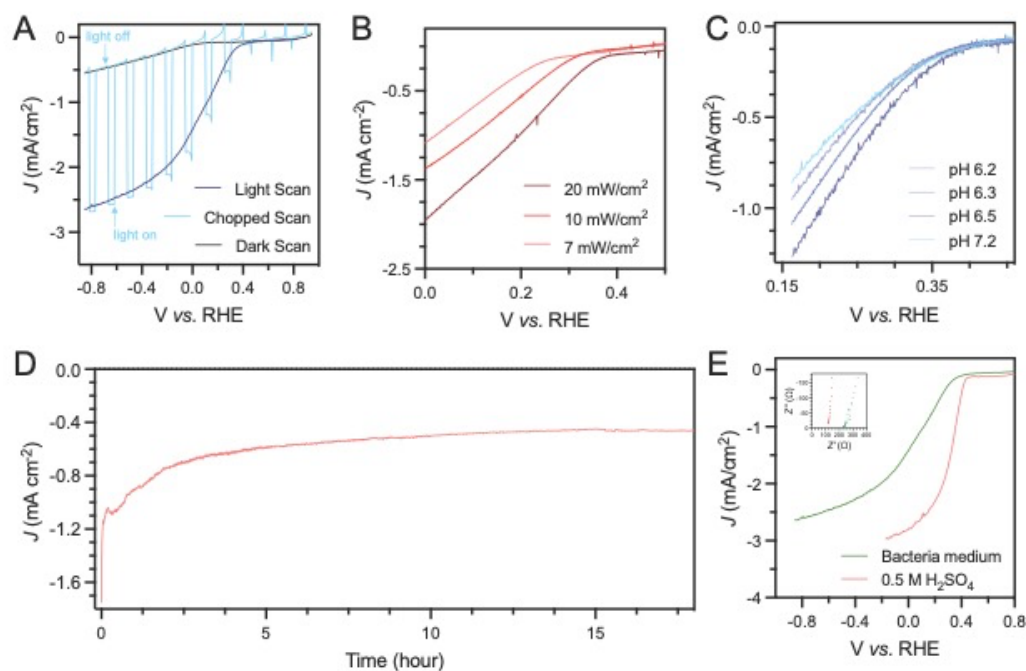


518

519 **Fig. 1. Overview of SiNW biophotochemical diodes for simultaneous CO₂RR and GOR.**

520 (A, B) Schematic current density-voltage curves of electrochemical (EC) and PEC conditions
521 for abiotic CO₂RR (grey), biotic CO₂RR (blue), GOR (green), and OER (orange). Predicted
522 operating photocurrent densities of bias-free systems are shown for PEC bioCO₂RR-OER ($J_{op, low}$)
523 and PEC bioCO₂RR-GOR ($J_{op, high}$). (C) Schematic energy diagram of a photochemical
524 diode under red light irradiation. A photovoltage of 0.4 V was harvested at the photocathode,
525 and a photovoltage of 0.45 V was harvested at the photoanode, coupling CO₂RR and GOR
526 under red light irradiation without an external bias. (D) Schematics of a bias-free
527 photochemical diode device consisting of a photocathode and a photoanode separated by a

528 bipolar membrane under red light irradiation. A magnified illustration of a p-type SiNW
529 biophotocathode (blue) and an n-type SiNW photoanode (green) shows the reaction interface
530 of the two photoelectrodes. *S. ovata* (pink) was used as a cathodic microbial catalyst for CO₂RR,
531 and co-sputtered Pt-Au was used as an anodic catalyst for GOR. **(E)** A photograph of a wafer-
532 scale nanofabricated 6-inch n⁺p-SiNW photocathode (left) and p⁺n-SiNW photoanode (right).
533 Scale bar, 5 cm **(E)**
534



536

537 **Fig. 2. Photoelectrochemistry of abiotic SiNW photocathodes in neutral pH buffer. (A)**538 Photocurrent densities versus bias (vs. RHE) of Pt/TiO₂/n⁺p-SiNW photocathodes under 20539 mW/cm² of 740 nm red light LED irradiation, chopped irradiation (light on/off), and dark

540 condition (B) Photocurrent densities versus bias (vs. RHE) of the SiNW photocathodes under

541 the different intensities of red light irradiation. (C) Photocurrent densities versus bias (vs. RHE)

542 of SiNW photocathodes under the different pH of electrolytes. (D) Current density traces

543 versus time for the SiNW photocathodes using the bacterial medium with pH 6.2 at the applied

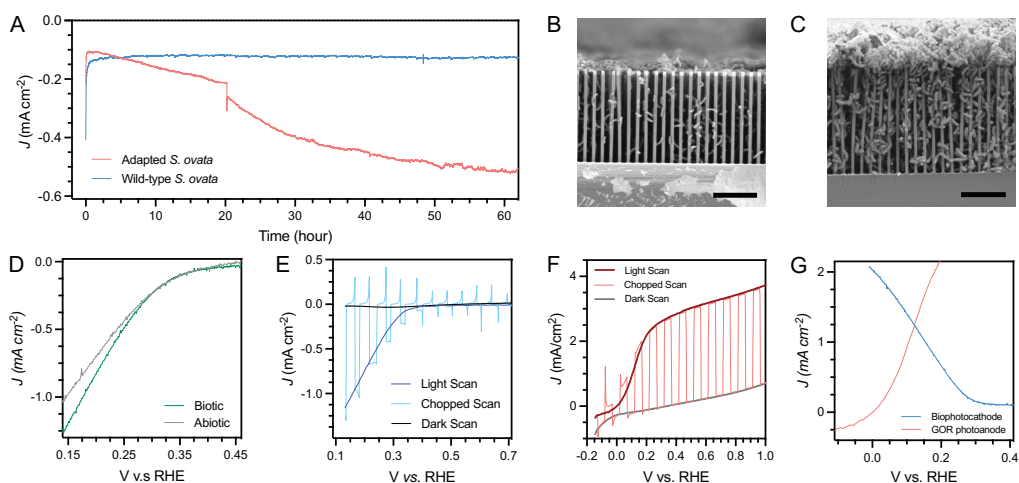
544 potential of 0.15 V vs. RHE. (E) Photocurrent densities versus applied bias (vs. RHE) using

545 0.5 M sulfuric acid (red) and the bacterial medium (green) with the SiNW photocathodes under

546 red light irradiation. The scan rate of all LSV measurements was 10 mV/sec. The catholyte was

547 continuously purged with an 80% N₂/20% CO₂ gas.

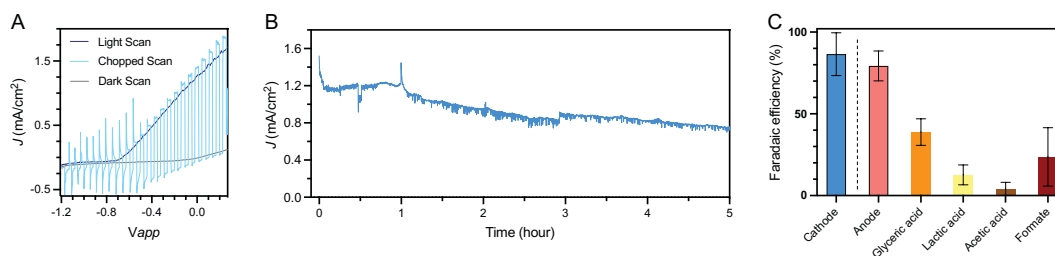
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549

550 **Fig. 3. SiNW biophotocathodes for CO₂RR and SiNW photoanodes for GOR.** (A) Time
 551 evolution of photocurrent densities of SiNW biophotocathodes using wild-type *S. ovata* (blue)
 552 and methanol-adapted *S. ovata* (red) at ~0.2 V vs. RHE. Cross-sectional SEM images of the
 553 biophotocathodes integrated with (B) wild-type *S. ovata* and (C) methanol-adapted *S. ovata*
 554 after ~62 hours of PEC operations. The SEM images shown in B and C are representative of at
 555 least three independent experiments. The scale bars are 10 μ m. (D) Representative
 556 photocurrent densities versus bias (vs. RHE) of SiNW photocathodes with (Biotic, green) and
 557 without (Abiotic, grey) adapted *S. ovata*. (E) Photocurrent densities versus bias (vs. RHE) of
 558 SiNW biophotocathodes with adapted *S. ovata* under continuous irradiation, chopped
 559 irradiation, and dark conditions. (F) Photocurrent densities versus bias (vs. RHE) of GOR using
 560 Pt-Au/TiO₂/p⁺n-SiNW photoanode in 1M KOH + 0.1M glycerol under continuous irradiation,
 561 chopped irradiation, and dark. (G) The overlap of *J-V* scans of the biophotocathode and the
 562 photoanode on an RHE scale. The current density of the biophotocathode was converted from
 563 negative to positive. A 20 mW/cm² of red light (740 nm) was used as a light source. The scan
 564 rate of all LSV measurements was 10 mV/sec. The catholyte was continuously purged with an
 565 80% N₂/20% CO₂ gas.

566



567

568 **Fig. 4. PEC performance of the biophotochemical diodes in a two-electrode**
 569 **configuration.** (A) Photocurrent densities versus applied bias (vs. RHE) of the
 570 biophotochemical diodes combining *S.ovata*/Pt/TiO₂/n⁺p-SiNW and Pt-Au/TiO₂/p⁺n-SiNW
 571 photoanode under continuous irradiation, chopped irradiation, and dark. An applied voltage
 572 of 0 V between two electrodes indicates the bias-free condition. (B) Photocurrent density
 573 traces of the bias-free biophotochemical diodes under continuous red light irradiation. (C)
 574 Faradaic efficiencies of the cathodic product (blue) and the total anodic products (pink) and
 575 each anodic product under the bias-free operation of the biophotochemical diodes. A 20
 576 mW/cm² of red light (740 nm) was used as a light source. The scan rate of all LSV
 577 measurements was 10 mV/sec. The bacterial medium, pH 6.2, was used as the catholyte,
 578 and 0.1M glycerol in 1M KOH was used as the anolyte. The catholyte was continuously
 579 purged with an 80% N₂/20% CO₂ gas. Error bars represent the standard deviation from three
 580 independent measurements.

581

582

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