Supporting Information

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SI Materials and Methods

Commercial Materials. Sodium chloride, magnesium sulfate heptahydrate, ammonium chloride, potassium phosphate monobasic, potassium phosphate dibasic, sodium phosphate monobasic, sodium phosphate dibasic, manganese(II) chloride tetrahydrate, methanol, and pressure-release aluminum crimp seals (20 mm) were purchased from Fisher Scientific. Calcium chloride dihydrate, iron(II) sulfate heptahydrate, nickel(II) chloride hexahydrate, boric acid, cobalt(II) chloride hexahydrate, copper(II) chloride dihydrate, sodium molybdate dihydrate, sodium sulfide, L-cysteine, biotin, folic acid, pyridoxine hydrochloride, thiamine hydrochloride, riboflavin, nicotinic acid, calcium D-(+)-pantothenate, vitamin B_{12}, *p*-aminobenzoic acid, and thioctic acid were purchased from Sigma-Aldrich. Yeast extract was purchased from EMD Biosciences. Casitone (pancreatic digest of casein) was purchased from BD. Zinc sulfate heptahydrate was purchased from Mallinckrodt Chemicals. Thioacetamide was purchased from Alfa Aesar. Resazurin was purchased from Eastman Kodak Company. Balch tubes (18 × 150 mm), anaerobic media bottles (250 mL and 2 L), and butyl rubber stoppers (20 mm) were purchased from Chemglass.

Medium Preparation. ATCC 1043 medium was used as the standard medium for the cultivation of *M. barkeri* ATCC 42431. To prepare the medium, all components (listed below) except iron sulfate, sodium bicarbonate, and reducing agent were dissolved in the appropriate volume of ddH_2O. The solution was brought to a vigorous boil while sparging with an 80% N_2/20% CO_2 gas mixture. Once boiling, iron sulfate and sodium bicarbonate were added and boiling was continued until the solution became a bright pink color. The solution was moved to an ice bath and cooled to room temperature under constant sparging with the above gas mixture. The medium was subsequently transferred to a N_2-degassed serum bottle using a modified Drummond Original Pipet-Aid Pipet Controller with the gas inlet line dispensing an 80% N_2/20% CO_2 gas mixture. The serum bottle was sealed with a butyl rubber stopper and aluminum crimp, and 10 mL reducing agent (see preparation below) were injected per liter of medium using a N_2-flushed syringe. The sealed medium was autoclaved, resulting in a light yellow solution.

A stock of reducing agent was prepared by adding a 0.01% (wt/vol) resazurin solution (200 μL) to ddH_2O (200 mL) and sparging the solution with N_2 for 20 min. Under continuous N_2 flow, L-cysteine (6 g) was added, followed by sodium sulfide nonahydrate (6 g). The N_2 sparge was continued until the sodium sulfide had dissolved and the solution was completely colorless. After preparation, the reducing agent was stored under N_2 atmosphere in a 250-mL serum bottle sealed with a butyl rubber stopper and aluminum crimp.

Per liter, the medium contains:

K_2HPO_4	348 mg
KH_2PO_4	227 mg
NH_4Cl	500 mg
$MgSO_4 \cdot 7H_2O$	500 mg
$CaCl_2 \cdot 2H_2O$	250 mg
NaCl	2.25 g
Yeast extract	2 g
Casitone	2 g
SL-6 trace elements solution	3 mL
Wolfe's vitamin solution	10 mL
Resazurin solution [0.01% (wt/vol)]	1 mL
$FeSO_4 \cdot 7H_2O$	2 mg
$NaHCO_3$	850 mg
Reducing agent	10 mL

Per liter, the SL-6 trace elements solution contains:

$ZnSO_4 \cdot 7H_2O$	100 mg
$MnCl_2 \cdot 4H_2O$	30 mg
H_3BO_3	300 mg
$CoCl_2 \cdot 6H_2O$	200 mg
$CuCl_2 \cdot 2H_2O$	10 mg
$NiCl_2 \cdot 6H_2O$	20 mg
$Na_2MoO_4 \cdot 2H_2O$	30 mg

To prepare a minimal (carbon-free) version of ATCC 1043 medium, yeast extract, casitone, and sodium bicarbonate were omitted from the standard recipe above. The sodium bicarbonate was replaced with a phosphate buffering system composed of $Na_2HPO_4 \cdot 7H_2O$ (4.84 g/L of media) and $NaH_2PO_4 \cdot H_2O$ (1.88 g/L of media). This medium was used for initial electrolysis experiments with Pt. Additionally, a N_2-sparged version of this medium was used for isotopic labeling studies.

Slight modifications were made to the minimal medium used for unassisted photochemical experiments. To prepare the catholyte, yeast extract, casitone, and resazurin were omitted from the standard medium recipe, although trace resazurin was still present from the reducing agent. In addition to sodium bicarbonate, the phosphate buffering system described above was added to increase ionic strength. The same medium was used to prepare the anolyte, except the reducing agent was omitted.

Design of Photo/Electrochemical Cells. Gas evolution experiments were conducted in custom-made two-compartment glass electrochemical cells (Adams and Chittenden Scientific Glass) (Fig. S1). The anode chamber (80 mL) (a) was closed at the top with a GL45 media bottle cap with silicone septum. The cathodic chamber (150 mL) (b) was sealed with a gas-tight lid possessing five distinct ports: (*i*) electrical connection to cathode (c), (*ii*) electrical connection to reference electrode (d), (*iii*) CO_2 line for solution sparging (e), (*iv*) connection to GC for headspace sampling (f), and (*v*) resealable septum for manual gas injection/sampling (g).

Ports d, e, and f on the lid (size Ace #7) were sealed with front-sealing PTFE bushing closures (5846-44) and port c (size Ace #15) was sealed with a rear-sealing PTFE bushing closure (5846-48) (Ace Glass). Port g (size Ace #7) was sealed with a front-sealing nylon bushing closure (5846-04, Ace Glass). Bushings for ports c–f were modified in the following manner: a 1/16-in hole was drilled all of the way through the center of the bushing, and 1/4-in -28 screw threads were drilled in the center, 8 mm deep from the outer side of the bushing. A 4-in-long stainless steel rod (1/16-in o.d.) was inserted through the bushings for ports c and d and further sealed using a 1/16-in Tefzel ferrule and flangeless male nut (P-200 and XP-235X, respectively; Upchurch Scientific) that could be screwed directly into the newly made opening on the bushing. Ports e and f were constructed in a similar manner, but replacing the stainless steel rods with 1/16-in-o.d. PEEK tubing (1531, Upchurch Scientific). The PEEK tubing was connected to Swagelok ball valves (40 series 1/8-in tube fitting; Swagelok) using PEEK unions (P-703, Upchurch Scientific), 1/8-in-o.d. stainless steel tubing, and 1/16-in and 1/8-in Tefzel ferrules and flangeless male nuts (P-300X and P-335X, respectively; Upchurch Scientific). A piece of 1/8-in-o.d. stainless steel tubing was used to connect the ball valve of port f to the stem of a Quick-Connect (SS-QM2-S-200, Swagelok), which could be attached directly to the GC inlet that had been modified with a

Quick-Connect body (SS-QM2-B-200, Swagelok). The bushing for port g was modified as follows: a 1/16-in hole was drilled all of the way through the center of the bushing, and a #8–32 screw thread was drilled in the center, 1/2-in deep from the outer side of the bushing. An 8-mm-diameter Teflon-coated silicone septum (Ace Glass) was placed behind the modified bushing of the manual gas injection port, and a 1/2-in #8–32 sealing socket head cap screw (95198A535, McMaster-Carr) was used to block access to the port when not in use. All electrodes used in the cathodic chamber were entirely contained within the chamber for the duration of the experiment to minimize leaks and were connected to a potentiostat via the stainless steel feed-through rods.

The headspace volume of the cathodic chamber was 100 mL. For electrochemical and photoelectrochemical experiments, the anode and cathode chambers were separated by a cation exchange membrane (Nafion 117, Sigma-Aldrich); for experiments with no externally applied potential, an anion exchange membrane was used (AMV membrane; AGC Engineering Co., Ltd.) to minimize pH changes.

Calculation of Overpotentials for Biological Galvanostatic Experiments. Potentials during galvanostatic experiments were measured with respect to a Ag/AgCl reference electrode that had been externally calibrated to $K_3[Fe(CN)_6]$ in pH 7 phosphate buffer [$E_{1/2}$ = 0.437 V vs. standard hydrogen electrode (SHE)]. Overpotentials were determined from the potentials measured at t = 5 min; we surmise that the decay in applied potential over time does not indicate instability of the catalyst but rather is caused by drift of the Ag/AgCl reference due to sulfide poisoning. Taking into consideration that CO_2-sparged 1043 medium has a pH of 6.5, overpotentials for CO_2 reduction to CH_4 (E = -0.21 V vs. SHE at pH 6.5, 25 °C, 1 atm) were calculated as follows:

$$\eta_{CH4} = -0.21 - (V \text{ vs SHE})_{t=5 \text{ min}}.$$

Headspace Analysis by GC. Headspace samples were analyzed with a multiple gas analyzer 8610C GC system equipped with a Haysep D column (1/8 in × 6 ft) and a 13X Mol Sieve column (1/8 in × 6 ft) (SRI Instruments). All gases were detected with a thermal conductivity detector with Ar as the carrier gas at a setpoint flow rate of 23 mL/min. The oven program was as follows: hold at 35 °C for 7.4 min, ramp to 60 °C (40 °C/min) followed by a hold for 4 min, and ramp to 220 °C (40 °C/min) followed by a hold for 2 min. Events were set as follows: valves 1 and 2 inject at 0.5 min; stop-flow solenoid is on at 3.2 min and off at 8.4 min, valve 1 returns to load at 8.4 min, and valve 2 returns to load at 15.5 min.

Helium (1 mL) was injected into the headspace of each experiment as an inert internal standard; He and H_2 peaks are adequately baseline-separated using the aforementioned method. Representative elution times for gases of interest are as follows: He standard (1.93 min), H_2 (2.16 min), CH_4 (5.98 min), CO_2 (9.31 min).

Headspace samples were introduced onto the GC by first using an evacuated 350-mL Strauss flask to evacuate the GC sample loop (1 mL), and then opening the sample loop to the headspace using the Swagelok ball valve located on the cap of the electrochemical cell. This procedure allowed for direct sampling of the headspace with little oxygen contamination.

Hydrogen and methane were quantified according to calibration curves prepared by injecting known volumes of H_2 and CH_4 into an electrochemical cell prepared identically to those used in gas measurement experiments (Fig. S2). At the start of each set of experiments, one sample of known H_2 and CH_4 concentration was run to ensure that the GC remained properly calibrated.

Calculation of Faradaic Efficiency for Methane. All CH_4 Faradaic efficiency calculations are based on cumulative measured CH_4 (V_T) over the duration of the experiment (3 d or 7 d). For each biological methane production experiment, a corresponding nonelectrolyzed/nonilluminated control with identical electrodes was performed to account for differences in residual methanol (a potential growth substrate) after washing of the culture. The cumulative amount of CH_4 measured in each control experiment is denoted as V_C. Faradaic efficiency (FE) for methane was calculated as follows:

$$\mathbf{FE}_{CH_4} = \frac{\mathbf{V}\mathcal{F}}{125\boldsymbol{Q}\boldsymbol{R}\boldsymbol{T}},$$

where $V = V_T - V_C$ in mL (assumed at 1 atm), $\mathcal{F}$ is Faraday's constant, Q is the charge passed in C, R is the universal gas constant (0.082 L atm K^{-1}·mol^{-1}), and T is the temperature (310 K). Error represents SDs.

Isotopic Quantification by High-Resolution Mass Spectrometry. The high-resolution GC-MS data were collected using an Agilent 7890A chromatograph and an AutoSpec Premier mass spectrometer (Waters) equipped with an electron impact ion source and Masslynx software. For gas chromatography, an HP-5 column (0.0250 mm × 30 m, 0.25-μm film thickness; Agilent) was used. The carrier gas was helium and the oven temperature was maintained at 50 °C. Samples were introduced directly to the column via a splitless manual injection using a 1-mL gas-tight Hamilton syringe (Hamilton Company) that had been flushed with N_2. For methane detection, 500 μL of electrolysis cell headspace was injected onto the instrument. The source temperature of the mass spectrometer was maintained at 150 °C and electron energy was set at 70 eV. For methane detection, the instrument was tuned to 10,000 resolution using the N_2 parent ion (28 m/z) and fragment (14 m/z). Methane was detected using voltage scanning from 8 to 33 m/z with water (18 m/z), an O_2 fragment (16 m/z), or a N_2 fragment (14 m/z) used as reference peaks as appropriate.

Limit of Detection Calculations for Isotopically Labeled Electrolysis Experiments. To determine the limit of detection of the high-resolution GC-MS, successively diluted samples of methane gas were injected onto the instrument until a methane signal could no longer be detected. The last concentration at which a methane peak was detectable was 0.5% (vol/vol). For each isotopically labeled electrolysis experiment, the sample was also analyzed using the SRI Instruments GC (as described above in *Headspace Analysis by GC*) after analyzing the headspace using the high-resolution GC-MS instrument. Using this method, the total volume of methane generated during the 3-d experiment could be quantified. To determine the percent of unlabeled methane potentially present in the system but undetectable by the high-resolution GC-MS, the volume equivalent to 0.5% of the 100-mL electrolysis cell headspace (500 μL) was divided by the total amount of detected methane.

General Characterization Methods for α-NiS. pXRD was performed on a Bruker GADDS Hi-Star D8 diffractometer using Co Kα radiation (1.790 Å). TEM and EDX spectroscopy were performed with a Hitachi TEM using copper grids (Ted Pella). HRTEM was performed with a 200-kV FEI monochromated F20 UT Tecnai instrument. TGA was performed with a TA Instruments Q5000 TGA.

Determination of Ni:S Ratio by ICP-OES. ICP-OES measurements were performed on a Perkin-Elmer Optima 5300 DV instrument with an internal standard containing 50 μg Sc^{3+}/mL. A calibration curve was made using [Ni] ($NiCl_2·6H_2O$) and [S] (H_2SO_4) concentrations of 1 μM, 10 μM, 100 μM, and 1 mM. α-NiS samples were dissolved in concentrated HNO_3 and then diluted to 7% (vol/vol) HNO_3 using ddH_2O. This solution was filtered before analysis using a 0.45-μm PVDF syringe filter (Whatman). The

nickel to sulfur ratio was found to be 0.80, with respective concentrations of 0.144 and 0.180 mM.

RDE Setup. For RDE experiments, a 1-M sodium phosphate buffer, pH 7 (10 mL), was degassed by sparging with N_2 for 15 min. A glassy carbon electrode (A = 0.071 cm^2) was polished before use, then coated with a 3-μL drop of NiS ink (see *Preparation of Pt and α-NiS/C Electrodes* below) and allowed to dry for 20 min in air. The rotation speed was set to 1,500 rpm. The reference electrode was an aqueous Ag/AgCl electrode (3.5 M KCl) purchased from BASi, which was referenced to $K_3[Fe(CN)_6]$ after the experiment. The counter electrode was a Pt wire, which was polished before use.

Preparation of Pt and α-NiS/C Electrodes. Platinum cathodes were fabricated from Pt foil (2.5 cm × 1.7 cm × 0.125–0.135 mm) (Sigma-Aldrich) and connected to stainless steel feed-through rods with Pt wire (Sigma-Aldrich). Before each experiment, Pt cathodes were cleaned by electrooxidation at 0.6 V vs. SHE for 2 min in 1 M HCl, followed by repeated rinsing with ddH_2O.

α-NiS/C cathodes were prepared by deposition of an ink of α-NiS on carbon cloth. α-NiS powder (5 mg) was weighed into a 4-mL sample vial using a microbalance. Ethanol (600 μL), ddH_2O (200 μL), and a solution of 5% (wt/vol) Nafion in aliphatic alcohols (Sigma-Aldrich) (40 μL) were added, and the vial was sonicated for 20–30 min. Meanwhile, Pt wire (0.5-mm diameter, Sigma-Aldrich) was threaded through the top of a 1.5 cm × 4.5-cm strip of carbon cloth (Fuel Cell Earth). This Pt wire was used only as an inert conductive material and was never submersed in electrolyte. α-NiS ink (240 μL) was applied to the bottom 3 cm of carbon cloth and allowed to dry for 2–4 h before use. Because both sides of the Pt and α-NiS/C electrodes are catalytically active, their geometric surface areas are 8.5 cm^2 and 9.0 cm^2, respectively.

Preparation of Silicon Photocathodes. Four-inch planar <100> *p*-silicon wafers (10–30 Ωcm) were cleaned in piranha solution and a 1:10 buffered hydrofluoric acid (HF) etch, followed by rinsing with dH_2O and centrifuge drying at room temperature. Arsenic doping was performed using a rapid temperature annealing (RTA) process. In preparation for this procedure, 6-in silicon handle wafers were spin-coated with arsenic dopant solution at 3,000 rpm for 1 min, followed by baking on a hotplate at 150 °C in air for 30 min. Immediately after cooling, a 6-in handle wafer and freshly cleaned 4-in wafer were placed together such that the arsenic-coated side was in contact with the wafer to be doped. After one or two dummy runs to ensure reliable heating and cooling profiles, the wafers were placed in the RTA chamber (Allwin21 Rapid Thermal Processing System) and purged with Ar for 5 min. Optimal doping conditions were found to vary from batch to batch, so normally 3–4 wafers were prepared using slightly different conditions and their photoactivity was evaluated at a later point. Standard RTA conditions were 900 °C for 3–4 min or 1,000 °C for 60–90 s. Following As doping, atomic layer deposition (ALD) of crystalline TiO_2 was performed to protect the photocathode from corrosion during illumination in neural aqueous media. Immediately preceding ALD, the doped silicon wafer was pretreated with 1:10 buffered HF to remove native oxide. ALD was performed using a home-built setup with $TiCl_4$ and H_2O as precursors; a typical recipe is 600 cycles at 300 °C.

A thin layer (10–20 nm) of nickel–molybdenum alloy was sputtered on top of the TiO_2 layer to act as an HER catalyst. For this step, it is imperative that the Ni–Mo layer not be too thick, as light transmission to the semiconductor may be impeded. Dummy runs were performed in advance to establish a suitable recipe. Rectangles of TiO_2-coated silicon (2.5 × 3 cm^2) were cleaned for 2 min with oxygen plasma to remove organics, then taped to a handle wafer around the edges using Kapton tape (to prevent side deposition, which may shunt the electrode). Sputtering was performed at 50-W dc (Ni target) and 150-W rf (Mo target) for 8 min with the Ni shutter open and the Mo shutter closed.

Electrical contact with the finished piece of silicon was made by first gently scratching a 2 × 2-cm^2 region on the backing of the silicon with a diamond scribe and then applying a thin layer of gallium–indium eutectic (Sigma-Aldrich). A roughly 1 × 1-cm^2 piece of conductive double-sided carbon tape was placed on the short edge of a 2.5 × 6-cm^2 piece of titanium foil (Sigma-Aldrich). Subsequently, a thin layer of silver paste (SPI Supplies) was applied on top of the GaIn eutectic, and the silicon chip was gently pressed onto the carbon sticker and Ti foil. Once dry, epoxy resin (Loctite Hysol 1C) was applied to the front and back of the silicon–titanium assembly, taking care to leave no gaps where water could enter the device. The electrode was allowed to dry at ambient temperature in air for at least 24 h before use. The photoactive geometric surface area of the finished cathodes was 7.0 cm^2. Before use in a biological experiment, the fabricated electrode was soaked in 1043 media for 24 h to remove any soluble fabrication materials that might be toxic to the cells.

Preparation of Indium Phosphide Photocathodes. A 5-nm layer of Zn and a 50-nm layer of Au were sequentially thermally evaporated onto the back side of an InP wafer, which was then subjected to an RTA process (450 °C for 30 min) to fabricate an ohmic contact. The annealing process transforms the Zn–Au layer into a Zn–Au alloy and a fraction of the Zn diffuses into the underlying InP layer, forming a p^+-InP layer. The presence of the Zn–Au alloy layer prevents oxidation of metallic Zn. During this step, the color of the film changes from golden yellow to silver. Next, the wafer was sonicated sequentially in acetone and isopropanol and blown dry with N_2. The wafer was etched in a 1:1 mixture of conc. HCl:conc. H_3PO_4 for 5–10 s, then rinsed with dH_2O water three times and blown dry. Immediately after this step, the sample was placed into the chamber of a home-built ALD and coated with 7–10 nm of amorphous TiO_2 at 150 °C ($TiCl_4$ and H_2O were used as precursors). The TiO_2-passivated wafer was sputtered with a 5-nm layer of Pt to act as an HER catalyst.

An ∼1.5 × 2-cm^2 piece of *p*-InP/Pt wafer was used to fabricate each electrode. A 1 × 1-cm^2 piece of conductive double-sided carbon tape was placed on the short edge of a 2 × 6-cm^2 piece of titanium foil (Sigma-Aldrich). Subsequently, a thin layer of silver paste (SPI Supplies) was applied to the back side of the indium phosphide and gently pressed onto the carbon sticker and Ti foil. Once dry, epoxy resin (Loctite Hysol 1C) was applied to the front and back of the InP/titanium assembly, taking care to leave no gaps where water could enter the device. The electrode was allowed to dry at ambient temperature in air for at least 24 h before use. The photoactive geometric surface area of the finished cathodes was 3.0 cm^2. Before use in a biological experiment, the fabricated electrode was soaked in 1043 media for 24 h to remove any soluble fabrication materials that might be toxic to the cells.

Preparation of Titanium Dioxide Photoanodes. Titanium dioxide nanowires were synthesized via hydrothermal methods according to published procedures (37, 75). A 3 × 4-cm^2 piece of FTO-coated glass was cleaned by sonicating first in acetone and then three times in isopropanol, then blown dry. The freshly cleaned FTO plates were placed in a Teflon-lined autoclave container, conductive side facing down. It was critical to mechanically remove any residual TiO_2 from the walls of the Teflon container by sonicating in dH_2O for at least 2 h, followed by sonication in 6 M HCl for 30 min and multiple rinses with dH_2O. In a typical synthesis, 0.5 mL titanium tetraisopropoxide (Sigma-Aldrich) was injected into 30 mL of 6 M HCl and shaken well before pouring into the Teflon container such that 75% of the FTO substrate was immersed. The assembled autoclave was placed into a preheated oven at 200 °C for 2–2.5 h. To terminate growth, the autoclave was removed from the oven and cooled to room temperature for 3 h before opening.

The coated FTO plates were removed and rinsed with copious dH_2O, then blown dry before being annealed in air (30-min ramp to 450 °C, 30-min anneal, followed by natural cooling). They were subsequently introduced into the chamber of a home-built ALD and coated with 10 nm of amorphous TiO_2 (precursors were $TiCl_4$ and H_2O).

To assemble the electrode, a 0.5 × 2-cm^2 piece of conductive double-sided carbon tape was placed in the region at the top of the anode that was not coated with *n*-TiO_2 nanowires (and hence remained conductive: average resistance should be < 100 Ω). Subsequently, a thin layer of silver paste (SPI Supplies) was applied to the conductive carbon and gently pressed onto a 2 × 4-cm^2 piece of Ti foil. Once dry, epoxy resin (Loctite Hysol 1C) was applied around the junction with the Ti foil, taking care to leave no gaps where water could enter the device. The electrode was allowed to dry at ambient temperature in air for at least 24 h before use. The photoactive geometric surface area of the finished cathodes was 9.0 cm^2.

Details of Photoelectrochemical Setup. Titanium wire (GalliumSource, LLC) and silver paste (SPI Supplies) were used to make an electrical connection between the titanium foil support of the photocathode and the stainless steel feed-through rod of the electrochemical cell. The entire photoactive region of the photocathode was submersed in media and illuminated with a 740-nm LED (Mightex Systems) with an intensity of 20 mW/cm^2. The electrolysis cell was heated to 37 °C in a water bath and stirred at 300 rpm for the duration of the experiment.

Details of Photochemical Setup. The standard electrochemical cell design described above was slightly modified for unassisted photochemical experiments. A 1-in-diameter quartz window was added to the anodic chamber, 180° from the membrane, to prevent initial filtering of the full-spectrum light by glass. The *n*-TiO_2 photoanode was placed in the center of the anodic compartment, and immediately behind it was added a 1-in-diameter 455-nm filter (Edmund Optics), which was necessary to prevent blue light from reaching the culture (70, 71). Instead of Nafion-117, an AMV anion exchange membrane was used (AGC Engineering Co., Ltd.). Titanium wire (GalliumSource, LLC) and silver paste (SPI Supplies) were used to make an electrical connection between the titanium foil support of the photocathode and the stainless steel feed-through rod of the electrochemical cell. A full-spectrum 300-W Xenon arc lamp (Newport Corp.) was used as a light source, with an intensity of 2.2 W/cm^2. The light beam passed first through the *n*-TiO_2 anode, then through the 455-nm filter and the membrane, before finally impinging on the cathode. The photoanode was illuminated with a 1-in-diameter light spot. The entire photoactive region of the photocathode was submersed in media and illuminated.

Photocurrent under illumination was measured with a BASi potentiostat using a standard two-electrode cell setup (reference and counter leads were shorted on the *n*-TiO_2 anode, and working lead was attached to the *p*-InP cathode).

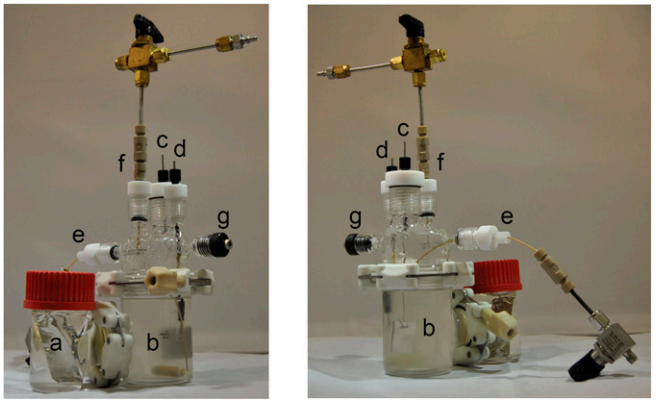


Fig. S1. Electrolysis cell photographs. The electrolysis cell as described above (see *Design of Photo/Electrochemical Cells*) viewed from different angles. Important design features are highlighted: (a) anode chamber with platinum anode visible, (b) cathode chamber with platinum cathode and Ag/AgCl reference electrode visible, (c) electrical connection to cathode, (d) electrical connection to reference electrode, (e) CO_2 line for solution sparging, (f) GC connection for headspace sampling, and (g) resealable septum for manual gas injection/sampling.

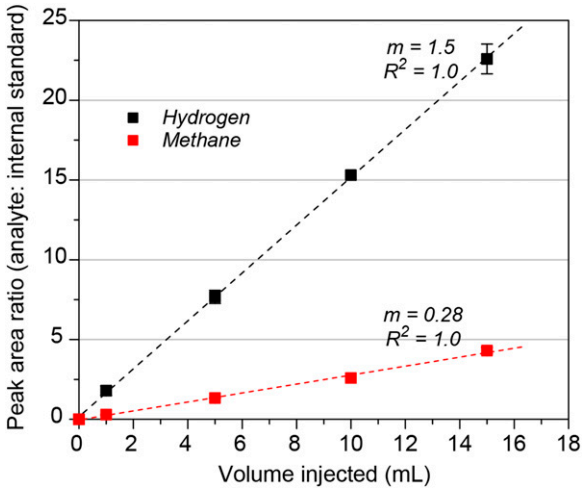
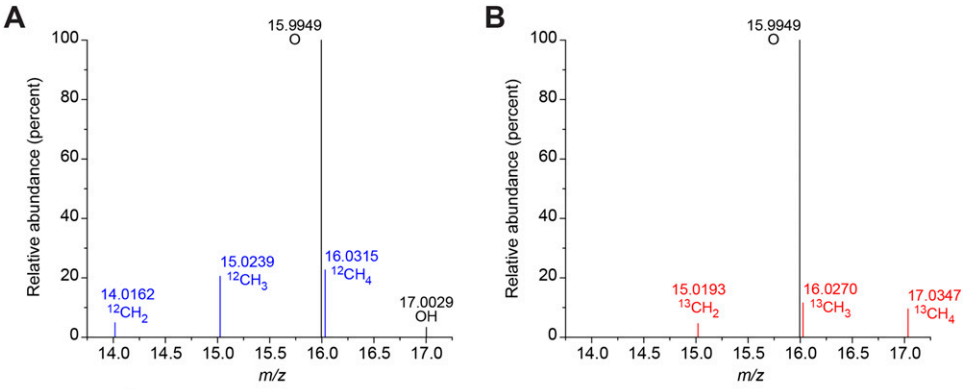


Fig. S2. GC calibration curve for H_2 and CH_4 quantification. Hydrogen and methane calibration curves were generated by injecting known amounts of H_2 and CH_4 into an electrochemical cell prepared identically to those used in gas measurement experiments. Headspace samples were introduced onto a GC by first evacuating the sample loop (1 mL) and subsequently opening it to the electrochemical cell. Peak areas determined by GC are reported as a ratio compared with the He internal standard (1 mL). Data are mean ± SD (n = 3).



C $^{12}CO_2$

m/z	Abundance	Formula
14.0162	4.91	$^{12}CH_2$
15.0239	20.55	$^{12}CH_3$
16.0315	22.70	$^{12}CH_4$

$^{13}CO_2$

m/z	Abundance	Formula
15.0193	4.62	$^{13}CH_2$
16.0270	11.55	$^{13}CH_3$
17.0347	9.57	$^{13}CH_4$

D $^{12}CO_2$

m/z	Abundance	Formula
14.0155	20.53	$^{12}CH_2$
15.0235	96.51	$^{12}CH_3$
16.0313	89.52	$^{12}CH_4$

$^{13}CO_2$

m/z	Abundance	Formula
15.0196	19.25	$^{13}CH_2$
16.0273	100.00	$^{13}CH_3$
17.0347	60.38	$^{13}CH_4$

Fig. S3. High-resolution mass spectra of headspace gases after electrolysis under $^{12}CO_2$ or $^{13}CO_2$ atmospheres. Experimental setup is as described. After setup under N_2 in the specified media, the headspace of the electrolysis cell was replaced with $^{12}CO_2$ or $^{13}CO_2$. He (1 mL) was added as an internal standard for final methane quantification. Each experiment was electrolyzed at 2.5 mA using a platinum cathode and anode. After 3 d, the headspace was analyzed using high-resolution mass spectrometry, with representative mass spectra presented below. (*A*) $^{12}CO_2$ headspace, carbon-free media, (*B*) $^{13}CO_2$ headspace, carbon-free media, (*C*) abundances of parent ions and fragments in carbon-free media, and (*D*) abundances of parent ions and fragments in rich media (see Fig. 2 *E* and *F* for corresponding spectra).

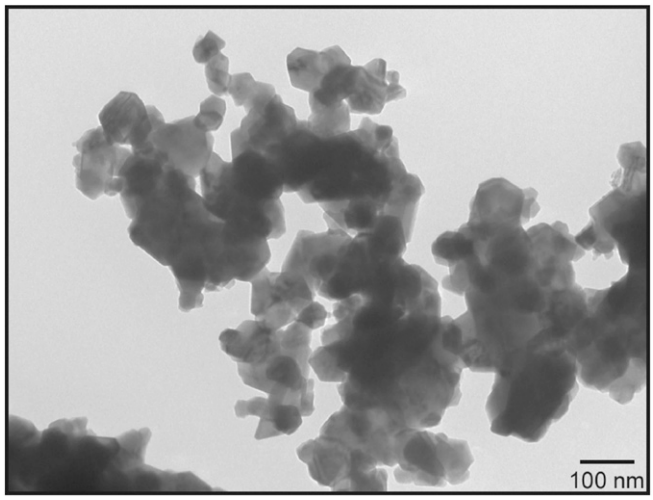


Fig. S4. TEM characterization of α-NiS nanoparticles. TEM image of α-NiS nanoparticles showing polydisperse hexagonal particles 20–100 nm in diameter.

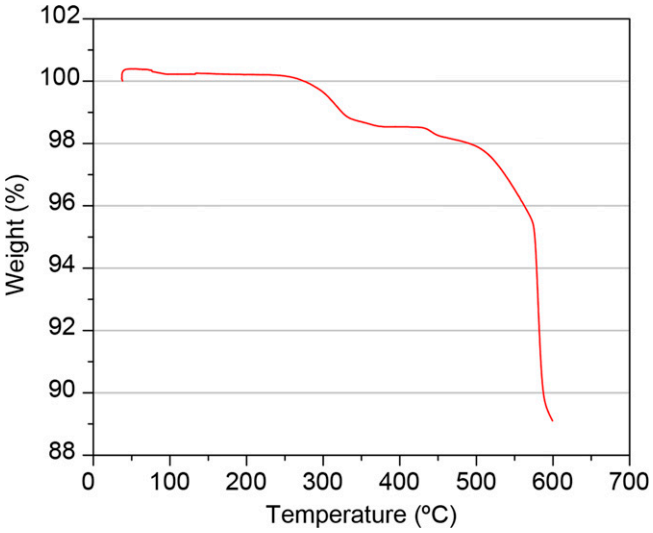


Fig. S5. TGA of α-NiS catalyst. The absence of a significant loss in mass until ~450 °C indicates a lack of surface-bound ligands on the α-NiS nanoparticles. Experiment was performed under an atmosphere of N_2 to prevent sample oxidation.

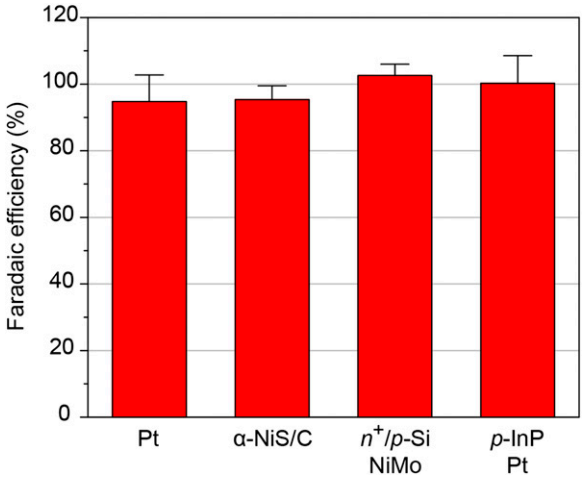


Fig. S6. FEs for H_2 generation for electrolysis, photoassisted electrolysis, and unassisted water splitting with Pt, α-NiS/C, n^+/*p*-Si/NiMo, and *p*-InP/Pt cathodes. Experimental setup is as described, except that no *M. barkeri* was inoculated into the electrolysis cell. A galvanostatic experiment was conducted using Pt, α-NiS/C, or illuminated n^+/*p*-Si/NiMo by passing a current of 2.5 mA for 23 h ($n = 3$ independent experiments). The *p*-InP/Pt cathodes were illuminated at 2.2 W/cm^2 for 1–6 h ($n = 4$ independent experiments). H_2 in the headspace was quantified by GC using He as an internal standard. FEs for H_2 were calculated according to the following equation: $\mathbf{FE}_{H_2} = \mathbf{V}\mathcal{F}/500\mathbf{QRT}$, where V is the volume of H_2 measured in mL (assumed at 1 atm), $\mathcal{F}$ is Faraday's constant, *Q* is charge passed in C, R is the universal gas constant (0.082 L atm K^{-1}·mol^{-1}), and T is the temperature (310 K). Error bars represent SDs.

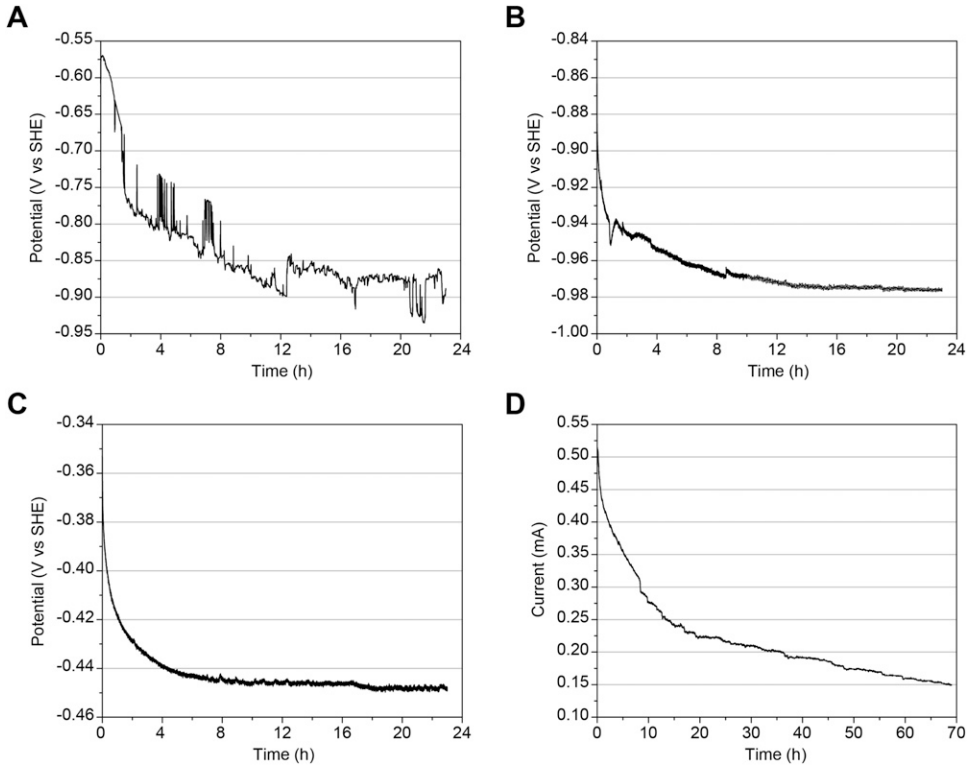


Fig. S7. Representative galvanostatic and potentiostatic traces for (photo)electrochemical and photochemical experiments with a *M. barkeri* culture. For each of the galvanostatic experiments shown above (*A*–*C*), a current of 2.5 mA was passed for 23 h. A standard three-electrode cell setup was used, where the anode is Pt mesh, and the cathode is as listed below. For the potentiostatic experiment (*D*), a two-electrode cell setup was used in which the counter and reference leads were shorted on the illuminated *n*-TiO_2 anode, and the working lead was attached to the illuminated *p*-InP/Pt cathode. The full cell potential was maintained at 0 V for 69 h. (*A*) Pt cathode, (*B*) α-NiS/C cathode, (*C*) n^+/*p*-Si/NiMo cathode illuminated at $\lambda = 740$ nm, and (*D*) *n*-TiO_2 and *p*-InP/Pt linked assembly illuminated with full spectrum and $\lambda > 455$ nm, respectively.

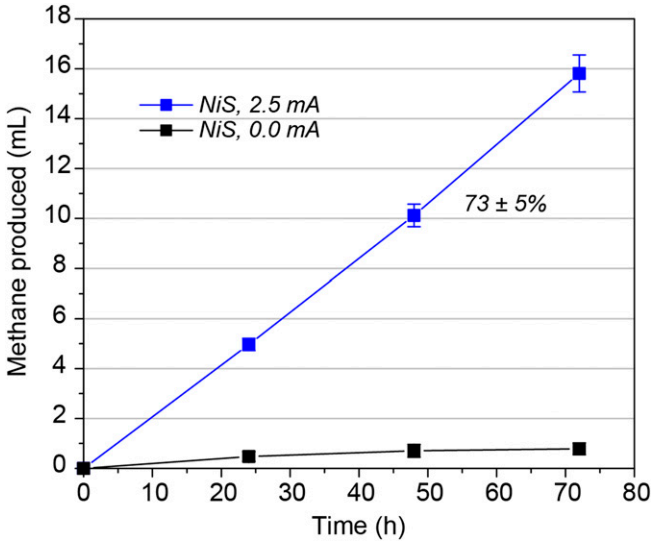


Fig. S8. Galvanostatic experiment (2.5 mA) with α-NiS/C cathode. Experimental setup and electrode preparation is as described. Cumulative methane generation and associated average FE in rich media are shown compared with a nonelectrolyzed control. Error bars represent SD with $n = 3$ independent experiments.

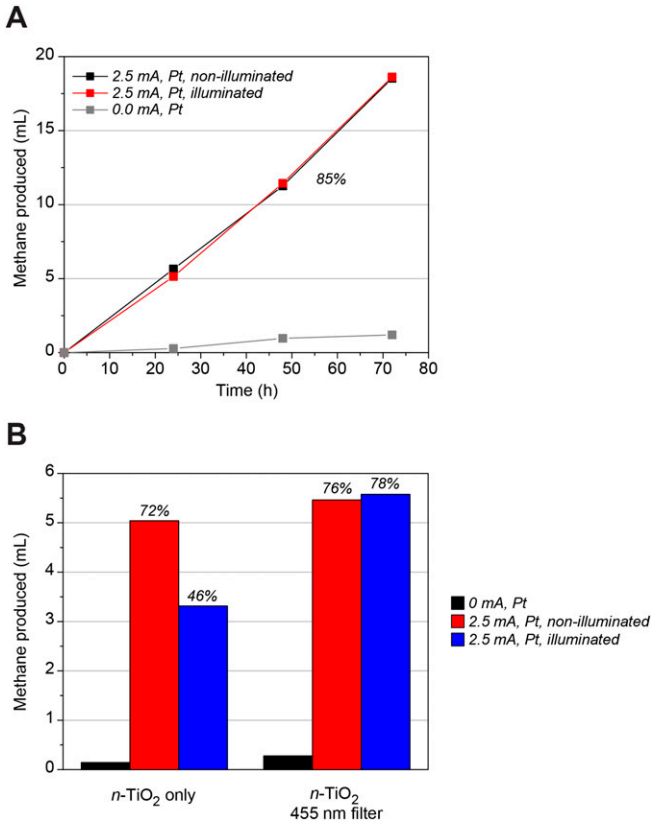


Fig. S9. Evaluation of microbial light toxicity. Experimental setup is as described. (*A*) Illuminated (λ = 740 nm) and nonilluminated galvanostatic electrolyses (2.5 mA, Pt cathode) show comparable methane production, indicating that illumination with this wavelength does not affect methane production over the course of 72 h ($n = 1$). (*B*) Illuminated (full-spectrum light) and nonilluminated galvanostatic electrolyses (2.5 mA, Pt cathode) were performed. When n-TiO_2/FTO was used as the only light filter, a lower than expected FE for methane was observed in the illuminated experiment. Upon addition of a 455-nm filter after the n-TiO_2/FTO, FEs for methane were similar between illuminated and nonilluminated experiments ($n = 1$).

Table S1. Comparison of various first-row transition metal HER catalysts at neutral pH

Catalyst	Onset, mV	η, mV, at 2 mA/cm^2	Tafel slope, mV/dec	j_o, mA/cm^2	Ref.
α-NiS	140	300	111	3.5×10^{-2}	This work
FeS	325	700	150	6.6×10^{-4}	63
Co_9S_8@C	100	190	—	—	65
FeP*	30	60	—	—	58
Ni_3S_2/Ni	180	~180	118	—	66
NiS_2	175	310	69	—	67
Co/P/O film	50	385	140	3.0×10^{-2}	57
Co–S film	43	83	93	0.256	62
Ni–S film	170	260	77	—	64

FEs for H_2 are quantitative in all cases. All values are reported at pH 7 unless otherwise noted.
*Values are reported at pH 6.5.