Self-Biased Solar-Microbial Device for Sustainable Hydrogen Generation

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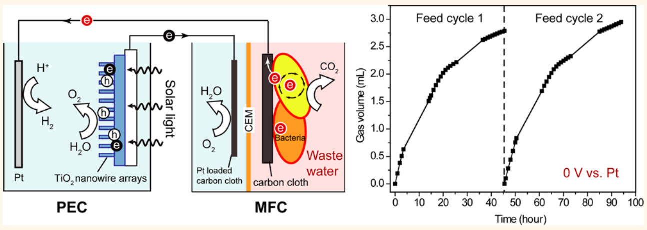
ABSTRACT Here we demonstrate the feasibility of continuous, self-sustained hydrogen gas production based solely on solar light and biomass (wastewater) recycling, by coupling solar water splitting and microbial electrohydrogenesis in a photoelectrochemical cell—microbial fuel cell (PEC-MFC) hybrid device. The PEC device is composed of a TiO_2 nanowire-arrayed photoanode and a Pt cathode. The MFC is an air cathode dual-chamber device, inoculated with either *Shewanella oneidensis* MR-1 (batch-fed on artificial growth medium) or natural microbial communities (batch-fed on local municipal wastewater). Under light illumination, the TiO_2 photoanode provided a photovoltage of ∼0.7 V that shifted the potential of the MFC bioanode to overcome the potential barrier for microbial electrohydrogenesis. As a result, under light illumination (AM 1.5G, 100 mW/cm^2) without external bias, and using wastewater as the energy source, we observed pronounced current generation as well as continuous production of hydrogen gas. The successful demonstration of such a self-biased, sustainable microbial device for hydrogen generation could provide a new solution that can simultaneously address the need of wastewater treatment and the increasing demand for clean energy.



KEYWORDS: microbial fuel cell · photoelectrochemical · hybrid · self-biased · sustainable hydrogen generation

With the drastic increase of human population, there is an ever-growing demand for energy and clean water for the continuous economic growth and suitable inhabitation on earth. Millions of tons of wastewater is produced from industrial and agricultural operations each year, and about 25 billion U.S. dollars are spent annually for wastewater treatment in the United States alone.[1] It is highly desirable to employ energy-efficient processes for wastewater treatment and simultaneously recover the energy contained as organic matter in wastewater. This can be achieved by microbial fuel cell (MFC) technology. MFCs are bioelectrochemical devices where electrogenic bacteria are used to oxidize the organic matter, transfer the electrons to an electrode. and generate electrical energy.[2−5] In addition to bioelectricity, the electrons produced by the microorganisms can also be used to produce various chemical fuels, depending on the electron acceptors used in the catholyte.[6,7] When protons serve as terminal electron acceptors, hydrogen gas will be produced at the cathode. While the microbial electrohydrogenesis process has been experimentally demonstrated using a wide range of microorganisms with various organic nutrients, thermodynamics constraints limit microbial electrogenesis and hydrogen production occurs simultaneously without the addition of an external bias.[8] To overcome the thermodynamic constraints and to compensate for the energy loss during the operation (*e.g.*, due to electrical resistance of the device), an external bias of 0.2 to 1.0 V is usually supplied to sustain the current/hydrogen generation.[9] Nevertheless, the requirement of external bias adds to the complexity and cost for hydrogen production, making it less attractive as a cost-effective energy solution. Considerable efforts have been made to minimize the energy loss through the optimization of MFC reactors,[10,11] electrodes,[12−15] as well as the type of metal catalysts on the cathode.[16,17] It has also been reported that microbial electrohydrogenesis can be driven by a solar cell or another MFC.[18−20] Recently, we also reported a solar-driven

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Received for review June 18, 2013 and accepted September 11, 2013.

10.1021/nn403082m

microbial photoelectrochemical cell that produces bioelectricity at zero external potential by integrating an electricigen-colonizing anode with a Cu_2O nanowire-arrayed cathode.[21] Lu *et al.* also demonstrated a light fuel cell device with rutile TiO_2 as cathode.[22] These microbial photoelectrochemical cells can open up many opportunities for microbial fuel cell technology because they combine respective advantages of semiconductor and microbial systems. Here we further extended this general concept to a hybrid device by interfacing a PEC device and an MFC device (denoted as PEC-MFC), which can generate hydrogen gas at zero external bias using biodegradable organic matter and solar light as the only energy sources.

RESULTS AND DISCUSSION

The configuration of the PEC-MFC device is illustrated in Figure 1a. The device is composed of a single-chamber PEC and an air cathode dual-chamber MFC. The MFC has an anode and a cathode chamber that was separated by a cation exchange membrane (CEM). Plain and Pt-loaded carbon cloth was used as anode and cathode electrodes in the MFC, respectively. The MFC was inoculated with either *Shewanella oneidensis* MR-1 or endogenous microorganisms from the municipal wastewater. PEC consists of an n-type TiO_2 nanowire-arrayed photoanode and a Pt counter electrode, filled with 0.5 M Na_2SO_4 aqueous solution as electrolyte. The MFC bioanode was connected to the PEC Pt electrode, while the MFC cathode was connected to the PEC TiO_2 photoanode. Upon light illumination, photoexcited electron−hole pairs are created at the TiO_2 photoanode and subsequently separated by the electric field at the anode/electrolyte interface. The holes stay at the surfaces of TiO_2 nanowires and oxidize water into oxygen. The electrons flow through the external circuit to the MFC cathode, where they reduce the dissolved oxygen in the MFC catholyte to water. Meanwhile, the electrogenic bacteria in the MFC oxidize the organic matter and produce bioelectrons, which are then transferred to the Pt counter of the PEC and reduce protons to hydrogen gas. Figure 1b shows the simplified energy diagram of the PEC-MFC device and the electron transfer pathway. Note the photovoltage generated by the TiO_2 photoanode shift the electrochemical potentials of MFC electrodes to a more negative value, so that the electrons generated at the MFC bioanode can reduce protons in the PEC chamber. Distinct from a conventional PEC that uses photoexcited electrons to produce hydrogen, the hydrogen production in the PEC-MFC device is sustained by the microbe-producing electrons. Our design aims to incorporate solar energy to boost the reduction capability of the bioanode, so that microbial electrohydrogenesis can be realized at zero external bias.

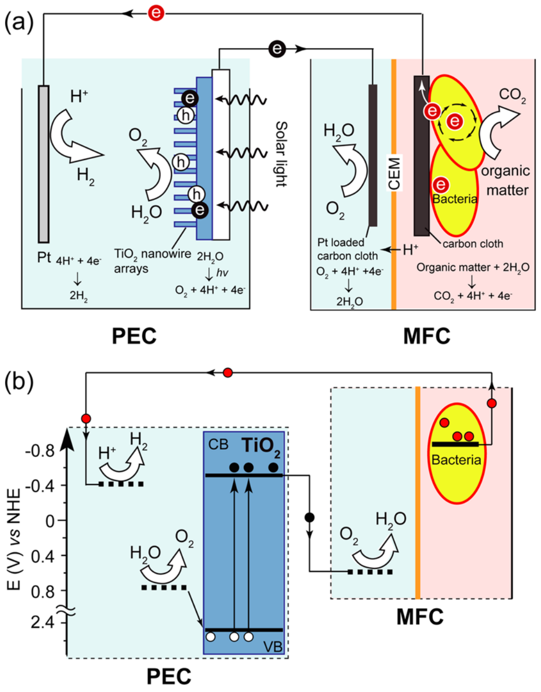

Figure 1. (a) Schematic configuration of a PEC-MFC device. (b) Corresponding energy diagram illustrates the carrier generation and transfer in this hybrid device. CB and VB are respective initials for conduction band and valence band. Solid and empty dots represent electrons and holes, respectively. Black and red dots highlight the electrons generated from TiO_2 photoanode and bacteria, respectively. Dashed lines represent the H^+/H_2, H_2O/O_2, and O_2/H_2O potentials *vs* NHE at pH 7.0.

We assembled and tested the PEC and MFC devices separately before integrating them into the hybrid device. For the PEC device, we used TiO_2 nanowires as the photoanode material because it is a preferred electrode material for PEC water oxidation,[23−27] due to its favorable band-edge positions, excellent chemical stability, and low cost. In addition, its one-dimensional structure provides an extremely large surface area for PEC water oxidation. Dense and vertically aligned TiO_2 nanowire arrays were grown on a fluorine-doped tin oxide (FTO)-coated glass substrate by hydrothermal synthesis (Experimental Method, Supporting Information).[28] Scanning electron microscopy (SEM) images collected from the growth substrate revealed a high-density growth of TiO_2 nanowire arrays (Figure 2a). The nanowires have an average diameter of 100−200 nm and an average length of 2−3 μm. X-ray diffraction (XRD) data collected from TiO_2 nanowire film can be indexed to the characteristic peaks of tetragonal rutile TiO_2 (JCPDS, No. 88-1175) (Figure S1, Supporting Information). PEC performance of the TiO_2 nanowire films was measured in a 0.5 M Na_2SO_4 aqueous solution (pH 7.0) in a two-electrode configuration using an electrochemical station coupled with a solar simulator with a Pt wire as the counter electrode (Supporting Information). As shown in Figure 2b, the TiO_2 nanowire

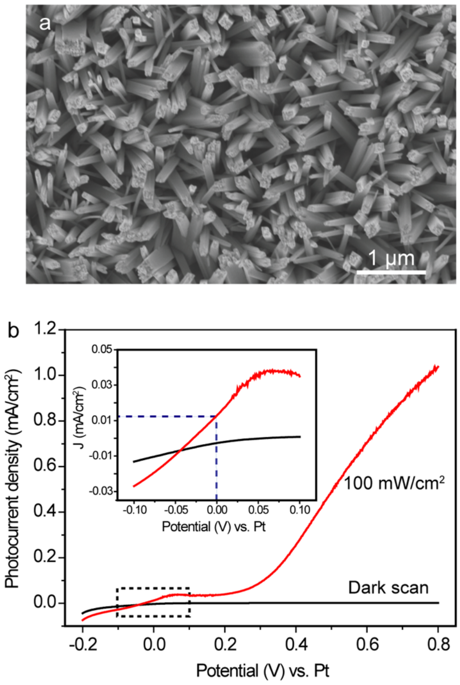

Figure 2. (a) SEM image of TiO_2 nanowire arrays grown on a FTO substrate. (b) Linear sweep voltammogram collected for TiO_2 nanowire-arrayed photoanode in a 0.5 M Na_2SO_4 aqueous solution in the dark and under illumination (150 W xenon lamp coupled with AM 1.5G filter, 100 mW/cm^2), at a scan rate of 20 mV/s. Inset: Magnified linear sweep voltammogram around zero bias.

photoanode showed pronounced photoresponse under 1 sun illumination (AM 1.5G, 100 mW/cm^2). At zero external bias (0 V *vs* Pt), the PEC device yielded a photocurrent density of 0.013 mA/cm^2. Gas bubbles were not observed at either electrode due to the low photocurrent.

For proof of concept, we fabricated several types of MFCs which were then assembled into the PEC-MFC device. We started with a 30 mL ferricyanide cathode dual-chamber MFC, which was inoculated with a pure strain of *Shewanella oneidensis* MR-1 (ATCC 700550) grown in trypticase soy broth (TSB, BD Biosciences, San Jose, CA). Buffered ferricyanide was supplied as catholyte. This MFC generated an open circuit voltage between 0.60 and 0.75 V. To monitor current generation, the MFCs were connected to a 1 K ohm external load and operated in a batch mode (Figure S2 and Experimental Method, Supporting Information). In each feeding cycle, a current of 0.1−0.6 mA was generated, which lasted for *ca.* 20 h before decreasing to the baseline (Figure S2, Supporting Information). Replenishment of fresh TSB medium led to a drastic current restoration, and bioelectricity generation was sustained for another 20 h. Polarization and power characterization revealed that these MFCs worked in the ohmic region and generated a peak power of 50 μW at a current of 0.3 mA (Figure 3a). SEM images of the bioanode after a few days of operation revealed that MR-1 cells grew on the carbon cloth electrode (Figure 3b).

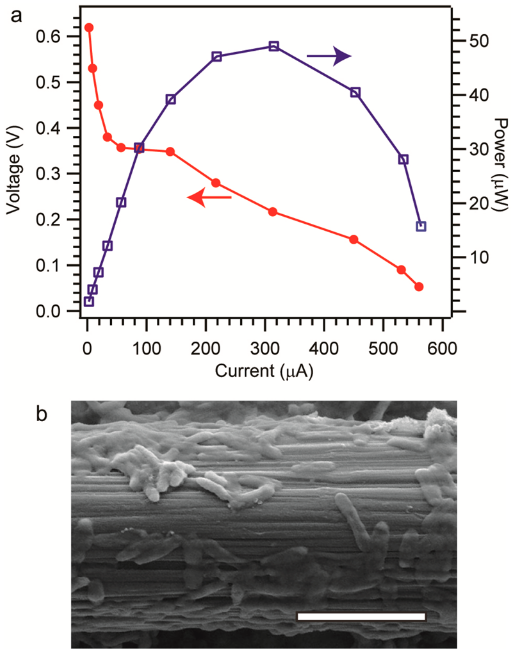

Figure 3. (a) Polarization (red symbol) and power (blue symbol) curves collected from a typical ferricyanide cathode MFC device inoculated with MR-1. (b) SEM image of a carbon cloth electrode colonized by MR-1. Scale bar is 5 μm.

To validate the concept of a PEC-MFC device, we interfaced the MFC with the PEC device by connecting the MFC bioanode to the PEC Pt cathode and the MFC cathode to the PEC TiO_2 photoanode (light projected area of 1.5−2.0 cm^2), respectively (Figure 1a). Figure 4a shows the linear sweep voltammograms collected from a representative PEC-MFC device in the dark and under 1 sun illumination. Significantly, the PEC-MFC device exhibited a remarkable current density of ~1.25 mA/cm^2 at zero bias (0 V *vs* Pt), which is substantially larger than the value of 0.013 mA/cm^2 obtained for the PEC alone at the same potential. Figure 4b shows the amperometric *I*−*t* curves recorded for the PEC and PEC-MFC devices at 0 V *versus* Pt with light on/off cycles. The current spikes occurred when the light was turned on, and then a steady-state current was obtained after several seconds of settling. This transient effect during power excitation could be due to the inefficient charge separation and transfer at the interface between the TiO_2 electrode and the electrolyte at zero bias.[29] Significantly, the PEC-MFC device showed reproducible photocurrent generation in response to light illumination. There was no obvious current drop within 600 s. These results suggest that the PEC-boosted microbial electrohydrogenesis was feasible and efficient. By coupling the MFC and PEC devices in series, the illuminated TiO_2 photoanode provided a photovoltage that shifted the potential of the MFC bioanode to a more negative value, and therefore, microbial electrohydrogenesis can occur at

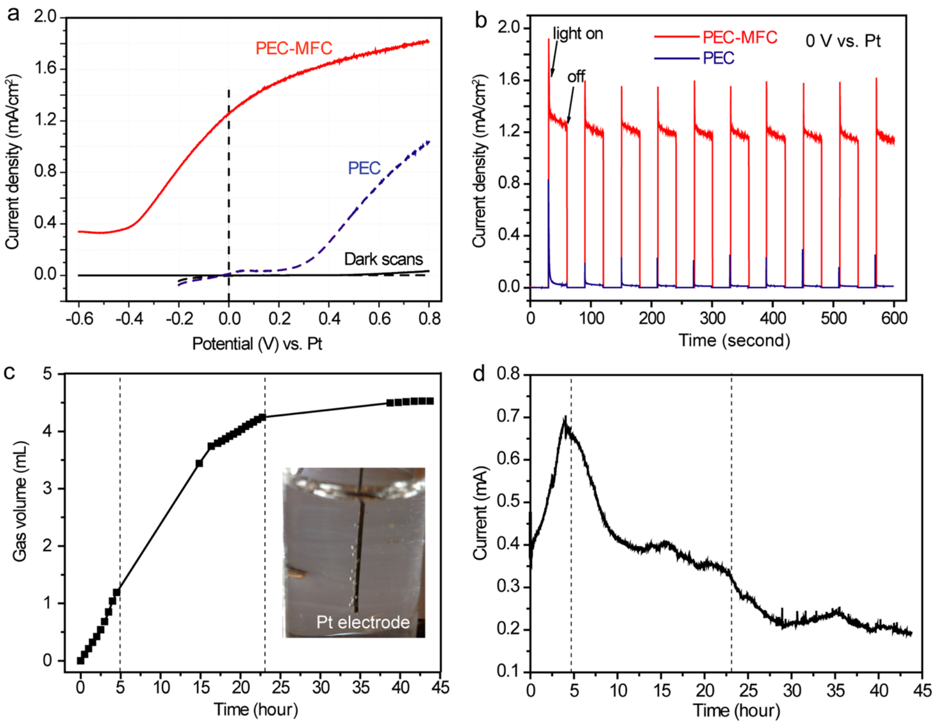

Figure 4. (a) Linear sweep voltammograms collected from a PEC device (blue line) and a PEC-MFC device (red line), at a scan rate of 20 mV/s in the dark (black lines) and under white light illumination (AM 1.5G, 100 mW/cm^2). The MFC device consists of a MR-1 colonized bioanode inoculated in TSB growth medium (anolyte) and a carbon cloth cathode with ferricyanide solution as catholyte. The PEC consists of a TiO_2 nanowire-arrayed photoanode and Pt wire as counter electrode in Na_2SO_4 electrolyte. (b) Amperometric *I*−*t* curves recorded for the PEC-MFC device (red line) and the PEC device (blue line) at 0 V *vs* Pt, with light on−off cycles. (c) Plot of gas production of the PEC-MFC device as a function of time, at 0 V *vs* Pt in 0.5 M Na_2SO_4 electrolyte. Inset: Digital image showing gas bubbles evolving from the Pt electrode during operation. (d) Corresponding current−time profile obtained for the PEC-MFC device during gas collection.

zero external bias (bioelectrons reduce protons to hydrogen gas). In other words, the MFC device served as a battery, which provided extra voltage for PEC hydrogen generation and shifted the entire current−voltage (*I*−*V*) curve to a more negative potential. The potential shift was measured to be around 0.7 V by comparing the onset potentials observed in *I*−*V* curves collected from the PEC and PEC-MFC devices. The solar-to-hydrogen (STH) conversion efficiency (η) of the PEC-MFC device can be calculated using the equation

$$\eta = I(1.23 - V)/J_{\mathrm{light}}$$

where 1.23 V is the theoretical potential for water splitting, *V* is the potential between the photoanode and Pt cathode, *I* is the photocurrent density at the measured potential, and J_{light} is the irradiance intensity of 100 mW/cm^2 (AM 1.5G). This hybrid device exhibits a STH conversion efficiency of 1.54% at 0 V *versus* Pt. Considering the fact that the theoretical STH efficiency of rutile TiO_2 is 2.3% under 1 sun illumination, given a band gap energy of 3.0 eV, we believe that the integration of PEC and MFC devices has enabled a high photoconversion efficiency of the TiO_2 electrode. More importantly, gas bubbles were observed to be continuously evolving on both the Pt electrode and TiO_2 photoanode under light illumination (Figure 4c, inset), indicative of hydrogen and oxygen generation. The gas bubbles were collected from the PEC device by a syringe and analyzed by gas chromatography, confirming the presence of H_2 (Figure S3, Supporting Information). We were not able to quantify the H_2/O_2 ratio due to the limitation of the instruments. Figure 4c, d shows the plots of gas volume produced (mixture of H_2 and O_2) and current (0 V *vs* Pt) as a function of time, respectively. Within the initial 5 h, the gas volume increased rapidly with the increase of the PEC-MFC device current; the gas production slowed when the current started to decline at later time points, due to the decreased activity of microorganisms as a result of depletion of nutrient in anolyte. After 45 h, the current decreased to baseline and the gas production ceased. On the basis of these results, we unambiguously demonstrated hydrogen generation from a self-biased, PEC-MFC device.

For practical applications, the sustainability of self-biased PEC-MFC devices is equally important to their electrochemical performance. While ferricyanide solution is an excellent catholyte for MFC devices, it is not renewable in practice and its production and use may cause environmental issues. Alternatively, oxygen can be used as an electron acceptor, which has been

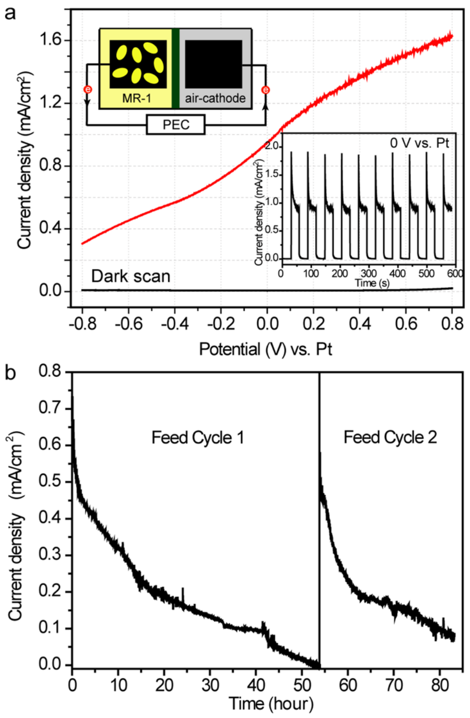

Figure 5. (a) Linear sweep voltammograms collected from a PEC-MFC device with air cathode and with S. oneidensis MR-1 in TSB medium, at a scan rate of 20 mV/s in the dark and under white light illumination of 100 mW/cm^2. Insets: Schematic diagram of the PEC-MFC device and the corresponding amperometric *I*−*t* curve recorded for the PEC-MFC device at 0 V *vs* Pt with light on−off cycles. (b) Current density *vs* time plot collected for the MFC-PEC device, operated in a batch-fed mode at 0 V *vs* Pt under the light illumination of 100 mW/cm^2.

demonstrated in a variety of air cathode MFCs.[30,31] Using an air cathode MFC eliminates the need for chemicals (*e.g.*, ferricyanide) and, therefore, can increase sustainability, reduce cost, and minimize the environmental impact of MFCs. To fabricate air cathode MFCs, we employed Pt nanoparticle-decorated carbon cloth (electrode 40% of Pt on carbon cloth, 0.5 mg/cm^2, Fuel Cell Earth, LLC, Stoneham, MA) as cathode to increase the efficiency of oxygen reduction (Figure S4, Supporting Information). The MFC was inoculated with MR-1 cells and fed with TSB medium. Linear sweep voltammograms were collected for the air cathode PEC-MFC device in the dark and under 1 sun illumination (Figure 5a). In comparison to the PEC-MFC device with ferricyanide solution as catholyte, the air cathode device exhibited slightly lower current density at the same potential. Although oxygen reduction should be more thermodynamically favorable (reduction potential 0.8 V *vs* NHE at pH 7.0) than the reduction of ferricyanide (0.4 V *vs* NHE at pH 7.0), the low concentration of dissolved oxygen and low oxygen mass transfer in water limit the rate of oxygen reduction and, thereby, the current density. The current generation was recorded as a function of time for an air cathode PEC-MFC device operated in a batch-fed mode at 0 V *versus* Pt under light illumination. Figure 5b shows the continuous current generation from the PEC-MFC device in two consecutive feeding cycles (under light illumination), which lasted for more than 80 h. The current decreased gradually due to the depletion of nutrients in the MFC, and the replenishment of fresh TSB medium led to current restoration. These results indicate that the overall current generation is determined by the MFC performance, which varies depending on the microbial activities of the bioanode. Importantly, the sustainability measurements indicate that the PEC-MFC device has the potential to be operated on a long time scale with continuous supply of organic substrates and light illumination.

On the basis of the success of the proof-of-concept device, we took a further step to replace the MFC anolyte of *S. oneidensis* MR-1 artificial growth medium with municipal wastewater collected from the Livermore Water Reclamation Plant (Livermore, California, USA) that contains mixed microbial populations of anaerobic and aerobic sludge. A mixture of anaerobic and aerobic sludge at 1:1 volume ratio was used to inoculate the air cathode MFC. Linear sweep voltammograms were collected from the air cathode PEC-MFC device fed with wastewater in the dark and under light illumination of 100 mW/cm^2 (Figure 6a). Significantly, the device also showed pronounced current at 0 V *versus* Pt, indicative of an efficient supply of bioelectrons from the wastewater MFC (Figure 6b). By using wastewater as anolyte, the PEC-MFC showed reduced current in comparison to the device with MR-1 in the TSB anolyte, at the same potential, which could be attributed to the relatively large electrolyte resistance (low conductivity) of the wastewater.[32] More importantly, we observed continuous evolution of H_2 bubbles from the Pt electrode at 0 V *versus* Pt under light illumination. Figure 6c,d shows the plot of gas production and current of a PEC-MFC device as a function of time. In each feeding cycle, the device started with a high initial gas generation rate and then decreased with the decease of current, as a result of depletion of nutrient in the wastewater of the MFC device. The replenishment of wastewater led to a complete restoration of current generation and gas production. These results proved that the PEC-MFC hybrid device is sustainable with the continuous supply of sunlight and wastewater. Moreover, the municipal wastewater has a measured soluble chemical oxygen demand (SCOD) of 500−600 mg/L. After the device operated for ∼48 h, the SCOD value decreased to ∼200 mg/L. This yielded a Coulombic efficiency of 64%, which is comparable to that of previously reported wastewater MFCs with Coulombic efficiency ranging from 40 to 90%.[33] Taken together, we demonstrate the nonbiased and sustainable microbial electrohydrogenesis process by coupling MFC and PEC

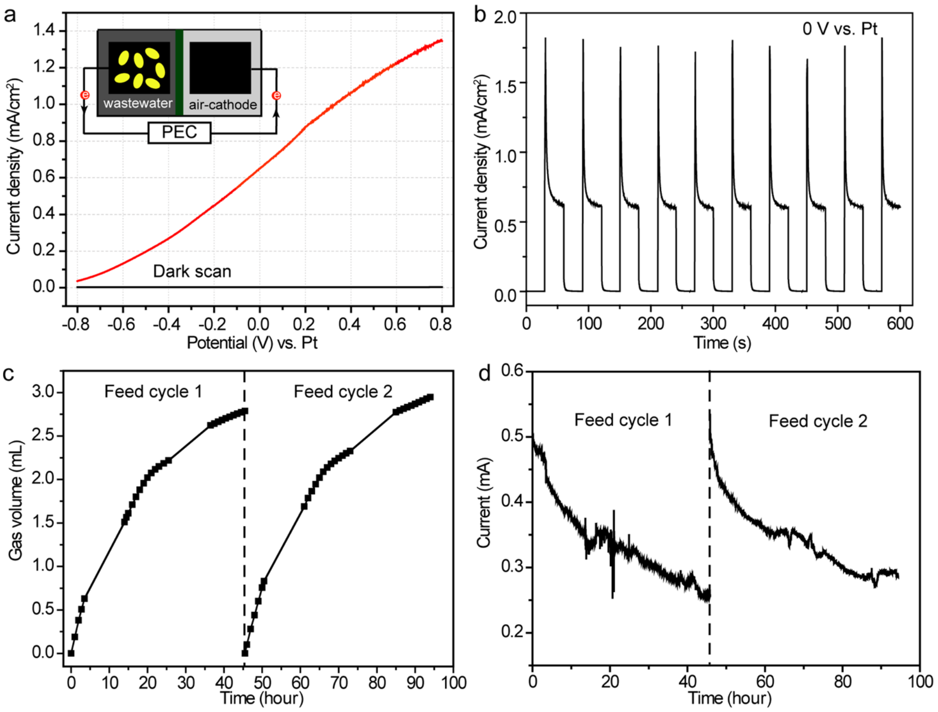

Figure 6. (a) Linear sweep voltammogram collected for PEC-MFC device with air cathode and wastewater as analyte, at a scan rate of 20 mV/s in the dark and under white light illumination of 100 mW/cm^2. Insets: Schematic diagram of the PEC-MFC device. (b) Amperometric *I*−*t* curve recorded for the PEC-MFC device at 0 V *vs* Pt with light on−off cycles. (c,d) Plot of gas production and current generation of the PEC-MFC device operated at 0 V *vs* Pt as a function of time.

devices, which only requires the supply of solar light and wastewater as energy sources, and can not only generate electricity and hydrogen gas but also treat wastewater at the same time.

CONCLUSION

In summary, we have developed a self-biased, sustainable PEC-MFC hybrid device for electricity and hydrogen generation, using wastewater and solar light as the only energy sources. By integrating an MFC device with a PEC device, the PEC device provides photovoltage that enables microbial electrohydrogenesis to occur without the need for an additional electrical bias. The results from this study provide new insights into the development of efficient energy solutions by integrating solar and microbial technology and may revolutionize the conventional wastewater treatment methodologies currently applied nationwide.

EXPERIMENTAL SECTION

Materials. Fluorine-doped tin oxide (FTO, TEC 8) glass substrates were purchased from Hartford Glass Company Inc. Titanium *n*-butoxide (99%), HCl (36.5−38% by weight), and potassium ferricyanide (99.9%) were from Fisher Scientific Company. Carbon cloth (CC6 Plain) and 40% Pt-decorated carbon cloth were purchased from Fuel Cell Earth LLC, Stoneham, MA. Wastewater containing the active sludge was supplied by the Livermore Water Reclamation Plant (Livermore, CA).

Synthesis of TiO_2 Nanowire Arrays. The synthesis of rutile TiO_2 nanowire arrays was based on a hydrothermal method reported previously.[34] Fifteen milliliters of concentrated hydrochloric acid was mixed with 15 mL of deionized water under stirring, followed by the addition of 0.475 mL of titanium *n*-butoxide. This precursor solution was poured into a 40 mL autoclave with a Teflon liner. A FTO glass substrate was cleaned and transferred into the autoclave with the conducting side facing down. The autoclave was heated at 150 °C in the electric oven for 5 h and then cooled to room temperature. The substrate was then washed with deionized water and air-dried. The substrate was covered with a white film of TiO_2 nanowire arrays. The nanowires were first calcined at 550 °C for 3 h in the air and then further annealed in a hydrogen atmosphere (in a home-built tube furnace filled with ultrapure hydrogen gas at a flow rate of 50 sccm) at 350 °C for 3 h.

Material Characterization. X-ray diffraction (XRD) spectra were obtained at room temperature on a Rigaku Americas Miniflex Plus powder diffractometer from a 2θ angle of 20−70° with a step size of 0.04° at a rate of 1°/min. Scanning electron microscopy (SEM) images were collected by a field-emission SEM (Hitachi S-4800 II).

Photoelectrochemical (PEC) Measurements. Linear sweep voltammograms were measured in a two-electrode configuration with a platinum wire as the counter electrode and TiO_2 nanowire samples as working electrode, at a scan rate of 20 mV/s, and 0.5 M Na_2SO_4 aqueous solution (pH 7.0) was used as electrolyte. TiO_2 photoanodes were fabricated by soldering a copper wire onto the bare edge of the FTO glass substrate and then sealing the FTO glass substrate and metal contact region with insulating epoxy resin. The exposed effective area for the TiO_2 working electrode is 0.15−0.2 cm^2. A 150 W Xe lamp (Newport 6255) coupled with an AM 1.5 global filter (Newport 81094) was used as the light source. The intensity of the incident light was measured with a digital power-meter and was controlled at 100 mW/cm^2. All PEC measurements were carried out with front side illumination. The gas produced on the Pt counter electrode was collected by a 1 or 3 mL gastight syringe and measured using a gas chromatograph (Agilent 3000) equipped with a thermal conductivity detector (100 °C, 150 mA) and Hayesep column (2.0 m, N 1/1600 80/100 mesh, set at 80 °C) with argon as carrier gas (30 mL/min).

Shewanella oneidensis MR-1 Bacterial Culture and MFC Operation. *Shewanella oneidensis* MR-1 (ATCC 700550) was cultured in tryptic soy broth (BD Biosciences, San Jose, CA) under aerobic conditions at room temperature for 24 h at 30 °C in an incubator shaker with shaking at 150 rpm. The culture was then transferred to the anode chamber of a dual-chamber MFC (chamber volume is ~25 mL). In the dual-chamber MFC, 25 mL of fresh catholyte solution, 50 mM ferricyanide in 100 mM phosphate buffer (K_2HPO_4 18.2 g/L, KH_2PO_4 2.56 g/L, $K_3Fe(CN)_6$ 15.6 g/L, pH 7.4), was injected to the cathode chamber using a syringe. An external resistor connects the anode and the cathode to complete the circuit, and the current generated in the MFC was monitored as a function of time. When the current dropped to the baseline level, fresh TSB medium was slowly injected into the anode chamber *via* a sterile syringe. For the MFC device with the air cathode, water was used as the catholyte, and oxygen dissolved in water was used as the electron acceptor, with air continuously bubbled into the water.

The current (I) generated in MFC was calculated according to Ohm's law, $I = V/R$, where V is the voltage and R is the external resistor. The power was then calculated as $P = V \times I$. The Coulombic efficiency (CE) of the MFC was calculated as the ratio of the transferred coulomb in the circuit to the total coulomb that was theoretically available from SCOD (*e.g.*, CE = $C_P/C_T \times 100\%$). C_P was calculated by integrating the current over time $\int I dt$ in the current–time plot, while C_T was calculated as $C_T = F \times b \times v \times \Delta COD/M$, where F is the Faraday's constant (96 500 C/mol), b is the number of moles of electrons produced per mol of oxygen ($b = 4$), v is the liquid volume of anolyte, ΔCOD is the COD removal after the treatment, and M is the molecular weight of oxygen ($M = 32$).

MFC with Wastewater as Anolyte. Anaerobic and aerobic sludge was obtained from the Livermore Water Reclamation Plant (Livermore, CA). A mixture of anaerobic and aerobic sludge at a 1:1 ratio was used to inoculate the MFC until the electrochemically active bacteria were enriched, leading to continuous current production. For SCOD analysis, the liquid samples were first filtered through a 0.22 μm pore diameter syringe filter then processed according to standard methods.[35]

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. We thank D.A. Stoops at Water Reclamation Plant (Livermore, CA) for providing municipal wastewater samples and helpful discussion. We thank Prof. J.Z. Zhang for offering a facility for GC measurements. Y.L. acknowledges the support of this work by NSF (CBET 1034222). F.Q. and Y.J. acknowledge support from LDRD Project 11-LW-054, performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DEAC52-07NA27344. Z.H. acknowledges the support by NSF (CBET 1033505).

Supporting Information Available: XRD, current *vs* time plot collected for a representative dual-chamber MFC with *Shewanella oneidensis* MR-1/TSB and ferricyanide/PSB, GC profiles, and schematic diagram and photograph of an air cathode MFC device using MR-1 cells. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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