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SANTA CRUZ

**SOLAR-DRIVEN MICROBIAL PHOTOELECTROCHEMICAL SYSTEM
FOR ENERGY CONVERSION**

A dissertation submitted in partial satisfaction
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

Hanyu Wang

June 2015

The Dissertation of Hanyu Wang
is approved:

Professor Yat Li, Chair

Professor Shaowei Chen

Professor Jin Z. Zhang

Tyrus Miller
Vice Provost and Dean of Graduate Studies

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SOLAR-DRIVEN MICROBIAL PHOTOELECTROCHEMICAL SYSTEM FOR ENERGY CONVERSION

Hanyu Wang

ABSTRACT

Ever growing demand for energy and clean water for the continuous economic growth and suitable inhabitation on earth are major global problems, especially with the drastic increase of human population. Over the years, distinct strategies have been applied to address these two needs separately: the municipal wastewater is collected by local wastewater plants for purification and subsequent reuse as reclaimed water, while the energy source is mainly based on fossil fuels as coal, natural gas, and crude oil. Apparently, these two strategies are decoupled. Additionally, the use of natural gas / petroleum generates a lot of greenhouse gas and toxic chemicals, which poses a serious threat to the environment, and also leads to additional cost to treat the pollution. Therefore, it's highly desirable to employ energy-efficient processes for wastewater treatment, and simultaneously recover the energy contained as organic matters in wastewater. This can be achieved by microbial fuel cell (MFC) technology, which is an electrochemical device that uses electrogenic bacteria as biocatalysts to decompose organic matter while simultaneously generating bioelectricity. Besides electricity, the bio-electrons generated in the microbial electrogenesis process at the anode can also be used to produce chemical fuels, such as hydrogen gas. However, microbial electrohydrogenesis process does not occur spontaneously due to the thermodynamic barrier for the conversion from protons to hydrogen gas, and

therefore an electrical bias has to be supplied to supplement the energy required for the proton reduction. The requirement of external bias adds to the complexity and cost for hydrogen production, making microbial electrohydrogenesis less attractive as a cost-effective energy solution. Alternatively, the energy required to overcome the barrier can be provided by a renewable energy source such as solar light, which is a promising approach that could fundamentally address this issue. In this thesis, I will give a detailed discussion on the development of a self-sustained and highly efficient solar-driven microbial device that could simultaneously address the increasing demand of clean water and energy. I have demonstrated a hybrid device by interfacing a photoelectrochemical cell (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. In addition to introducing the self-sustained microbial photoelectrochemical system (MPS), the efficiencies of MFC and PEC devices can be enhanced by chemical modification on anode materials of both MFC device and PEC device, separately. Moreover, based on the success of the hybrid PEC-MFC device, I have further studied the investigation of interplay between light, a hematite nanowire-arrayed photoelectrode, and *Shewanella oneidensis* MR-1 bacteria in a single solar-assisted MPS device. In the end, I will give a final summary and outlook on the solar-assisted MFC device for recovering energy from wastewater and simultaneously removing organic wastes.

**DEDICATED
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Chapter 1: H. Wang, F. Qian and Y. Li* "Solar-Assisted Microbial Fuel Cells for Bioelectricity and Chemical Fuel Generation" *Nano Energy*, 8, 264-273 (2014)

Chapter 2: H. Wang, F. Qian, G. Wang, Y. Jiao, Z. He and Y. Li* "Self-Biased Solar-Microbial Device for Sustainable Hydrogen Generation" *ACS Nano*, 7, 8728-8735 (2013)

Chapter 3: H. Wang, G. Wang, Y. Ling, F. Qian, Y. Song, X. Lu, S. Chen, Y. Tong and Y. Li* “High Power Density Microbial Fuel Cell with Flexible 3D Graphene-Nickel Foam as Anode” *Nanoscale*, 5, 10283-10290 (2013)

Chapter 4: H. Wang, G. Wang, Y. Ling, M. Lepert, C. Wang, J. Z. Zhang and Y. Li* “Photoelectrochemical Study of Oxygen Deficient TiO₂ Nanowire Arrays with CdS Quantum Dots Sensitization” *Nanoscale*, 4, 1463-1466 (2012)

Chapter 5: F. Qian,[†] H. Wang,[†](equal contribution) Y. Ling, G. Wang, M. P. Thelen and Y. Li* “Photo-Enhanced Electrochemical Interaction between *Shewanella* and a Hematite Photoanode” *Nano Lett.*, 14, 3688-3693 (2014)

Chapter 1

Introduction of Solar-Assisted Microbial Photoelectrochemical System and Chemical Modified Titanium Oxide Nanostructure for Photoelectrochemical Water Splitting

1.1 Background

Clean water crisis and steadily increased energy demanding are becoming one of the most urgent issues in today's society. Microbial Fuel cell (MFC) converts the energy stored in chemical bonds from organic compounds in wastewater to electrical energy through the catalytic reactions by microorganisms. This technology has generated considerable interests among academic researchers in recent years. The discovery that microbial metabolism in MFC could provide energy in the form of an electrical current and the wastewater treatment has led to a dramatic raise in the number of publications in the field of MFC research. In 2009, Time Magazine highlighted MFC technology as one of the top 50 most important inventions.¹ These systems are very adaptable and hold much promise to provide energy in a sustainable fashion even major improvements are still required for widespread applications.

In addition to bioelectricity, the electrons generated by the microorganisms can also be used to produce various chemical fuels, depending on the electron acceptors used in the catholyte. If protons serve as the electron acceptor, hydrogen gas will be generated at the cathode. This type of MFC device is called microbial electrolysis cell (MEC).² Although MEC technology represents an environmental friendly approach for hydrogen generation, major improvements are required since additional energy input is needed to overcome the thermodynamic energy barrier of converting protons to hydrogen gas. Nevertheless, the requirement of external bias adds to the complexity and cost for the MEC systems, making them less attractive in terms of cost-effectiveness.

To address this issue, researchers have proposed to use a renewable energy source to substitute the electrical energy input, such as solar light. Coupling of the renewable solar energy with the metabolic reaction of microorganisms for bioelectricity or hydrogen production leads to a new type of MFC device. This new type of solar-assisted MFC opens up new perspectives to simultaneously address the need of wastewater treatment and the increasing demand for clean energy.

Among different solar energy conversion devices, photoelectrochemical (PEC) cell is capable of converting the sun's rays into electrical or chemical energy in a direct manner. PEC utilizes the sustainable solar energy to convert water to a clean, renewable and carbon-free burning fuel, hydrogen gas. In PEC compartment, an electrical bias generated from solar light supplements the energy requirement to concur the thermodynamic barrier of microbial electrohydrogenesis process in MFC. Development of advanced anode materials in MFC is an effective approach to lower the energy barrier towards bioelectricity or hydrogen production. Meanwhile, chemical modification of photoanode in PEC promises desirable energy to assist the metabolic reaction of microorganisms in MFC. Thus, integrating an MFC device and a PEC device with improved anode materials is a new solution for electricity and hydrogen generation, using wastewater and solar light as the only energy sources.

This microbial photoelectrochemical system can open up many opportunities for microbial fuel cell technology because it combines respective advantages of microbial systems and semiconductor. In this part, I will give an overview of the basic mechanism of microbial fuel cell and photoelectrochemical water splitting, the

semiconductor material selection criteria, with an emphasis of the recent accomplishments in chemically modified nanostructure semiconductors for PEC and the solar-assisted MFC technology.³⁻⁵

1.2 The Basic Mechanism of Microbial Fuel Cell

Figure 1.1a shows the schematic diagram of a typical dual-chamber MFC device.⁶⁻⁸ The MFC chambers can be constructed by a number of materials, such as glass, polycarbonate, as well as plexiglass.^{9, 10} The essential physical components of the MFC are the anode electrode, cathode electrode, and anion exchange membrane that allows specific ions to diffuse from one chamber to the other. The anode electrode materials must be conductive, biocompatible, and chemically stable in the bacterial culture. Carbon-based materials such as carbon cloth, carbon paper, graphite, graphite felt and graphite brush are commonly used as anode electrode for MFC.¹¹⁻¹⁴ The cathode electrodes are typically carbon-based materials as well. For air-cathode, platinum (Pt) or Pt black-catalyst materials are commonly used to suppress the overpotential for oxygen reduction.^{15, 16} Anode chamber is filled with organic substrates that can be degraded by electrogenic microorganisms. The microorganisms that have been reported for use in MFCs include pure bacterial strains, e.g. *Geobacter*,¹⁷⁻²⁰ and *Shewanella* species,²¹⁻²³ or the mixed culture, e.g. natural microbial community domestic wastewater, sediment from marine and lake, as well as brewery wastewater.²⁴⁻²⁶ The cathode chamber is filled with solution containing an electron acceptor. The anode and the cathode are connected via an

external load to complete the circuit. As shown in Figure 1.1a, when the MFC is in operation, protons migrate from the anode to the cathode chamber through proton exchange membrane (PEM). Meanwhile, the microbially generated electrons flow through the external circuit from the anode to the cathode, where they are subsequently used to reduce electron acceptor, such as ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-}$) or permanganate (MnO_4^-), in the cathode chamber. While these chemical solutions serve as excellent catholytes for MFC devices, they are not sustainable and may cause environmental issues.^{27, 28} Alternatively, oxygen is a better electron acceptor for MFCs, due to its abundance sustainability and environmental cleanliness.²⁹ Figure 1.1b shows the digital image of a real dual-chamber MFC device with an air cathode (blue cap bottle) and a bacteria-colonizing anode (yellow cap bottle). Air was continuously bubbled into the catholyte (water). The anode was inoculated with anaerobic digester sludge from a sewage treatment plant (black solution in the beaker). The microbes in anode oxidized the organic wastes and converted the black wastewater solution into an almost clear solution. Table1 summarizes a few recently developed MFC devices using different electrogenic microorganisms and system design.

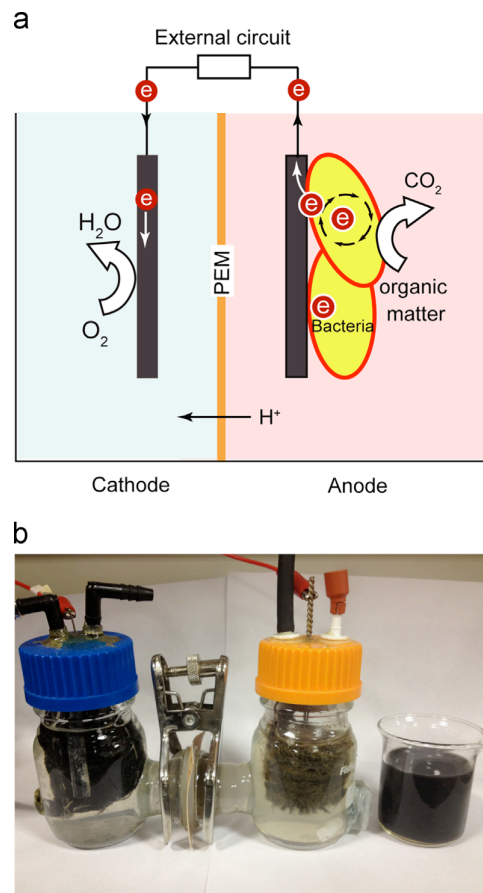


Figure 1.1 (a) Schematic illustration and (b) digital picture of a conventional microbial fuel cell device with an air cathode.

Table 1.1 A summary of recently developed MFC devices

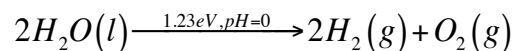
Culture/ Inoculum	<i>Geobacter sulfurreducens</i>		<i>Shewanella oneidensis</i> MR-1		Wastewater/Anaerobic sludge			
System design	Dual Chamber stacked cell	Dual chamber H-shaped cell	Single chamber air-cathode	Dual chamber channelled-cell	Single chamber air-cathode	Single chamber air-cathode	Dual chamber H-shaped cell	Dual chamber H-shaped cell
Anode material	Graphite cloth	Graphite	Carbon fiber brush	Graphene-Ni foam	Double carbon cloth electrode assemblies	Graphite rods (8)	Crumpled graphene-carbon cloth	Graphene-sponge
Cathode material	Graphite cloth	Graphite	Pt-carbon cloth	Carbon cloth	Pt-carbon cloth	Pt-carbon cloth	Pt/C carbon cloth	Pt-carbon cloth
Exchange membrane	Nafion 117	Nafion 117	None	CMI-7000S	None-woven cloth	Nafion 117	CMI-7000	AMI-7001
Medium	Acetate	Acetate	Lactate	Trypticase soy broth	Acetate	Untreated	Acetate	Glucose
Conditions	Anaerobic	Strictly anaerobic	Anaerobic	Semi-anaerobic	N/A	Untreated	Anaerobic	Untreated
Power output ¹	2.15 kWm ⁻³	65 mA m ⁻²	332 mW m ⁻²	27 W m ⁻³	4.30 W m ⁻²	26 mWm ⁻²	4.8 W m ⁻³	1.57 Wm ⁻²
Reference	19	20	22	23	34	40	41	49

¹ Power output was calculated based either on the electrode surface area or on the chamber volume.

The utilization of MFC as an alternative energy source was limited by its relative low power output for most practical applications. Therefore, significant efforts have been made in improving the current densities and power densities of MFCs, including modification of the architecture of MFC device,³⁰⁻³⁴ optimization of the microbial activities,^{35, 36} increasing of the effective surface area of both anode³⁷⁻⁴⁰ and cathode,^{41, 42} as well as the incorporation of various oxygen reduction reaction catalysts on cathode electrodes, such as Ni,^{43, 44} Co^{45, 46} and Au.^{11, 47} The rapid development of nanostructured electrodes also opens up new opportunities of enhancing the performance of MFCs. For instance, 3D porous materials with extremely large surface area are emerging as a new class of electrode materials for MFCs.^{23, 48-52} A 3D porous conductive scaffold not only considerably increases the effective surface area for microbial colonization, but also allows efficient electron transfer and mass transport of both nutrients and metabolites. A high power density microbial fuel cell with flexible 3D graphene-nickel foam as anode will be discussed in the thesis.

1.3 The Principle of Photoelectrochemical Water Splitting

Water cannot be directly decomposed by light, because it is transparent to visible light.⁵³ In photoelectrochemical water splitting cell, specialized semiconductors use solar energy to directly dissociate water into the form of hydrogen gas and oxygen gas. This PEC water splitting process is a long-term technology pathway with no greenhouse gas emission, which is known to be an endothermic process:



Although the minimum required band gap for successful water splitting at pH = 0 is 1.23 eV, which is equal to the driving voltage from the irradiance energy with a wavelength 1008 nm, water splitting is only observable when the wavelength is shorter than 380 nm due to the slow kinetics. However, if light can be effectively used in the electrochemical system it should be possible to achieve water splitting under visible light. Figure 1.2 shows the schematic diagram of a PEC cell. In a typical PEC cell, an n-type semiconductor works as photoanode, and a Pt electrode acts as a counter electrode. The n-type semiconductor photoanode is immersed into a water-based electrolyte, where sunlight energizes the water-splitting process. When photon falls on the semiconductor, the photo-excited electron-hole pairs can be created at the junction of two different materials. Two redox systems involve in the cell: one reacting with the holes at the surface of the photoanode to generate oxygen and the other reacting with the electrons through the counter-electrode to get hydrogen at the cathode. The overall reaction is the cleavage of water by sunlight.⁵⁴ Semiconductors used in PEC water splitting need to fulfill the band requirements mentioned previously and typically to optimize their performance resulting in they are either doped or have co-catalysts. Most semiconductors with suitable band structures to split water absorb mostly UV light; in order to absorb visible light, it is necessary to narrow the band gap. Titanium dioxide (TiO₂) is a typical n-type semiconductor with the proper band structure in PEC system. However, due to the relatively positive conduction band (CB) of TiO₂ (CB at -0.2 eV vs. NHE pH=0), the driving force for

H₂ production is so little that TiO₂ is usually used with a co-catalyst such as platinum (Pt) to increase the rate of H₂ generation.

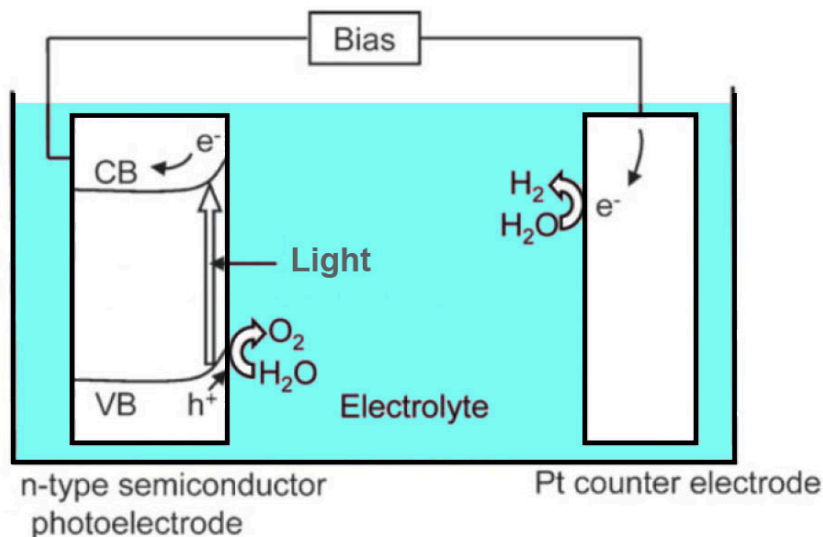


Figure 1.2 Principle of operation of photoelectrochemical cells based on n-type semiconductors. A cell that generates a chemical fuel, hydrogen, through the photo-cleavage of water.

1.4 Selection Criteria for Semiconductors for Photoelectrochemical Water Splitting

To achieve high solar-to-hydrogen (STH) efficiency of PEC water splitting, there are some very important properties for semiconductors used in PEC cell. First of all, those semiconductor materials should have suitable band edge position as the conduction band (CB) and valence band (VB) of semiconductors should straddle the electrochemical potentials of $E^{\circ}(\text{H}^{+}/\text{H}_2)$ (0 V vs. NHE) and $E^{\circ}(\text{O}_2/\text{H}_2\text{O})$ (1.23 V vs. NHE). Specifically, E_{CB} should be above $E^{\circ}(\text{H}^{+}/\text{H}_2)$ and E_{VB} should be below $E^{\circ}(\text{O}_2/\text{H}_2\text{O})$ to drive the photo-excited electrons and holes to split water into hydrogen gas and oxygen gas without external bias applied.^{55, 56} Secondly, solar light

absorption, especially in visible range by semiconductors, should be sufficient. Thirdly, semiconductors should have high chemical stability in electrolyte under either dark or light illumination. Besides, efficient charge transport across the semiconductor is required to avoid recombination of photo-excited electrons and holes, as well as compete with photocorrosion. Last, the semiconductors should have low overpotential for reduction/oxidation reaction. Comparing to the theoretical band gap of semiconductor required for PEC water splitting (1.23 eV), the actual used energy in PEC is relatively more than thermodynamically expected to drive a reaction, resulting in extra/missing energy is lost as heat. This potential difference is overpotential and it varies in each case. This energy loss contributes to photo-excited electrons and holes recombination, polarization within PEC cell and the resistance between electrode and contact.⁵⁷

1.5 Advances of Using Titanium Oxide as Photoanode and Its Chemical Modification

In 1972, Honda and Fujishima proposed the first artificial photosynthesis of H₂ via photoelectrochemical water splitting, using a TiO₂ photoanode in a PEC cell.⁵⁸ Inspired by the pioneer study, lots of efforts have been dedicated to develop PEC with TiO₂ and a number of other semiconductor materials for water splitting.⁵⁹⁻⁷⁰ To date, metal oxides are the most commonly-used materials for PEC water splitting, including TiO₂, Fe₂O₃,⁷¹⁻⁷⁶ BiVO₄,⁷⁷⁻⁸² ZnO⁸³⁻⁹⁰ and WO₃,⁹¹⁻⁹⁷ metal nitrides and phosphides such as Ta₃N₅,⁹⁸⁻¹⁰¹ GaP^{102, 103} and GaN,^{104, 105} metal oxynitrides such as TaON,^{106, 107} as well as both n type and p type silicon.¹⁰⁸⁻¹¹⁰

Among these semiconductors, TiO_2 is the most widely investigated as a photoanode for PEC water splitting, due to its abundance, low cost, strong optical absorption, favorable band edge alignments with water redox potentials, especially its excellent stability over a wide range of pH and applied potential than others.^{63, 65} However, the slightly large band gap and fast electron-hole recombination limits its extensively spread. Hence, large number of researches has been carried out to improve the visible light absorption of large band gap. For example, elemental doping and/or sensitization with small band gap semiconductors, such as CdS and CdSe.^{64, 65} These approaches could narrow band gap and improve the STH efficiency of titanium dioxide photoanode via modifying its optical absorption coefficient and wavelength. Recently, our group proposed that hydrogen treatment on TiO_2 semiconductor could fundamentally improve the PEC performance for water oxidation. The enhancement of photoactivity was ascribed to the increased oxygen vacancies during the hydrogen treatment process, resulting in the increased donor density of titanium dioxide photoanode. In this thesis, different methods of introducing oxygen vacancies were further investigated, and these new approaches were all shown improved photoactivity, comparable to reported TiO_2 with hydrogen treatment.

1.6 Recent Accomplishments of Solar-Driven Microbial Fuel Cell Technology

In 2009, Chae *et al.* demonstrated a dye-sensitized solar cell (DSSC)-powered microbial electrolysis cell for hydrogen production.³ The DSSC harvests renewable solar energy and provides the required energy for bioelectrochemical hydrogen production. Figure 1.3a illustrates the mechanism of electron transfer in the DSSC-

powered MEC hybrid device. This hybrid device operated in a manner analogous to the photosystem II in natural photosynthesis. Under light illumination, the photo-excited electrons in the surface-absorbed dye molecules transfer to the conduction band of TiO₂ nanoparticles, and then to the cathode of MEC via the external circuit, where the hydrogen evolution reaction happens (Figure 1.3a). At the same time, the bio-electrons generated in the anode of the MEC diffuse into the DSSC through the external circuit, where I³⁻ is reduced to I⁻. The dye molecules can be regenerated upon receiving electrons from iodide ions, results in oxidizing iodide ions back to triiodide ions. Hydrogen gas evolution was observed under light illumination. This work demonstrated that solar energy can be coupled into MFC device and provide a critical driving force for the bioelectrochemical reaction. In 2010, Qian *et al.* reported a microbial photoelectrochemical cell (denoted as MPC) that interfacing the inorganic photocathode and bio-anode, and allow them to work synergistically to combine the energy from solar light and organic substrate.⁴ Figure 1.3b shows the energy diagram of the solar MPC device. This work demonstrated for the first time of interfacing an inorganic photocathode with a bacterial colonizing bioanode. The semiconductor band edge positions relative to the redox potential of bacterial cells are favorable for the microbial electrons transport to the valence band of semiconductor. Under light illumination, photoexcited holes can recombine with the bio-electrons generated at the anode, while the photoexcited electrons reduce proton to produce hydrogen gas.

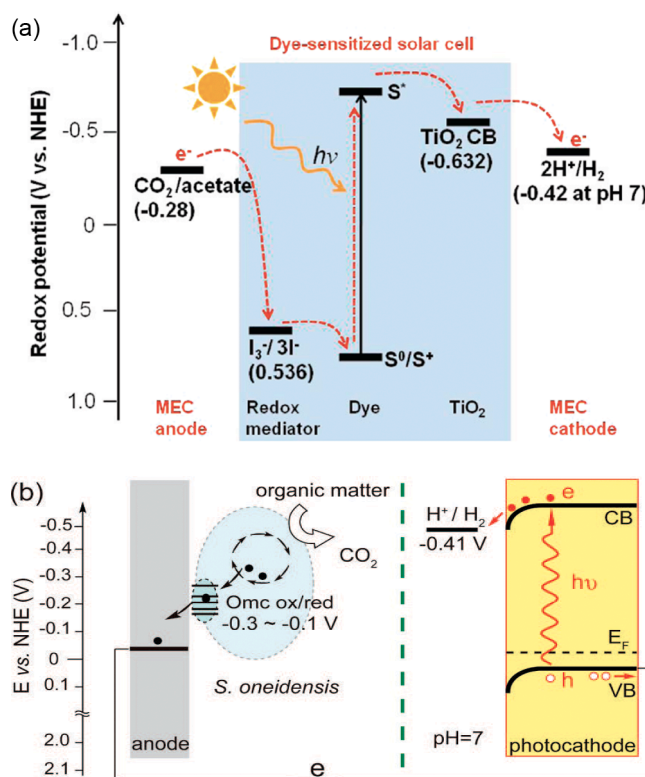


Figure 1.3 (a) Schematic diagram of electron transfer in the solar-powered MEC. Reprinted with permission from Ref (3). Copyright (2009) American Chemical Society. (b) Corresponding energy diagram illustrates the carrier generation and charge transfer at the virtual interface between microbial and semiconductor systems. CB, VB, and E_F are respective initials for conduction band, valence band, and Fermi level. Solid and empty red dots represent photogenerated electrons and holes. Black dots represent electrons generated from bacterial cells. Reprinted with permission from Ref (4). Copyright (2010) American Chemical Society.

Despite the MPS system provides a solution on the need of wastewater treatment and the increasing demand for clean energy, some challenges in practical use still exist. I will give a detailed discuss on the current challenges and future opportunities in the end of this thesis.

Reference

1. Time The 50 Best Inventions of 2009, http://content.time.com/time/specials/packages/article/0,28804,1934027_1934003_1933965,00.html.
2. Cheng, S.; Logan, B. E., Sustainable and Efficient Biohydrogen Production via Electrohydrogenesis. *PNAS* **2007**, *104*, 18871-18873.
3. Chae, K. J.; Choi, M. J.; Kim, K. Y.; Ajayi, F. F.; Chang, I. S.; Kim, I. S., A Solar-Powered Microbial Electrolysis Cell with a Platinum Catalyst-Free Cathode to Produce Hydrogen. *Environ. Sci. Technol.* **2009**, *43*, 9525-9530.
4. Qian, F.; Wang, G.; Li, Y., Solar-Driven Microbial Photoelectrochemical Cells with a Nanowire Photocathode. *Nano Lett.* **2010**, *10*, 4686-4691.
5. Wang, H.; Qian, F.; Wang, G.; Jiao, Y.; He, Z.; Li, Y., Self-Biased Solar-Microbial Device for Sustainable Hydrogen Generation. *ACS Nano* **2013**, *7*, 8728-8735.
6. Logan, B. E.; Hamelers, B.; Rozendal, R.; Schroder, U.; Keller, J.; Freguia, S.; Aelterman, P.; Verstraete, W.; Rabaey, K., Microbial Fuel Cells: Methodology and Technology. *Environ. Sci. Technol.* **2006**, *40*, 5181-5192.
7. Li, F.; Sharma, Y.; Lei, Y.; Li, B.; Zhou, Q., Microbial Fuel Cells: The Effects of Configurations, Electrolyte Solutions, and Electrode Materials on Power Generation. *Appl. Microbial Biotechnol.* **2010**, *160*, 168-181.
8. Kim, D.; An, J.; Kim, B.; Jang, J. K.; Kim, B. H.; Chang, I. S., Scaling-Up Microbial Fuel Cells: Configuration and Potential Drop Phenomenon at Series Connection of Unit Cells in Shared Anolyte. *ChemSusChem* **2012**, *5*, 1086-1091.
9. Das, S.; Mangwani, N., Recent Developments in Microbial Fuel Cells: A Review. *J. Sci. Ind. Res.* **2010**, *69*, 727-731.
10. Rhoads, A.; Beyenal, H.; Lewandowski, Z., Microbial Fuel Cell using Anaerobic Respiration as an Anodic Reaction and Biomineralized Manganese as a Cathodic Reactant. *Environ. Sci. Technol.* **2005**, *39*, 4666-4671.
11. Wei, J.; Liang, P.; Huang, X., Recent Progress in Electrodes for Microbial Fuel Cells. *Bioresour. Technol.* **2011**, *102*, 9335-9344.
12. Zhou, M.; Chi, M.; Luo, J.; He, H.; Jin, T., An Overview of Electrode Materials in Microbial Fuel Cells. *J. Power Sources* **2011**, *196*, 4427-4435.

13. Zhang, Y.; Min, Z.; Yang, Z.; Xie, J.; Li, Y., Effects of Electrode Materials on Electricity of Microbial Fuel Cell. *Adv. Mater. Res.* **2011**, 183-185, 1549-1552.
14. Sangeetha, T.; Muthukumar, M., Influence of Electrode Material and Electrode Distance on Bioelectricity Production from Sago-Processing Wastewater Using Microbial Fuel Cell. *Environ. Prog. Sustain. Energy* **2013**, 32, 390-395.
15. Pant, D.; Van Bogaert, G.; Porto-Carrero, C.; Diels, L.; Vanbroekhoven, K., Anode and Cathode Materials Characterization for a Microbial Fuel Cell in Half Cell Configuration. *Waer Sci. Technol.* **2011**, 63, 2457-2461.
16. Cheng, S.; Liu, H.; Logan, B. E., Power Densities Using Different Cathode Catalysts (Pt and CoTMPP) and Polymer Binders (Nafion and PTFE) in Single Chamber Microbial Fuel Cells. *Environ. Sci. Technol.* **2006**, 40, 364-369.
17. Lovley, D. R.; Giovannoni, S. J.; White, D. C.; Champine, J. E.; Philips, E. J.; Gorby, Y. A.; Goodwin, S., *Geobacter Metallireducens* gen. nov. sp. nov., a Microorganism Capable of Coupling the Complete Oxidation of Organic Compounds to the Reduction of Iron and Other Metals. *Arch. Microbiol.* **1993**, 159, 336-344.
18. Lovley, D. R.; Ueki, T.; Zhang, T.; Malvankar, N. S.; Shrestha, P. M.; Flanagan, K. A.; Aklujkar, M.; Butler, J. E.; Giloteaux, L.; Rotaru, A.-E.; Holmes, D. E.; Franks, A. E.; Orellana, R.; Risso, C.; Nevin, K. P., *Geobacter*: the Microbe Electric's Physiology, Ecology and Practical Applications. *Adv. Microb. Physiol.* **2011**, 59, 1-100.
19. Nevin, K. P.; Richter, H.; Covalla, S. F.; Johnson, J. P.; Woodard, T. L.; Orloff, A. L.; Jia, H.; Zhang, M.; Lovley, D. R., Power Output and Columbic Efficiencies from Biofilms of *Geobacter sulfurreducens* Comparable to Mixed Community Microbial Fuel Cells. *Environ. Microbiol.* **2008**, 10, 2505-2514.
20. Bond, D. R.; Lovley, D. R., Electricity Production by *Geobacter sulfurreducens* Attached to Electrodes. *Appl. Environ. Microbiol.* **2003**, 69, 1548-1555.
21. Gorby, Y. A.; Yanina, S.; McLean, J. S.; Rosso, K. M.; Moyles, D.; Dohnalkova, A.; Beveridge, T. J.; Chang, I. S.; Kim, B. H.; Kim, K. S.; Culley, D. E.; Reed, S. B.; Romine, M. F.; Saffarini, D. A.; Hill, E. A.; Shi, L.; Elias, D. A.; Kennedy, D. W.; Pinchuk, G.; Watanabe, K.; Ishii, S.; Logan, B. E.; Nealon, K. H.; Fredrickson, J. K., Electrically Conductive Bacterial Nanowires Produced by *Shewanella oneidensis* Strain MR-1 and Other Microorganisms. *PNAS* **2006**, 103, 11358-11363.

22. Watson, V. J.; Logan, B. E., Power production in MFCs Inoculated with *Shewanella oneidensis* MR-1 or Mixed Cultures. *Biotechnol. Bioengin.* **2010**, *105*, 489-498.
23. Wang, H.; Wang, G.; Ling, Y.; Qian, F.; Song, Y.; Lu, X.; Chen, S.; Tong, Y.; Li, Y., High Power Density Microbial Fuel Cell with Flexible 3D Graphene-Nickel Foam as Anode. *Nanoscale* **2013**, 10283-10290.
24. Feng, Y.; Wang, X.; Logan, B. E.; Lee, H., Brewery Wastewater Treatment Using Air-Cathode Microbial Fuel Cells. *Appl. Microbial Biotechnol.* **2008**, *78*, 873-880.
25. Rabaey, K.; Verstraete, W., Microbial Fuel Cells: Novel Biotechnology for Energy Generation. *TRENDS Biotechnol.* **2005**, *23*, 291-298.
26. Logan, B. E., Simultaneous Wastewater Treatment and Biological Electricity Generation. *Water Sci. Technol.* **2005**, *52*, 31-37.
27. Wei, L.; Han, H.; Shen, J., Effects of Cathodic Electron Acceptors and Potassium Ferricyanide Concentrations on the Performance of Microbial Fuel Cell. *Int. J. Hydrogen Energy* **2012**, *37*, 12980-12986.
28. Pham, T. H.; Jang, J. K.; Chang, I. S.; Kim, B. H., Improvement of Cathode Reaction of a Mediatorless Microbial Fuel Cell. *J. Microbiol. Biotechnol.* **2004**, *14*, 324-329.
29. Oh, S.; Min, B.; Logan, B. E., Cathode Performance as a Factor in Electricity Generation in Microbial Fuel Cells. *Environ. Sci. Technol.* **2004**, *38*, 4900-4904.
30. Zhang, X.; Sun, H.; Liang, P.; Huang, X.; Chen, X.; Logan, B. E., Air-Cathode Structure Optimization in Separator-Coupled Microbial Fuel Cell. *Biosens. Bioelectron.* **2011**, *30*, 267-271.
31. Hu, H.; Fan, Y.; Liu, H., Hydrogen Production Using Single-Chamber Membrane-Free Microbial Electrolysis Cells. *Water Res.* **2008**, *42*, 4172-4178.
32. Qian, F.; Baum, M.; Gu, Q.; Morse, D. E., A 1.5 μ L Microbial Fuel Cell for On-Chip Bioelectricity Generation. *Lab Chip* **2009**, *9*, 3076-3081.
33. Zhang, F.; Ge, Z.; Grimaud, J.; He, Z., Improving Electricity Production in Tubular Microbial Fuel Cell through Optimizing the Anolyte Flow with Spiral Spacers. *Bioresour. Technol.* **2013**, *134*, 251-256.
34. Fan, Y.; Han, S.-K.; Liu, H., Improved Performance of CEA Microbial Fuel Cells with Increased Reactor Size. *Energy Environ. Sci.* **2012**, *5*, 8273-8280.

35. R., K. J.; Min, B.; Logan, B. E., Evaluation of Procedures to Acclimate a Microbial Fuel Cell for Electricity Production. *Appl. Microbiol. Biotechnol.* **2005**, *68*, 23-30.
36. Liu, H.; Cheng, S.; Logan, B. E., Power Generation in Fed-Batch Microbial Fuel Cells as a Function of Ionic Strength, Temperature, and Reactor Configuration. *Environ. Sci. Technol.* **2005**, *39*, 5488-5493.
37. Ci, S.; Wen, Z.; Chen, J.; He, Z., Decorating Anode with Bamboo-Like Nitrogen-Doped Carbon Nanotubes for Microbial Fuel Cells. *Electrochem. Commun.* **2012**, *14*, 71-74.
38. Chen, S.; He, G.; Liu, Q.; Harnisch, F.; Zhou, Y.; Chen, Y.; Hanif, M.; Wang, S.; Peng, X.; Hou, H.; Schroder, U., Layered Corrugated Electrode Macrostructures Boost Microbial Bioelectrocatalysis. *Energy Environ. Sci.* **2012**, *5*, 9769-9772.
39. Chen, S.; Hou, H.; Harnisch, F.; Patil, S. A.; Carmona-Martinez, A. A.; Agarwal, S.; Zhang, Y.; Sinha-Ray, S.; Yarin, A. L.; Greiner, A.; Schroder, U., Electrospun and Solution Blown Three-Dimensional Carbon Fiber Nonwovens for Application as Electrodes in Microbial Fuel Cells. *Energy Environ. Sci.* **2011**, *4*, 1417-1421.
40. Liu, H.; Ramnarayanan, R.; Logan, B. E., Production of Electricity during Wastewater Treatment Using a Single Chamber Microbial Fuel Cell. *Environ. Sci. Technol.* **2004**, *38*, 2281-2285.
41. Xiao, L.; Damien, J.; Luo, J.; Jang, H. D.; Huang, J.; He, Z., Crumpled Graphene Particles for Microbial Fuel Cell Electrodes. *J. Power Sources* **2012**, *208*, 187-192.
42. Xiao, L.; Wen, Z.; Ci, S.; Chen, J.; He, Z., Carbon/Iron-Based Nanorod Catalysts for Hydrogen Production in Microbial Electrolysis Cells. *Nano Energy* **2012**, *1*, 751-756.
43. Wang, C.-T.; Chen, Y.-M.; Qi, Z.-Q.; Yang, Y.-C., Carbon Nanotube Planted on Ni-Based Alloy in Microbial Fuel Cell. *J. Nano Mat.* **2013**, *2013*, 435960.
44. Liu, X.; Du, X.; Wang, X.; Li, N.; Xu, P.; Ding, Y., Improved Microbial Fuel Cell Performance by Encapsulating Microbial Cells with a Nickel-Coated Sponge. *Biosens. Bioelectron.* **2012**, *41*, 848-851.
45. Wang, X.; Cheng, S.; Zhang, X.; Li, X.-Y.; Logan, B. E., Impact of Salinity on Cathode Catalyst Performance in Microbial Fuel Cells (MFCs). *Int. J. Hydrogen Energy* **2011**, *36*, 13900-13906.

46. Cheng, S.; Logan, B. E., Evaluation of Catalysts and Membranes for High Biohydrogen Production via Electrohydrogenesis in Microbial Electrolysis Cells (MECs). *Water Sci. Technol.* **2008**, *58*, 853-857.
47. Brondani, D.; Zapp, E.; Vieira, I. C.; Dupont, J.; Scheeren, C. W., Gold Nanoparticles in an Ionic Liquid Phase Supported in a Biopolymeric Matrix Applied in the Development of a Rosmarinic Acid Biosensor. *Analyst* **2011**, *136*, 2495-2505.
48. Xie, X.; Ye, M.; Hu, L.; Liu, N.; McDonough, J. R.; Chen, W.; Alshareef, H. N.; Criddle, C. S.; Cui, Y., Carbon Nanotube-Coated Macroporous Sponge for Microbial Fuel Cell Electrodes. *Energy Environ. Sci.* **2012**, *5*, 5265-5270.
49. Xie, X.; Yu, G.; Liu, N.; Bao, Z.; Criddle, C. S.; Cui, Y., Graphene-Sponges as High-Performance Low-Cost Anodes for Microbial Fuel Cells. *Energy Environ. Sci.* **2012**, *5*, 6862-6866.
50. Yong, Y.-C.; Dong, X.-C.; Chan-Park, M. B.; Song, H.; Chen, P., Macroporous and Monolithic Anode Based on Polyaniline Hybridized Three-Dimensional Graphene for High-Performance Microbial Fuel Cells. *ACS Nano* **2012**, *6*, 2394-2400.
51. Qiao, Y.; Bao, S.-J.; Li, C. M.; Cui, X.-Q.; Lu, Z.-S.; Guo, J., Nanostructured Polyaniline/Titanium Dioxide Composite Anode for Microbial Fuel Cells. *ACS Nano* **2008**, *2*, 113-119.
52. Gadhamshetty, V.; Koratkar, N., Nano-Engineered Biocatalyst-Electrode Structures for Next Generation Microbial Fuel Cell. *Nano Energy* **2012**, *1*, 3-5.
53. Coehn, A., Photochemical Equilibria. IV. Detonating Gas and Water Vapor. *Berichte der Deutschen Chemischen Gesellschaft* **1910**, *43*, 880.
54. Grätzel, M., Photoelectrochemical Cells. *Nature* **2001**, *414*, 338-344.
55. Abe, R., Recent Progress on Photocatalytic and Photoelectrochemical Water Splitting under Visible Light Irradiation. *J. Photochem. Photobiol. C* **2010**, *11*, 179-209.
56. Li, Y.; Zhang, J. Z., Hydrogen Generation from Photoelectrochemical Water Splitting Based on Nanomaterials. *Laser & Photonics Rev.* **2010**, *4*, 517-528.
57. Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C., Photo-Electrochemical Hydrogen Generation from Water Using Solar Energy. Materials Related Aspects. *Int. J. Hydrogen Energ.* **2002**, *27*, 991-1022.

58. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37-38.
59. Park, J. H.; Kim, S.; Bard, A. J., Novel Carbon-Doped TiO₂ Nanotube Arrays with High Aspect Ratios for Efficient Solar Water Splitting. *Nano Lett.* **2006**, *6*, 24-28.
60. Lu, N.; Quan, X.; Li, J.; Chen, S.; Yu, H.; Chen, G., Fabrication of Boron-Doped TiO₂ Nanotube Array Electrode and Investigation of Its Photoelectrochemical Capability. *J. Phys. Chem. C* **2007**, *111*, 11836-11842.
61. Rockafellow, E. M.; Stewart, L. K.; Jenks, W. S., Is Sulfur-Doped TiO₂ an Effective Visible Light Photocatalyst for Remediation? *Applied Catalysis B: Environmental* **2009**, *91*, 554-562.
62. Park, Y.; Kim, W.; Park, H.; Tachikawa, T.; Majima, T.; Choi, W., Carbon-Doped TiO₂ Photocatalyst Synthesized without Using an External Carbon Precursor and the Visible Light Activity. *Appl. Catalysis B-Environ.* **2009**, *91*, 355-361.
63. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated TiO₂ Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, *11*, 3026-3033.
64. Hensel, J.; Wang, G.; Li, Y.; Zhang, J. Z., Synergistic Effect of CdSe Quantum Dot Sensitization and Nitrogen Doping of TiO₂ Nanostructures for Photoelectrochemical Solar Hydrogen Generation. *Nano Lett.* **2010**, *10*, 478-483.
65. Wang, H.; Wang, G.; Ling, Y.; Lepert, M.; Wang, C.; Zhang, J. Z.; Li, Y., Photoelectrochemical Study of Oxygen Deficient TiO₂ Nanowire Arrays with Cds Quantum Dot Sensitization. *Nanoscale* **2012**, *4*, 1463-1466.
66. Wang, G.; Ling, Y.; Lu, X.; Wang, H.; Qian, F.; Tong, Y.; Li, Y., Solar Driven Hydrogen Releasing from Urea and Human Urine. *Energy Environ. Sci.* **2012**, *5*, 8215-8219.
67. Hoang, S.; Berglund, S. P.; Hahn, N. T.; Bard, A. J.; Mullins, C. B., Enhancing Visible Light Photo-Oxidation of Water with TiO₂ Nanowire Arrays via Cotreatment with H₂ and NH₃: Synergistic Effects between Ti³⁺ and N. *J. Am. Chem. Soc.* **2012**, *134*, 3659-62.
68. Hwang, Y. J.; Hahn, C.; Liu, B.; Yang, P., Photoelectrochemical Properties of TiO₂ Nanowire Arrays: A Study of the Dependence on Length and Atomic Layer Deposition Coating. *ACS Nano* **2012**, *6*, 5060-5069.

69. Xu, M.; Da, P.; Wu, H.; Zhao, D.; Zheng, G., Controlled Sn-Doping in TiO₂ Nanowire Photoanodes with Enhanced Photoelectrochemical Conversion. *Nano Lett.* **2012**, *12*, 1503-1508.
70. Hwang, Y. J.; Boukai, A.; Yang, P., High Density n-Si/n-TiO₂ Core/Shell Nanowire Arrays with Enhanced Photoactivity. *Nano Lett.* **2009**, *9*, 410-415.
71. Wang, G.; Ling, Y.; Wheeler, D. A.; George, K. E. N.; Horsley, K.; Heske, C.; Zhang, J. Z.; Li, Y., Facile Synthesis of Highly Photoactive α -Fe₂O₃-Based Films for Water Oxidation. *Nano Lett.* **2011**, *11*, 3503-3509.
72. Ling, Y.; Wang, G.; Reddy, J.; Wang, C.; Zhang, J. Z.; Li, Y., The Influence of Oxygen Content on the Thermal Activation of Hematite Nanowires. *Angew. Chem. Int. Ed.* **2012**, *51*, 4074-4079.
73. Lin, Y.; Zhou, S.; Sheehan, S. W.; Wang, D., Nanonet-Based Hematite Heteronanostructures for Efficient Solar Water Splitting. *J. Am. Chem. Soc.* **2011**, *133*, 2398-2401.
74. Li, L.; Yu, Y.; Meng, F.; Tan, Y.; Hamers, R. J.; Jin, S., Facile Solution Synthesis of α -FeF₃·3H₂O Nanowires and Their Conversion to α -Fe₂O₃ Nanowires for Photoelectrochemical Application. *Nano Lett.* **2012**, *12*, 724-731.
75. Goncalves, R. H.; Lima, B. H. R.; Leite, E. R., Magnetite Colloidal Nanocrystals: A Facile Pathway To Prepare Mesoporous Hematite Thin Films for Photoelectrochemical Water Splitting. *J. Am. Chem. Soc.* **2011**, *133*, 6012-6019.
76. Vayssieres, L.; Sathe, C.; Butorin, S. M.; Shuh, D. K.; Nordgren, J.; Guo, J., One-Dimensional Quantum-Confinement Effect in α -Fe₂O₃ Ultrafine Nanorod Arrays. *Adv. Mater.* **2005**, *17*, 2320-2323.
77. Sayama, K.; Nomura, A.; Arai, T.; Sugita, T.; Abe, R.; Yanagida, M.; Oi, T.; Iwasaki, Y.; Abe, Y.; Sugihara, H., Photoelectrochemical Decomposition of Water into H₂ and O₂ on Porous BiVO₄ Thin-Film Electrodes under Visible Light and Significant Effect of Ag Ion Treatment. *J. Phys. Chem. B* **2006**, *110*, 11352-11360.
78. Ng, Y. H.; Iwase, A.; Kudo, A.; Amai, R., Reducing Graphene Oxide on a Visible-Light BiVO₄ Photocatalyst for an Enhanced Photoelectrochemical Water Splitting. *J. Phys. Chem. Lett.* **2010**, *1*, 2607-2612.
79. Mingce; Weimin; Kisch, H., Visible Light Induced Photoelectrochemical Properties of n-BiVO₄ and n-BiVO₄/p-Co₃O₄. *J. Phys. Chem. C* **2008**, *112*, 548-554.

80. ChatChai, P.; Murakami, Y.; Kishioka, S.; Nosaka, A. Y.; Nosaka, Y., Efficient Photocatalytic Activity of Water Oxidation over WO₃/BiVO₄ Composite under Visible Light Irradiation. *Electrochim. Acta* **2009**, *54*, 1147-1152.
81. Iwase, A.; Kudo, A., Photoelectrochemical Water Splitting Using Visible-Light-Responsive BiVO₄ Fine Particles Prepared in an Aqueous Acetic Acid Solution. *J. Mater. Chem.* **2010**, *20*, 7536-7542.
82. Zhong, D.; Choi, S.; Gamelin, D. R., Near-Complete Suppression of Surface Recombination in Solar Photoelectrolysis by "Co-Pi" Catalyst-Modified W:BiVO₄. *J. Am. Chem. Soc.* **2011**, *133*, 18370-18377.
83. Cooper, J. K.; Ling, Y.; Longo, C.; Li, Y.; Zhang, J. Z., Effects of Hydrogen Treatment and Air Annealing on Ultrafast Charge Carrier Dynamics in ZnO Nanowires Under in Situ Photoelectrochemical Conditions. *J. Phys. Chem. C* **2012**, *116*, 17360-17368.
84. Yang, X.; Wolcott, A.; Wang, G.; Sobo, A.; Fitzmorris, R. C.; Qian, F.; Zhang, J. Z.; Li, Y., Nitrogen-Doped ZnO Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2009**, *9*, 2331-2336.
85. Wang, G.; Yang, X.; Qian, F.; Zhang, J. Z.; Li, Y., Double-Sided CdS and CdSe Quantum Dot Co-Sensitized ZnO Nanowire Arrays for Photoelectrochemical Hydrogen Generation. *Nano Lett.* **2010**, *10*, 1088-1092.
86. Qiu, Y.; Yan, K.; Deng, H.; Yang, S., Secondary Branching and Nitrogen Doping of ZnO Nanotetrapods: Building a Highly Active Network for Photoelectrochemical Water Splitting. *Nano Lett.* **2012**, *12*, 407-413.
87. Shi, J.; Starr, M. B.; Xiang, H.; Hara, Y.; Anderson, M. A.; Seo, J.-H.; Ma, Z.; Wang, X., Interface Engineering by Piezoelectric Potential in ZnO-Based Photoelectrochemical Anode. *Nano Lett.* **2012**, *11*, 5587-5593.
88. Xie, S.; Lu, X.; Zhai, T.; Li, W.; Yu, M.; Liang, C.; Tong, Y., Enhanced Photoactivity and Stability of Carbon and Nitrogen Co-Treated ZnO Nanorod Arrays for Photoelectrochemical Water Splitting. *J. Mater. Chem.* **2012**, *22*, 14272-14275.
89. Li, H.; Cheng, C.; Li, X.; Liu, J.; Guan, C.; Tay, Y. Y.; Fan, H. J., Composition-Graded Zn_xCd_{1-x}Se@ZnO Core-Shell Nanowire Array Electrodes for Photoelectrochemical Hydrogen Generation. *J. Phys. Chem. C* **2012**, *116*, 3802-3807.
90. Lin, Y.-G.; Hsu, Y.-K.; Chen, Y.-C.; Chen, L.-C.; Chen, S.-Y.; Chen, K.-H., Visible-Light-Driven Photocatalytic Carbon-Doped Porous ZnO Nanoarchitectures for Solar Water-Splitting. *Nanoscale* **2012**, *4*, 6515-6519.

91. Wang, G.; Ling, Y.; Wang, H.; Yang, X.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated WO₃ Nanoflakes Show Enhanced Photostability. *Energy Environ. Sci.* **2012**, *5*, 6180.
92. Zhang, X.; Lu, X.; Shen, Y.; Han, J.; Yuan, L.; Gong, L.; Xu, Z.; Bai, X.; Wei, M.; Tong, Y.; Gao, Y.; Chen, J.; Zhou, J.; Wang, Z. L., Three-Dimensional WO₃ Nanostructures on Carbon Paper: Photoelectrochemical Property and Visible Light Driven Photocatalysis. *Chem. Commun.* **2011**, *47*, 5804-5806.
93. Liu, X.; Wang, F.; Wang, Q., Nanostructure-Based WO₃ Photoanodes for Photoelectrochemical Water Splitting. *Phys. Chem. Chem. Phys.* **2012**, *14*, 7894-7911.
94. Esposito, D. V.; Forest, R. V.; Chang, Y.; Gaillard, N.; McCandless, B. E.; Hou, S.; Lee, K. H.; Birkmire, R. W.; Chen, J. G., Photoelectrochemical Reformation of Glucose for Hydrogen Production Using a WO₃-Based Tandem Cell Device. *Energy Environ. Sci.* **2012**, *5*, 9091-9099.
95. Cristino, V.; Caramori, S.; Argazzi, R.; Meda, L.; Marra, G. L.; Bignozzi, C. A., Efficient Photoelectrochemical Water Splitting by Anodically Grown WO₃ Electrodes. *Langmuir* **2011**, *27*, 7276-7284.
96. Hill, J. C.; Choi, K.-S., Effect of Electrolytes on the Selectivity and Stability of n-type WO₃ Photoelectrodes for Use in Solar Water Oxidation. *J. Phys. Chem. C* **2012**, *116*, 7612-7620.
97. Kronawitter, C. X.; Vayssieres, L.; Shen, S.; Guo, L.; Wheeler, D. A.; Zhang, J. Z.; Antoun, B. R.; Mao, S. S., A Perspective on Solar-Driven Water Splitting with All-Oxide Heteronanostructures. *Energy Environ. Sci.* **2011**, *4*, 3889-3899.
98. Feng, X.; Latempa, T. J.; Basham, J. I.; Mor, G. K.; Varghese, O. K.; Grimes, C. A., Ta₃N₅ Nanotube Arrays for Visible Light Water Photoelectrolysis. *Nano Lett.* **2010**, *10*, 948-952.
99. Cong, Y.; Park, H. S.; Wang, S.; Dang, H. X.; Fan, F.-R.; Mullins, C. B.; Bard, A. J., Synthesis of Ta₃N₅ Nanotube Arrays Modified with Electrocatalysts for Photoelectrochemical Water Oxidation. *J. Phys. Chem. C* **2012**, *116*, 14541-14550.
100. Yang, Y.; Ling, Y.; Wang, G.; Lu, X.; Tong, Y.; Li, Y., Growth of Gallium Nitride and Indium Nitride Nanowires on Conductive and Flexible Carbon Cloth Substrates. *Nanoscale* **2013**, *5*, 1820-1824.
101. Li, Y.; Takata, T.; Cha, D.; Takanabe, K.; Minegishi, T.; Kubota, J.; Domen, K., Vertically Aligned Ta₃N₅ Nanorod Arrays for Solar-Driven Photoelectrochemical Water Splitting. *Adv. Mater.* **2013**, *25*, 125-131.

102. Sun, J.; Liu, C.; Yang, P., Surfactant-Free, Large-Scale, Solution-Liquid Growth of Gallium Phosphide Nanowires and Their Use for Visible -Light-Driven Hydrogen Production from Water Reduction. *J. Am. Chem. Soc.* **2011**, *133*, 19306-19309.
103. Liu, C.; Sun, J.; Tang, J.; Yang, P., Zn-Doped p-Type Gallium Phosphide Nanowire Photocathodes from a Surfactant-Free Solution Synthesis. *Nano Lett.* **2012**, *12*, 5407-5411.
104. Wang, D.; Pierre, A.; Kibria, M. G.; Cui, K.; Han, X.; Bevan, K. H.; Guo, H.; Paradis, S.; Hakima, A. R.; Mi, Z., Wafer-Level Photocatalytic Water Splitting on GaN Nanowire Arrays Grown by Molecular Beam Epitaxy. *Nano Lett.* **2011**, *11*, 2353-2357.
105. Kibria, M. G.; Nguyen, H. P. T.; Cui, K.; Zhao, S.; Liu, D.; Guo, H.; Trudeau, M. L.; Paradis, S.; Hakima, A.-R.; Mi, Z., One-Step Overall Water Splitting under Visible Light Using Multiband InGaN/GaN Nanowire Heterostructures. *ACS Nano* **2013**, *7*, 7886-7893.
106. Banerjee, S.; Mohapatra, S. K.; Misra, M., Synthesis of TaON Nanotube Arrays by Sonoelectrochemical Anodization Followed by Nitridation: a Novel Catalyst for Photoelectrochemical Hydrogen Generation from Water. *Chem. Commun.* **2009**, 7137-7139.
107. Higashi, M.; Domen, K.; Abe, R., Highly Stable Water Splitting on Oxynitride TaON Photoanode System under Visible Light Irradiation. *J. Am. Chem. Soc.* **2012**, *134*, 6968-6971.
108. Reece, S. Y.; Hamel, J. A.; Sung, K.; Jarvi, T. D.; Esswein, A. J.; Pijpers, J. J. H.; Nocera, D. G., Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts. *Science* **334**, 645-648.
109. Abdi, F. F.; Han, L.; Smets, A. H. M.; Zeman, M.; Dam, B.; Krol, R. v. d., Efficient Solar Water Splitting by Enhanced Charge Separation in a Bismuth Vanadate-Silicon Tandem Photoelectrode. *Nat. Comm.* **2013**, *4*, 2195.
110. Liu, C.; Tang, J.; Chen, H. M.; Liu, B.; Yang, P., A Fully Integrated Nanosystem of Semiconductor Nanowires for Direct Solar Water Splitting. *J. Am. Chem. Soc.* **2013**, *135*, 2989-2992.

Chapter 2

A Self-Biased Solar-Microbial Device for Sustainable Hydrogen Generation

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 TiO₂ 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 TiO₂ photoanode provided a photovoltage of ~0.7 V that shifted the potential of MFC bioanode to overcome the potential barrier for microbial electrohydrogenesis. As a result, under light illumination (AM 1.5G, 100 mW/cm²) 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.

2.1 Introduction

With the drastically 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 tons of wastewater is produced from industrial and agricultural operations each year, and about 25 billion US 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 matters in wastewater. This can be achieved by microbial fuel cell (MFC) technology. MFCs are bio-electrochemical 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 microbial electrohydrogenesis process has been experimentally demonstrated using a wide range of microorganisms with various organic nutrients, thermodynamics constraints limit microbial electrogensiss and hydrogen production occur simultaneously without the addition of an external bias.⁸ To overcome the thermodynamic constrains 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 are 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 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.

2.2 Experimental Section

2.2.1 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%) 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).

2.2.2 Synthesis of TiO_2 Nanowire Arrays

The synthesis of rutile TiO_2 nanowire arrays was based on a hydrothermal method reported previously.²³ 15 mL concentrated hydrochloric acid was mixed with 15 mL deionized water under stirring, follow by the addition of 0.475 mL 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 conducting side facing down. The autoclave was heated at 150 °C in the electric oven for 5 h and then cooled down to room temperature. The substrate was then washed with deionized water, and air-dried. The substrate was covered with a white film of TiO₂ 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 ultra-pure hydrogen gas at a flow rate of 50 sccm) at 350 °C for 3 h.

2.2.3 *Material Characterization*

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

2.2.4 *Photoelectrochemical (PEC) Measurements*

Linear sweep voltammograms were measured in a two-electrode configuration with a platinum wire as counter electrode, and TiO₂ nanowire samples as working electrode, at a scan rate of 20 mV/s. 0.5 M Na₂SO₄ aqueous solution (pH 7.0) was used as electrolyte. TiO₂ photoanodes were fabricated by soldering a copper wire onto the bare edge of FTO glass substrate, and then sealing the FTO glass substrate and metal contact region with insulating epoxy resin. The exposed effective area for the TiO₂ working electrode is 0.15-0.2 cm². 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/cm². 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 gas-tight 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).

2.2.5 *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 fresh catholyte solution, 50 mM ferricyanide in 100 mM phosphate buffer (K₂HPO₄ 18.2 g/L, KH₂PO₄ 2.56 g/L, K₃Fe(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 air cathode, water was used as the catholyte, and oxygen dissolved in water was used as 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 was the voltage and R was 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 was the Faraday's constant (96,500 C/mol), b was 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 were 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.²⁴

2.3 Results and Discussion

The configuration of PEC-MFC device is illustrated in Figure 2.1a. 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 bio-electrons, which are then transferred to the Pt counter of the PEC and reduce protons to hydrogen gas. Figure 2.1b 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 MFC bioanode can reduce protons in the PEC chamber. Distinct from a conventional PEC that uses photo-excited 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 bioanode, so that microbial electrohydrogenesis can be realized at zero external bias.

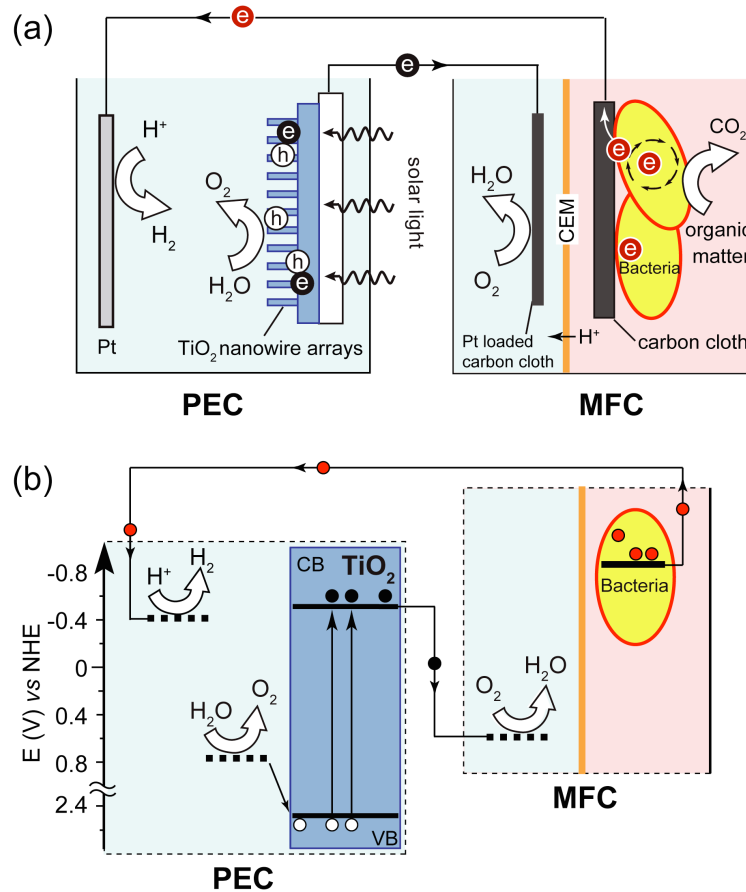


Figure 2.1 (a) Schematic configuration of a PEC-MFC device. (b) Corresponding energy diagram illustrates the carrier generation and transfer in this hybrid device. CB and VB are respective initials for conduction band and valence band. Solid and empty dots represent electrons and holes, respectively. Black and red dots highlight the electrons generated from TiO₂ photoanode and bacteria, respectively. Dashed lines represent the H⁺/H₂, H₂O/O₂ and O₂/H₂O 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 PEC device, we used TiO₂ nanowires as the photoanode material, because it is a preferred electrode material for PEC water oxidation,²⁵⁻²⁹ due to its favorable band-edge positions, excellent chemical stability and low cost. In addition, its one-dimensional structure provides extremely large

surface area for PEC water oxidation. Dense and vertically aligned TiO₂ nanowire arrays were grown on fluorine-doped tin oxide (FTO) coated glass substrate by hydrothermal synthesis.³⁰ X-ray diffraction (XRD) data collected from TiO₂ nanowire film can be indexed to the characteristic peaks of tetragonal rutile TiO₂ (JCPDS, No. 88-1175) (Figure 2.2a). Scanning electron microscopy (SEM) images collected from the growth substrate revealed a high-density growth of TiO₂ nanowire arrays (Figure 2.2b). The nanowires have an average diameter of 100-200 nm and an average length of 2-3 μ m. PEC performance of the TiO₂ nanowire films were measured in a 0.5 M Na₂SO₄ aqueous solution (pH 7.0) in a two-electrode configuration using electrochemical station coupled with a solar simulator, with a Pt wire as the counter electrode. As shown in Figure 2.2c, the TiO₂ nanowire photoanode showed pronounced photo-response under 1-sun illumination (AM 1.5, 100 mW/cm²). At zero external bias (0 V vs. Pt), the PEC device yielded a photocurrent density of 0.013 mA/cm², and no gas generation was observed at either electrode due to such low gas evolution efficiency.

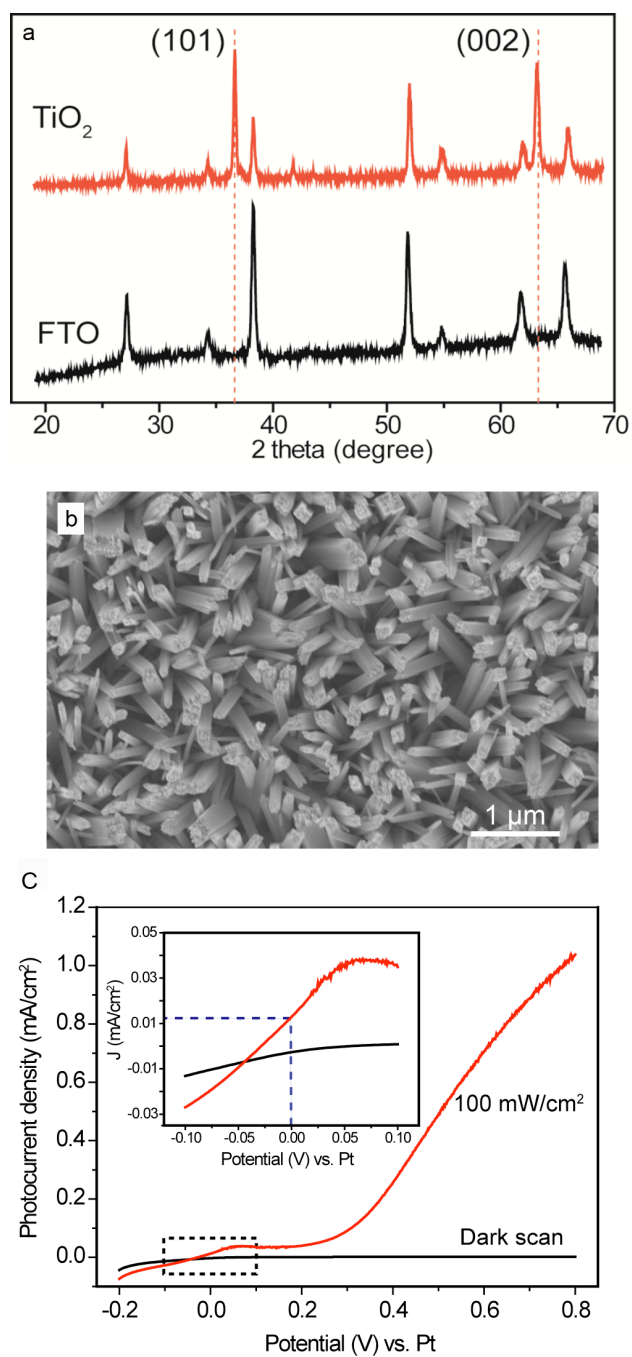


Figure 2.2 (a) XRD spectra collected for the TiO₂ nanowire film grown on the FTO substrate and blank FTO substrate control without the nanowire. The two diffraction peaks centered at 2θ angles of 36.5° and 63.2° (highlighted by dashed lines) are indexed to be tetragonal rutile TiO₂ (JCPDS, No. 88-1175). (b) SEM image of TiO₂ nanowire arrays grown on a FTO substrate. (c) Linear sweep voltammogram

collected for TiO₂ nanowire-arrayed photoanode in a 0.5 M Na₂SO₄ aqueous solution in the dark and under illumination (150 W xenon lamp coupled with AM 1.5G filter, 100 mW/cm²), at a scan rate of 20 mV/s. Inset: Magnified linear sweep voltammogram around zero bias.

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 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 - 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 2.3 and Experimental Method). In each feeding cycle, a current of 0.1-0.6 mA was generated, which lasted for c.a. 20 h before decreasing to the baseline (Figure 2.3). Replenishment of fresh TSB medium led to a drastic current restoration, and bioelectricity generation sustained for another 20 h.

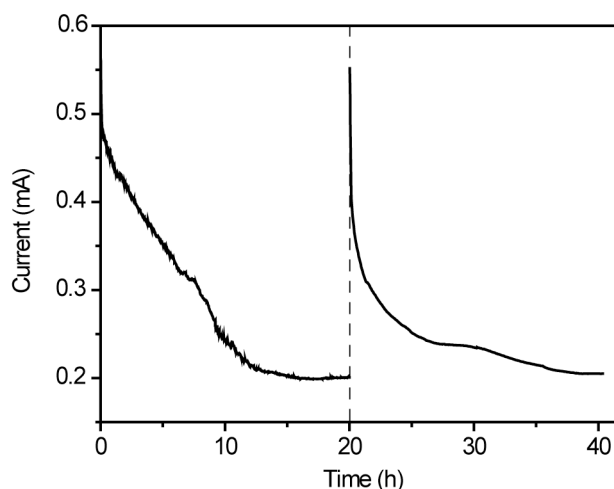


Figure 2.3 Current vs. time plot collected for a representative dual-chamber MFC, with *Shewanella oneidensis* MR-1 in TSB medium as anolyte and buffered ferricyanide as catholyte, operated in a batch-fed

mode, showing sustainable current generation in response to substrate addition at 20 h.

Polarization and power characterization revealed these MFCs worked in the ohmic region and generated a peak power of 50 μW at a current of 0.3 mA (Figure 2.4a). SEM images of the bioanode after a few days operation revealed MR-1 cells grew on the carbon cloth electrode (Figure 2.4b).

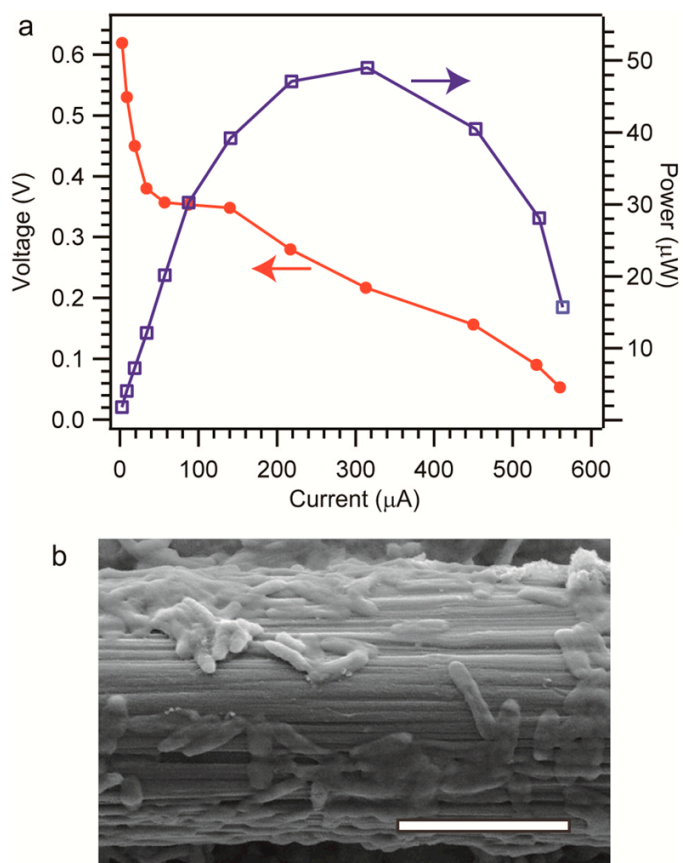


Figure 2.4 (a) Polarization (red symbol) and power (blue symbol) curves collected from a typical ferricyanide-cathode MFC device inoculated with MR-1. (b) SEM image of a carbon cloth electrode colonized by MR-1. Scale bar is 5 μm .

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 TiO₂ photoanode (light projected area of 1.5 ~ 2.0 cm²), respectively (Figure 2.1a). Figure 2.5a 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/cm² at zero bias (0 V vs. Pt), which is substantially larger than the value of 0.013 mA/cm² obtained for the PEC alone at the same potential. Figure 2.5b shows the amperometric *I-t* curves recorded for the PEC and PEC-MFC devices at 0 V vs. 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 TiO₂ electrode and the electrolyte at zero bias.³¹ 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, illuminated TiO₂ photoanode provided a photovoltage that shifted the potential of the MFC bioanode to a more negative value, and therefore, microbial electrohydrogenesis can occur at zero external bias (bio-electrons 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

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

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/cm² (AM 1.5G). This hybrid device exhibits an STH conversion efficiency of 1.54% at 0 V vs. Pt. Considering the fact that the theoretical STH efficiency of rutile TiO₂ 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 TiO₂ electrode. More importantly, gas bubbles were observed continuously evolving on both Pt electrode and TiO₂ 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 H₂ (Figure 2.6). We were not able to quantify the H₂/O₂ ratio due to the limitation of instrument. Figures 2.5c and 2.5d show the plots of gas volume produced (mixture of H₂ and O₂) and current (0 V vs. Pt) as a function of time, respectively. Within the initial 5 hours, the gas volume increased rapidly with the increase of PEC-MFC device current; the gas production slowed down 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 hours, the current decreased to baseline and the gas production ceased. Based on these results,

we unambiguously demonstrated hydrogen generation from a self-biased, PEC-MFC device.

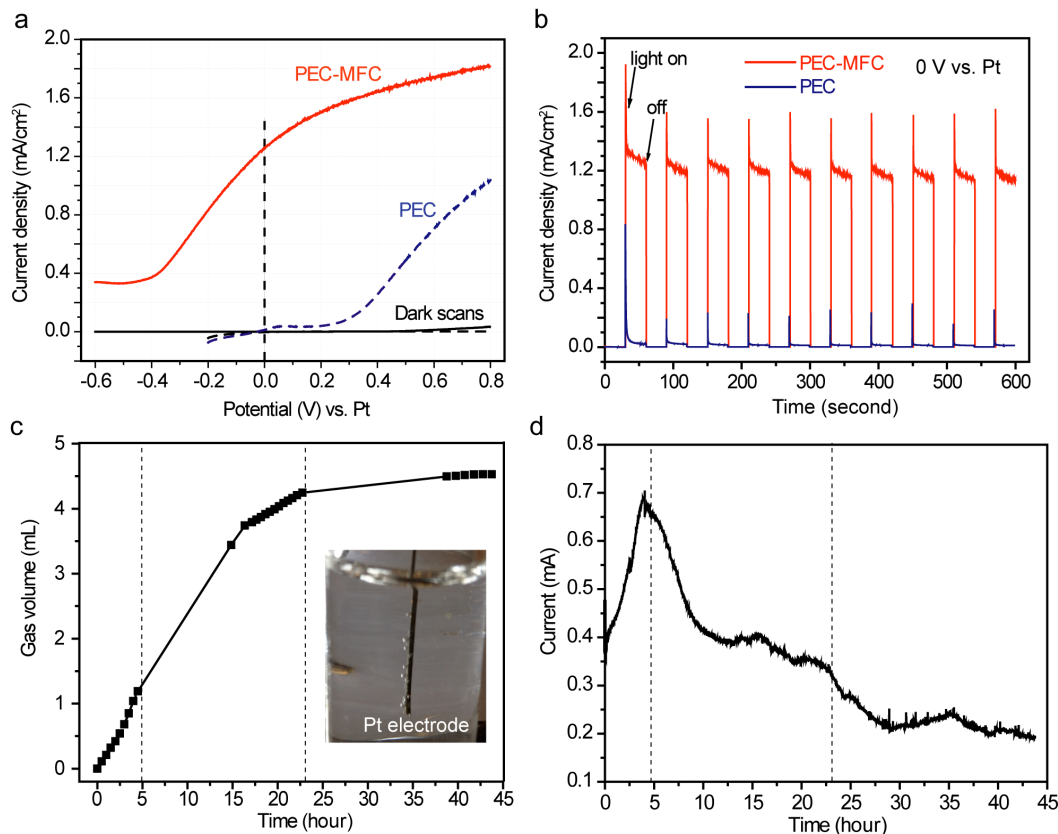


Figure 2.5 (a) Linear sweep voltammograms collected from a PEC device (blue line) and a PEC-MFC device (red line), at a scan rate of 20 mV/s in the dark (black lines) and under white light illumination (AM 1.5G, 100 mW/cm^2). The MFC device consists of a MR-1 colonized bioanode inoculated in TSB growth 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) The 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) The corresponding current-time profile obtained for the PEC-MFC device during gas collection.

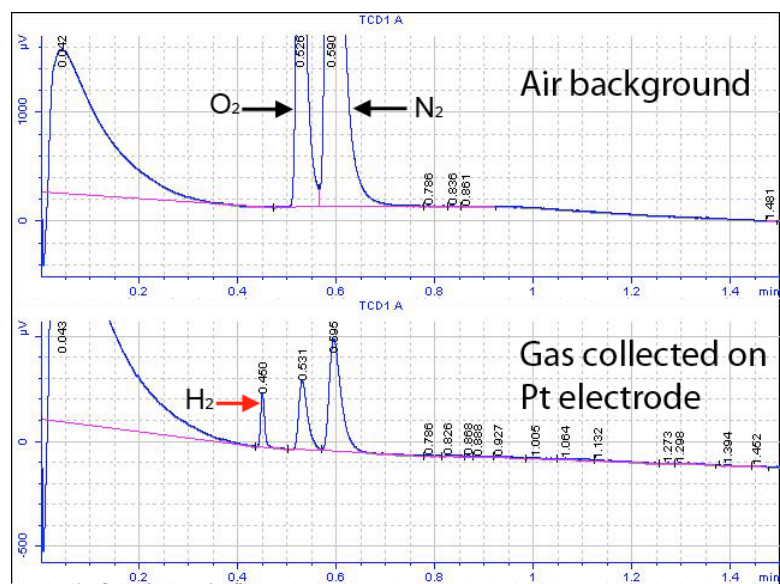


Figure 2.6 GC profiles collected from a blank air sample and the gas collected on the Pt electrode. Note that the N₂ and O₂ background signals are always present in the GC system and the injection of H₂ gas sample did not change the N₂/O₂ ratio.

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 demonstrated in a variety of air-cathode MFCs.^{32, 33} Using an air-cathode MFC eliminates the need of chemicals (e.g., ferricyanide), and therefore can increase sustainability, reduce cost, and minimize 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/cm², Fuel Cell Earth, LLC, Stoneham, MA) as cathode to increase the efficiency of oxygen reduction (Figure 2.7).

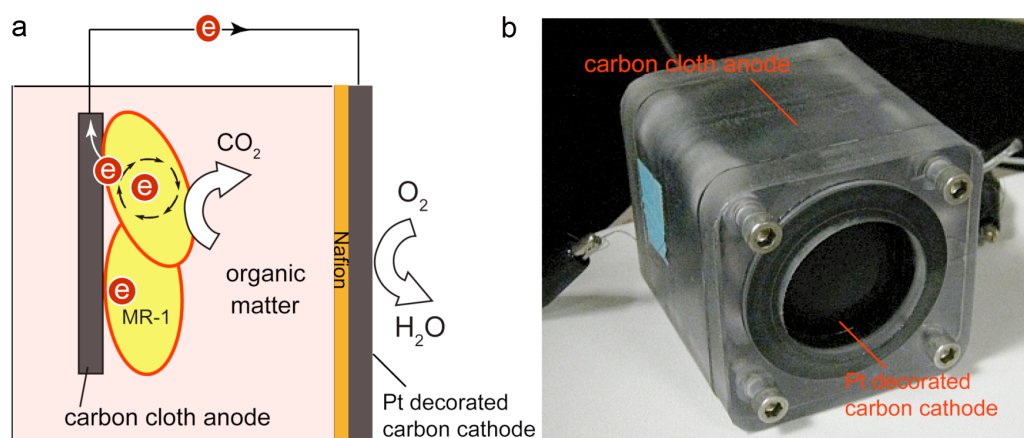


Figure 2.7 Schematic diagram (a) and photograph (b) of an air-cathode MFC device using MR-1 cells. The carbon cloth was used as the anode (the area of the carbon cloth anode was about 70 cm²), and carbon cloth with 40% Pt (0.5 mg/cm²) was used as the cathode.

The MFC was inoculated with MR-1 cells and fed with TSB medium. Linear sweep voltammograms were collected for air-cathode PEC-MFC device in the dark and under 1 sun illumination (Figure 2.8a). 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 *vs.* Pt under light illumination. Figure 2.8b 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 nutrient 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 bio-anode. 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.

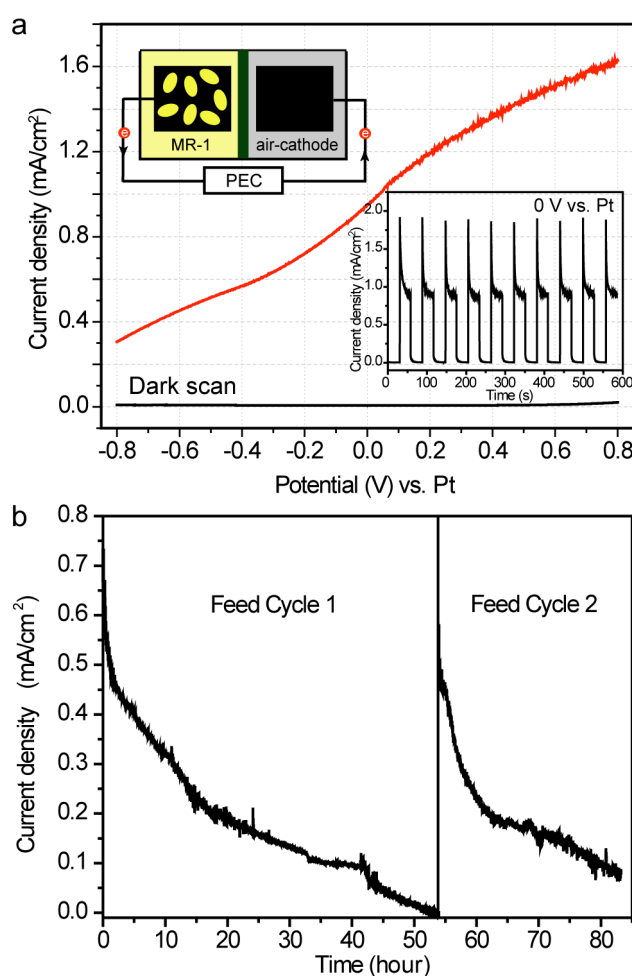


Figure 2.8 (a) Linear sweep voltammograms collected from a PEC-MFC device with air-cathode and with *S. oneidensis* MR-1 in TSB medium, at a scan rate of 20 mV/s in the dark and under white light illumination of 100 mW/cm^2 . Insets: schematic diagram of the PEC-

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) The 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/cm².

Based on 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 on with wastewater in the dark and under light illumination of 100 mW/cm² (Figure 2.9a). Significantly, the device also showed pronounced current at 0 V *vs.* Pt, indicative of efficient supply of bioelectrons from the wastewater MFC (Figure 2.9b). By using wastewater as anolyte, the PEC-MFC showed reduced current in comparison to the device with MR-1 in TSB anolyte, at the same potential, which could be attributed to the relatively large electrolyte resistance (low conductivity) of the wastewater.³⁴ More importantly, we observed continuous evolution of H₂ bubbles from the Pt electrode at 0 V *vs.* Pt under light illumination. Figures 2.6c and 2.6d show 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 decrease 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 operating for ~48 hours, the SCOD value decreased to ~200 mg/L. This yielded a Coulombic efficiency of 64%, which is comparable to previously reported wastewater MFCs with Coulombic efficiency ranging from 40 to 90%.³⁵ Taken together, we demonstrate the non-biased and sustainable microbial electrohydrogenesis process by coupling MFC and PEC 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.

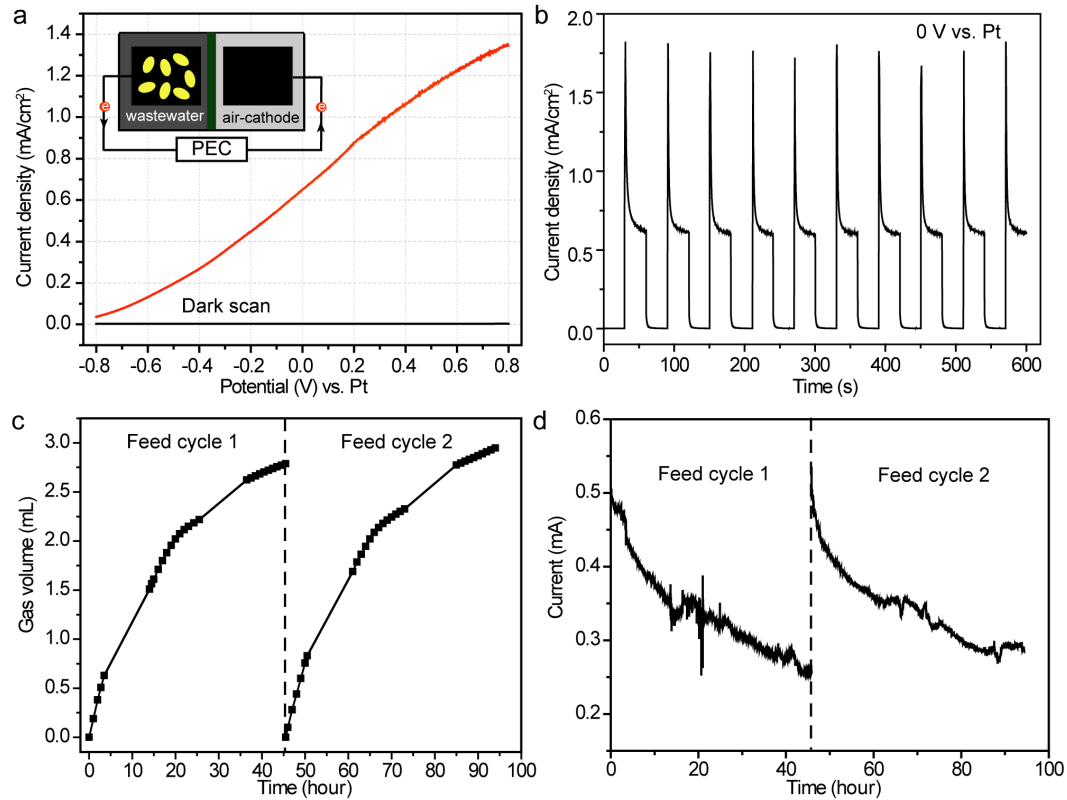


Figure 2.9 (a) Linear sweep voltammogram collected for PEC-MFC device with air-cathode and wastewater as anolyte, at a scan rate of 20 mV/s in the dark and under white light illumination of 100 mW/cm². Insets: schematic diagram of the PEC-MFC device. (b) Amperometric *I-t* curve recorded for the PEC-MFC device at 0 V *vs.* Pt with light on-off cycles. (c) and (d) Plot of gas production and current generation of the PEC-MFC device operated at 0 V *vs.* Pt as a function of time.

2.4 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 of 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.

Reference

1. Dentel, S. K.; Strogen, B.; Chiu, P., Direct Generation of Electricity from Sludges and Other Liquid Wastes. *Water Sci. Technol.* **2004**, *50*, 161-168.
2. Logan, B. E.; Hamelers, B.; Rozendal, R.; Schroder, U.; Keller, J.; Freguia, S.; Aelterman, P.; Verstraete, W.; Rabaey, K., Microbial Fuel Cells: Methodology and Technology. *Environ. Sci. Technol.* **2006**, *40*, 5181-5192.
3. Berk, R. S.; Canfield, J. H., Bioelectrochemical Energy Conversion. *Appl. Microbiol.* **1964**, *12*, 10-12.
4. Davis, J. B.; Yarbrough, H. F., Preliminary Experiments on a Microbial Fuel Cell. *Science* **1962**, *137*, 615-616.
5. Yuan, S. J.; Sheng, G. P.; Li, W. W.; Lin, Z. Q.; Zeng, R. J.; Tong, Z. H.; Yu, H. Q., Degradation of Organic Pollutants in a Photoelectrocatalytic System Enhanced by a Microbial Fuel Cell. *Environ. Sci. Technol.* **2010**, *44*, 5575-5580.
6. Wang, G.; Qian, F.; Saltikov, C. W.; Jiao, Y.; Li, Y., Microbial Reduction of Graphene Oxide by *Shewanella*. *Nano Res.* **2011**, *4*, 563-570.
7. Jiao, Y.; Qian, F.; Li, Y.; Wang, G.; Saltikov, C. W.; Granick, J. A., Deciphering the Electron Transport Pathway for Graphene Oxide Reduction by *Shewanella Oneidensis* MR-1. *J. Bacteriol.* **2011**, *193*, 3662-3665.
8. Cheng, S.; Logan, B. E., Sustainable and Efficient Biohydrogen Production via Electrohydrogenesis. *Proc. Natl. Acad. Sci.* **2007**, *104*, 18871-18873.
9. Liu, H.; Grot, S.; Logan, B. E., Electrochemically Assisted Microbial Production of Hydrogen from Acetate. *Environ. Sci. Technol.* **2005**, *39*, 4317-4320.
10. Zhang, X.; Sun, H.; Liang, P.; Huang, X.; Chen, X.; Logan, B. E., Air-Cathode Structure Optimization in Separator-Coupled Microbial Fuel Cell. *Biosens. Bioelectron.* **2011**, *30*, 267-271.
11. Hu, H.; Fan, Y.; Liu, H., Hydrogen Production Using Single-Chamber Membrane-Free Microbial Electrolysis Cells. *Water Res.* **2008**, *42*, 4172-4178.
12. Xiao, L.; Damien, J.; Luo, J.; Jang, H. D.; Huang, J.; He, Z., Crumpled Graphene Particles for Microbial Fuel Cell Electrodes. *J. Power Sources* **2012**, *208*, 187-192.

13. Hays, S.; Zhang, F.; Logan, B. E., Performance of Two Different Types of Anodes in Membrane Electrode Assembly Microbial Fuel Cells for Power Generation from Domestic Wastewater. *J. Power Sour.* **2011**, *196*, 8293-8300.
14. Xie, X.; Ye, M.; Hu, L.; Liu, N.; McDonough, J. R.; Chen, W.; Alshareef, H. N.; Criddle, C. S.; Cui, Y., Carbon Nanotube-Coated Macroporous Sponge for Microbial Fuel Cell Electrodes. *Energy Environ. Sci.* **2012**, *5*, 5265-5270.
15. Xie, X.; Yu, G.; Liu, N.; Bao, Z.; Criddle, C. S.; Cui, Y., Graphene-Sponges as High-Performance Low-Cost Anodes for Microbial Fuel Cells. *Energy Environ. Sci.* **2012**, *5*, 6862-6866.
16. Wang, X.; Cheng, S.; Zhang, X.; Li, X.-Y.; Logan, B. E., Impact of Salinity on Cathode Catalyst Performance in Microbial Fuel Cells (MFCs). *Int. J. Hydrogen Energy* **2011**, *36*, 13900-13906.
17. Selembo, P. A.; Merrill, M. D.; Logan, B. E., Hydrogen Production with Nickel Powder Cathode Catalysts in Microbial Electrolysis Cells. *Int. J. Hydrogen Energ.* **2010**, *35*, 428-437.
18. Chae, K. J.; Choi, M. J.; Kim, K. Y.; Ajayi, F. F.; Chang, I. S.; Kim, I. S., A Solar-Powered Microbial Electrolysis Cell with a Platinum Catalyst-Free Cathode to Produce Hydrogen. *Environ. Sci. Technol.* **2009**, *43*, 9525-9530.
19. Sun, M.; Sheng, G. P.; Zhang, L.; Xia, C. R.; Mu, Z. X.; Liu, X. W.; Wang, H. L.; Yu, H. Q.; Qi, R.; Yu, T., An MEC-MFC-Coupled System for Biohydrogen Production from Acetate. *Environ. Sci. Technol.* **2008**, *42*, 8095-8100.
20. Wang, A.; Sun, D.; Cao, G.; Wang, H.; Ren, N.; Wu, W.-M.; Logan, B. E., Integrated Hydrogen Production Process from Cellulose by Combining Dark Fermentation, Microbial Fuel Cells, and a Microbial Electrolysis Cell. *Bioresource Technol.* **2011**, *102*, 4137-4143.
21. Qian, F.; Wang, G.; Li, Y., Solar-Driven Microbial Photoelectrochemical Cells with a Nanowire Photocathode. *Nano Lett.* **2010**, *10*, 4686-4691.
22. Lu, A.; Li, Y., Light Fuel Cell (LFC): A Novel Device for Interpretation of Microorganisms-Involved Mineral Photochemical Process. *Geomicrobiology Journal* **2012**, *29*, 236-243.
23. Liu, B.; Aydil, E. S., Growth of Oriented Single-Crystalline Rutile TiO₂ Nanorods on Transparent Conducting Substrates for Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2009**, *131*, 3985-3990.

24. American Public Health Association; America Water Works Association; Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 20th edn. American Public Health Association: Washington, DC, **1998**.
25. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, 238, 37-38.
26. Khan, S. U. M.; Al-shahry, M.; Ingler Jr., W. B., Efficient Photochemical Water Splitting by a Chemically Modified n-TiO₂. *Science* **2002**, 297, 2243-2245.
27. Lin, Y.; Zhou, S.; Liu, X.; Sheehan, S.; Wang, D., TiO₂/TiSi₂ Heterostructures for High-Efficiency Photoelectrochemical H₂O Splitting. *J. Am. Chem. Soc.* **2009**, 2772-273.
28. Mor, G. K.; Varghese, O. K.; Wilke, R. H. T.; Sharma, S.; Shankar, K.; Latempa, T. J.; Choi, K.-S.; Grimes, C. A., p-Type Cu-Ti-O Nanotube Arrays and Their Use in Self-Biased Heterojunction Photoelectrochemical Diodes for Hydrogen Generation. *Nano Lett.* **2008**, 8, 1906-1911.
29. Zhou, H.; Qu, Y.; Zeid, T.; Duan, X., Towards Highly Efficient Photocatalysts Using Semiconductor Nanoarchitectures. *Energy Environ. Sci.* **2012**, 5, 6732-6743.
30. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated TiO₂ Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, 11, 3026-3033.
31. Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P., Nanowire Dye-Sensitized Solar Cells. *Nat. Mater.* **2005**, 4, 455-459.
32. Liu, H.; Logan, B. E., Electricity Generation Using an Air-Cathode Single Chamber Microbial Fuel Cell in the Presence and Absence of a Proton Exchange Membrane. *Environ. Sci. Technol.* **2004**, 38, 4040-4046.
33. Park, D. H.; Zeikus, J. G., Improved Fuel Cell and Electrode Designs for Producing Electricity from Microbial Degradation. *Biotechnol. Bioeng.* **2003**, 81, 348-355.
34. Huang, L.; Logan, B. E., Electricity Generation and Treatment of Paper Recycling Wastewater Using a Microbial Fuel Cell. *Appl. Microbiol. Biotechnol.* **2008**, 80, 349-355.
35. Du, Z.; Li, H.; Gu, T., A state of the Art Review on Microbial Fuel Cells: A Promising Technology for Wastewater Treatment and Bioenergy. *Biotechnol. Adv.* **2007**, 25, 464-482.

Chapter 3

High Power Density Microbial Fuel Cell with Flexible 3D Graphene-Nickel

Foam as Anode

Abstract

The structure and electrical conductivity of anode play a significant role in the power generation of microbial fuel cells (MFCs). In this study, we developed a three-dimensional (3D) reduced graphene oxide-nickel (denoted as rGO-Ni) foam as an anode for MFC through controlled deposition of rGO sheets onto the nickel foam substrate. The loading amount of rGO sheets and electrode surface area can be controlled by the number of rGO loading cycles. 3D rGO-Ni foam anode provides not only a large accessible surface area for microbial colonization and electron mediators, but also a uniform macro-porous scaffold for effective mass diffusion of the culture medium. Significantly, at a steady state of the power generation, the MFC device with flexible rGO-Ni electrodes produced an optimal volumetric power density of 661 W/m³ calculated based on the volume of anode material, or 27 W/m³ based on the volume of anode chamber. These values are substantially higher than that of plain nickel foam, and other conventional carbon based electrodes (e.g., carbon cloth, carbon felt, and carbon paper) measured in the same conditions. To our knowledge, this is the highest volumetric power density reported for mL-scale MFC device with pure strain of *Shewanella oneidensis* MR-1. We also demonstrated that the MFC device can be operated effectively in batch-mode at least for a week. These new 3D rGO-Ni electrodes show great promise for improving the power generation of MFC devices.

3.1 Introduction

Microbial fuel cells (MFCs) employ electrogenic bacteria to recover chemical energy stored in biodegradable organic materials to electrical energy via bio-oxidation process, which holds great potentials to simultaneously address the needs for energy regeneration and organic waste treatment.¹⁻⁵ However, the relatively low power output of MFCs restricts their practical application. A number of methods have been used in improving MFC power output, including optimization of microbial activities,^{6, 7} and MFC device configuration,⁸⁻¹¹ activation of cathode electrode by incorporating various catalysts such as Au,¹²⁻¹⁴ Pd,^{15, 16} and Ni,^{17, 18} as well as enhancement of effective surface area of both anode¹⁹⁻²³ and cathode. The rapid advancement of nanostructured electrodes opens up new opportunities in the development of high performance MFCs.

Carbon-based materials such as carbon cloth, carbon paper, carbon felt and graphite brush are most commonly used anode materials for MFCs.²⁴ These commercially available electrode materials are chemical inert, highly conductive and inexpensive. However, these microstructures have relatively small surface area for bacterial colonization, and thus, limit the power density of MFC device. Previous studies have demonstrated that the power density of MFC can be enhanced by modifying the electrodes with nanostructures to increase the accessible surface area for bacterial colonization. For example, carbon electrodes modified with Au and Pd nanoparticles shown improved power densities.²⁵ Roh *et al.* reported that the power density of carbon paper was improved by decorating it with multi-walled carbon

nanotube /polyacrylonitrile composite.²⁶ To further improve the performance of anode, 3D structures with potentially larger surface area are emerging as new electrode materials for MFCs. For instance, Higgins *et al.* reported the preparation of 3D chitosan-carbon nanotube scaffolds, with a pore size distribution between 10 μm and 120 μm , as MFC anode.²⁷ Xie *et al.* reported the fabrication of single-walled carbon nanotubes, graphene-coated textile,²⁸ and sponge^{29, 30} bio-electrodes for MFCs. Recently, Yong *et al.* developed a 3D conducting graphene-polyaniline scaffold as MFC anode.¹⁹ These MFC devices with 3D electrodes shown significantly enhanced power output and suggests the potential of 3D conducting scaffold for MFC electrodes.

Here, we report the fabrication of a flexible and high performance MFC anode by employing nickel foam as a 3D conducting scaffold and coated with reduced graphene oxide (rGO) sheets to increase its accessible surface area for bacteria colonization and electron mediators. Significantly, the rGO-nickel foam (denoted as rGO-Ni) anode produced a remarkable volumetric power density of 661 W/m^3 (27 W/m^3) at a stable state of power generation, calculated based on the volume of anode material (based on the anode chamber volume). These values are substantially higher than that of plain nickel foam, and conventional carbon based electrodes (e.g., carbon cloth, carbon felt and carbon paper) electrodes measured in the same conditions.

3.2 Experimental Section

3.2.1 Preparation of Graphene Oxide (GO)

GO was prepared from graphite powder using Hummer's method. Graphite powder (0.5 g) was mixed with 23 mL concentrated H_2SO_4 and 10 mL concentrated HNO_3 in a container that was cooled in an ice bath. KMnO_4 (3 g) was slowly added to the mixture. After the addition of KMnO_4 , the solution was heated at 35 °C for 3 h, and then diluted with 40 mL of deionized water. After 12 hours, the solution was further diluted by adding an additional 200 mL of deionized water, followed by slow addition of 3.0 mL of H_2O_2 (30% v/v). The solution with black graphite suspension was gradually converted into a bright yellow graphite oxide solution. The precipitate of graphite oxide was isolated by centrifugation at 1500 rpm for 30 min, and washed with deionized water, and then re-suspended in 500 mL deionized water. The concentration of the graphite oxide solution is ~ 1 mg/mL. The aqueous graphite oxide solution was vigorously sonicated for 2-4 h to exfoliate stacked graphite oxide sheets into monolayer or multi-layered GO sheets.

3.2.2 Deposition of rGO Sheets onto Nickel Foam

A nickel foam substrate was transferred into an autoclave (with Teflon liner) filled with 25 mL aqueous GO solution. The autoclave was heated at 120 °C for 5 hrs and allowed it to cool down at room temperature. The yellowish nickel foam substrate turned into black color (covered with rGO sheets). The substrate was then washed with deionized water, and then air-dried. To improve the electrical conductivity of

rGO sheets, the rGO-Ni substrate was annealed at 400 °C in hydrogen atmosphere in a home-built quartz tube furnace for 30 minutes.

3.2.3 Fabrication of MFC Anode

rGO-Ni composite anodes were fabricated by attaching a Ti wire (the diameter of Ti wire is 0.25 mm) onto the Ni foam substrate by silver conductive epoxy (Ted Pella, Inc., Redding, CA). Carbon felt (GF-S6, Electrolytica, Inc., Amherst, NY), carbon paper (SGL Group, Germany), and carbon cloth (CC6 Plain, Fuel Cell Earth LLC, Stoneham, MA) electrodes were fabricated by directly attaching a Ti wire onto the carbon-based substrates. The projected areas of all anodes are in the range of 7-10 cm². The thickness of rGO-Ni electrodes is 1 mm. The thickness of carbon felt electrodes is 6 mm. The thickness of carbon paper and carbon cloth electrodes is 0.5 mm.

3.2.4 *Shewanella oneidensis* MR-1 Bacterial Culture and MFC Operation

Shewanella oneidensis MR-1 (ATCC 700550) was cultured in trypticase soy broth (TSB) (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). 25 mL solution of 50 mM ferricyanide in 100 mM phosphate buffer (K₂HPO₄ 18.2 g/L, KH₂PO₄ 2.56 g/L, K₃Fe(CN)₆ 15.6 g/L, pH 7.4) was used as catholyte. The voltage of MFC device across an external resistor (1000 Ω) was monitored using a precision multimeter/data acquisition system (2700, Keithley, OH). When the current dropped to the baseline level, fresh TSB medium was slowly

injected into the anode chamber via a sterile syringe. The current (I) generated in MFC was calculated according to Ohm's law, $I = V/R$, where V was the voltage and R was the external resistor. The power was then calculated as $P = V \times I$. The power densities were calculated based on the volume of the electrodes or the volume of anode chamber (~25 mL).

3.2.5 Methylene Blue Absorption Measurement

The initial concentration of the MB aqueous solution was 2 mg/L. The plain nickel foam and rGO-X-Ni composite foams were immersed separately in MB aqueous solution. The solutions were stirred in the dark for 24 hrs to allow reaching absorption-desorption equilibrium. Then, the substrates were removed from the MB solutions. Absorption spectra were collected for the original and these MB solutions using an ATI Unicam UV4 spectrometer by using a 1-cm quartz cuvette with a resolution of 2 nm.

3.2.6 Electrochemical Impedance Spectroscopy (EIS)

The electrochemical characterization was carried out on CHI 660D electrochemical station using impedance-potential technique under whole cell conditions. EIS measurements were conducted in a two-electrode mode by recording the impedance spectrum of the anode as working electrode, with the cathode acting as a counter electrode and reference electrode. The impedance spectra were collected at the open-circuit potential by applying a sine wave (5 mV) at a frequency range from 1000 kHz to 10 mHz. The data was analyzed using ZView by fitting the EIS spectra with an equivalent circuit.

3.2.7 Material Characterization

SEM images were collected by a field-emission SEM (Hitachi S-4800 II). XPS analysis was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) using Mg-monochromatic X-ray at a power of 25 W with an X-ray-beam diameter of 10 mm, and a pass energy of 29.35 eV. The pressure of analyzer chamber was maintained below 5×10^{-8} Pa during the measurement. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as reference.

3.3 Results and Discussion

rGO-Ni anodes were prepared by refluxing a nickel foam substrate (45-103, Lyrus New Material) in an aqueous graphene oxide (GO) solution at 120 °C in an autoclave (Figure 3.1a), followed by annealing in hydrogen atmosphere at 400 °C (Experimental Section). The conversion of GO into rGO by hydrothermal method has been reported elsewhere.²⁹ Scanning electron microscopy (SEM) image showed that the nickel foam is a continuous 3D scaffold with pore size in a range between 100 and 500 μm (Figure 3.1b). The large pore size allows bacteria colonization in the inner structure of the 3D electrode and efficient mass transfer of nutrient. The specific surface area of the nickel foam was estimated to be $\sim 3000 \text{ m}^2$ per cubic meter based on its weight and size of the framework. More importantly, it offers a continuous 3D highly conductive surface for rGO coating. We aimed to increase the accessible surface area for bacteria colonization and electron mediator through controlled loading rGO sheets on the nickel foam. After refluxing the nickel foam in GO solutions for 5 hrs, its color changed from yellowish silver to black. As shown in

Figure 3.1c, the entire nickel foam scaffold was covered with rGO sheets. rGO-Ni foams were further reduced in a hydrogen atmosphere at 400 °C in a home-built quartz tube furnace to increase their electrical conductivities. Previously studies has demonstrated that bio-electrons generated from bacteria can be effectively transferred to GO and rGO.^{31, 32} Therefore, the conductive rGO coating is expected to serve as a good electron transfer layer that could facilitate bacterial colonization and power generation.^{33, 34} Furthermore, the rGO-Ni foam preserves the excellent mechanical properties of the nickel skeleton. It is flexible and can be bent and folded into various shapes (Figure 3.1d), which enables it to fit in different MFC devices. Importantly, we did not observe fragmentation of rGO sheets when it was bent repeatedly, suggesting the affinity between rGO and nickel skeleton is strong and the composite structure is stable. Moreover, we have demonstrated the feasibility to scale up the fabrication of rGO-Ni electrode for large-scale MFC devices. Figure 3.1e shows a 25 cm × 20 cm rGO-Ni foam. The electrode size can be further increased, and practically it is only limited by the size of container for refluxing process.

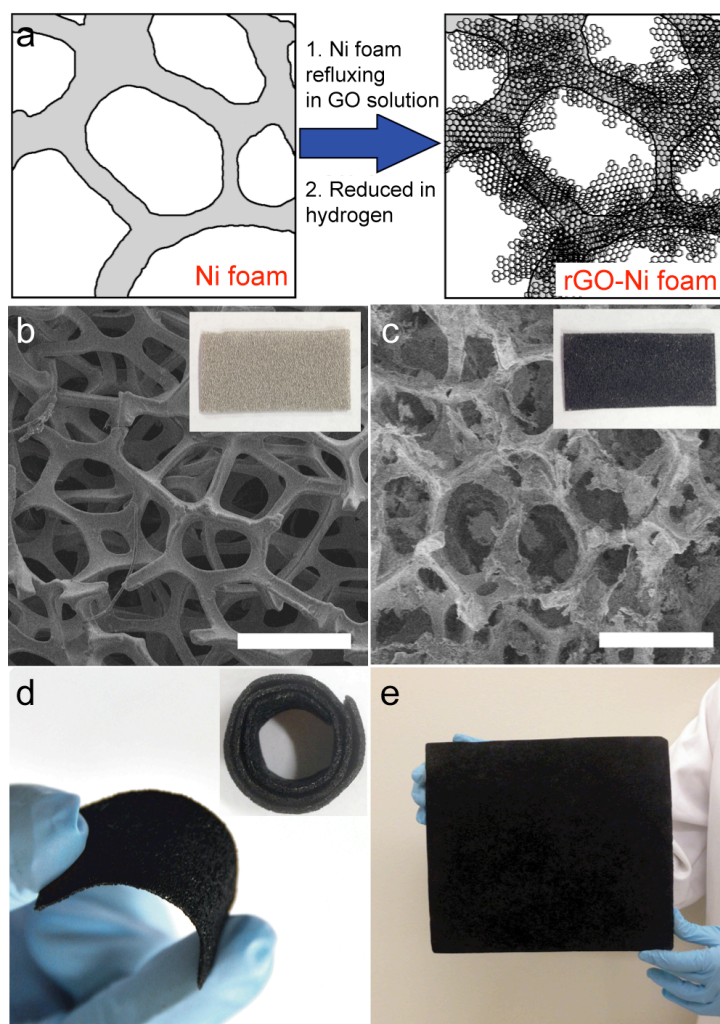


Figure 3.1 (a) A schematic diagram illustrates the preparation of rGO-Ni anode. (b,c) SEM images and digital pictures (insets) of plain nickel foam and rGO-Ni foam. Scale bars are 200 μm . (d) Digital picture of a curved rGO-Ni foam. Inset: rGO-Ni foam rolled up into a cylindrical shape. (e) Digital picture of a 25 cm $\times$ 20 cm rGO-Ni foam.

The capability of developing a highly conductive electrode with large effective surface area is essential to the success of developing a high-performance bioanode. To characterize the chemical nature of rGO coating, core level C 1s X-ray photoelectron spectroscopy (XPS) spectra were collected for rGO-Ni structures before and after hydrogen reduction. As shown in Figure 3.2 rGO sheets before

hydrogenation showed a broad peak centered at 284.8 eV with a shoulder at higher binding energy, which suggests the existence of more than one chemical state of carbon.³⁵ The broad peak was deconvoluted into four peaks. The main peak at 284.7 eV can be attributed to the graphite-like sp^2 hybridized carbon, indicating most carbon atoms are arranged in honeycomb lattice.³⁶ The synthetic peak centered at 285.5 eV is consistent with the sp^3 hybridization of C-C or C-H bonds.³⁷ Small peaks located at the high-energy tail (286.2 eV and 288.9 eV) can be ascribed to the carbon signal in carbon-oxygen compounds such as C-O bond or carboxylate carbon (O-C=O), respectively.³⁸ Importantly, the intensity of the signals associated with C-O and O-C=O bonds dropped substantially upon hydrogenation, suggesting these surface oxygen containing groups have been reduced.

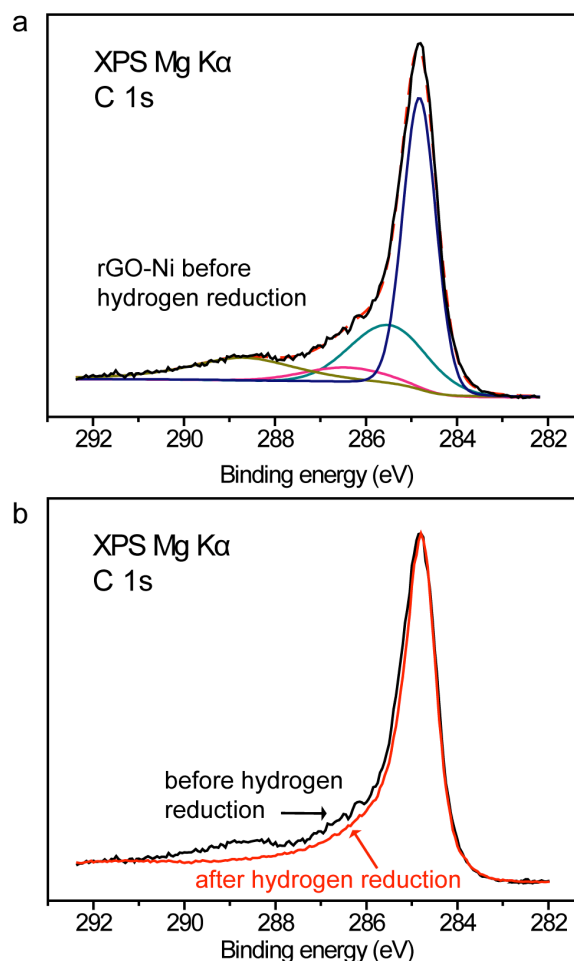


Figure 3.2 (a) XPS C 1s spectrum of rGO-Ni foam before hydrogen reduction. The black curve is the experimental result. The red dashed curve is the summation of four synthetic peaks centered at 284.7 eV (green curve), 285.5 eV (blue curve), 286.2 eV (pink curve), and 288.9 eV (yellow curve). (b) Normalized C 1s XPS spectra collected for rGO-Ni foam before and after hydrogen reduction.

Moreover, the electrode surface area is expected to be related to the loading amount of rGO sheets, which can be controlled by number of loading cycles. Nickel foam reflux in GO solution at 120 °C for 5 hrs is counted as one loading cycle. Figure 3.3 shows the SEM images collected for a plain nickel foam and rGO-X-Ni (X = the number of loading cycles) electrodes prepared with different number of loading

cycles. Before loading of rGO sheets, the nickel foam has a smooth surface (Figure 3.3a). After refluxing in GO solution, the nickel foam was covered with rGO sheets. The thickness and roughness of rGO coating increased with the number of loading cycles.

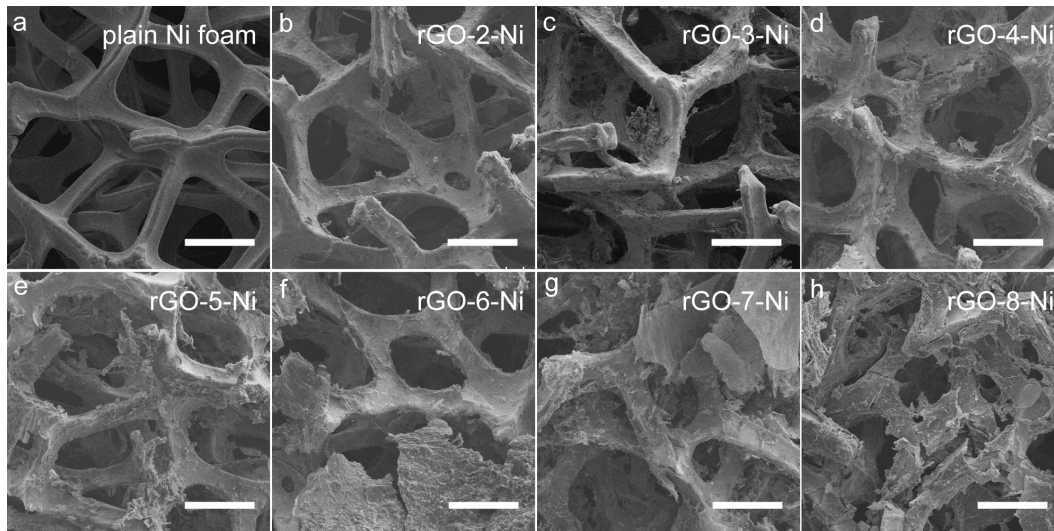


Figure 3.3 SEM images of (a) plain nickel foam, and (b-h) rGO-X-Ni (X = the number of loading cycles) foams. Scale bars are 200 μm .

Furthermore, the amount of rGO loading increases with the number of loading cycles as expected (Figure 3.4a). It is noteworthy that the deposition of rGO sheets did not significantly change the pore size, and thus, it seems not likely to affect the mass diffusion of bacterial culture medium. However, we observed that rGO-Ni electrodes became fragile after repeating the loading process for 6 times or above (Figure 3.4b). This could be due to the chemical dissolution of nickel in acidic GO aqueous solution (pH $\sim$ 5).

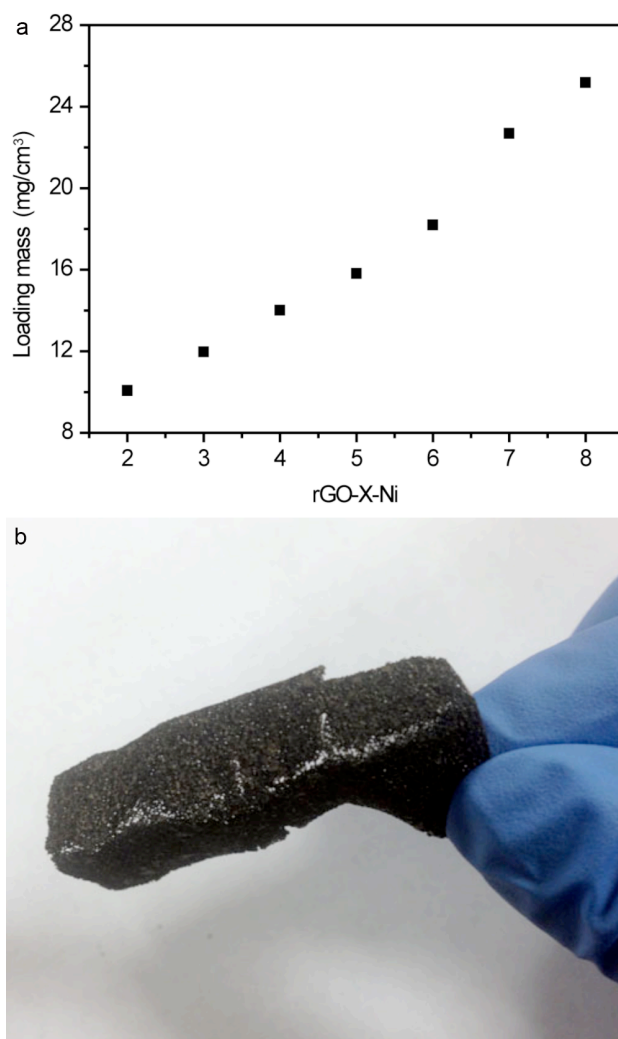


Figure 3.4 (a) The amount of rGO loading plots as a function of the number of loading cycles. (b) Digital picture shows the structurally collapsed rGO-8-Ni foam. rGO-Ni electrodes became fragile after repeating the loading process for 6 times or above due to the chemical dissolution of nickel in acidic GO aqueous solution (pH ~5).

To test our hypothesis that the effective electrode surface area can be increased by increasing the number of rGO loading cycles, we investigated the surface area for rGO-X-Ni structures. Since nickel substrate slowly dissolved in GO solution during the refluxing process, the quantitative determination of specific surface area for rGO-X-Ni electrodes by Brunauer-Emmett-Teller method is

impossible. Alternatively, we estimated the surface area of rGO-X-Ni electrodes by dye absorption experiment. Methylene blue (MB) is a dye that has been widely used for determining surface area of solid absorber.³⁹ The absorption measurements were started with a 2 mg/L MB aqueous solution. The plain nickel foam and rGO-X-Ni electrodes were immersed in the MB aqueous solution for 24 h. The solutions were stirred in the dark to establish an adsorption/desorption equilibrium for MB on the electrode surface. UV-vis absorption spectra collected for these solutions revealed characteristic absorption peaks of MB (Figure 3.5). More importantly, the absorption intensity (665 nm) decreases almost linearly with the increased number of loading cycles (Figure 3.5, inset). These results clearly support our hypothesis that the electrode surface area can be increased and controlled by the number of loading cycles.

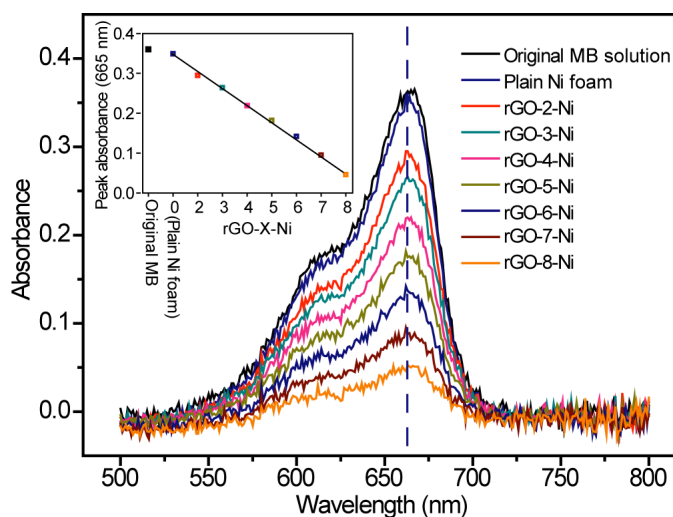


Figure 3.5 UV-vis absorption spectra collected for the original MB solution (2 mg/L in water) and the MB solutions after reacting with rGO-X-Ni foams for 24 hrs. Inset: The absorption peak intensity (665 nm, highlighted by dashed line) of rGO-X-Ni foams plot as a function

of number of rGO loading cycles. A line of best-fit by eye was drawn through the data points.

We investigated the interplay between the performance of rGO-X-Ni anode and the number of rGO loading cycles. rGO-X-Ni anodes were tested in a conventional, dual-chamber MFC device. The configuration of MFC device is illustrated in Figure 3.6a. The dual-chamber MFC devices were built with glass tubes jointed by a cation exchange membrane (CEM) (CMI 7000S, Membranes International Inc., Ringwood, NJ, USA). Each chamber had a liquid volume of ~25 mL. In anode chamber, pure strain of *Shewanella oneidensis* MR-1 (ATCC 700550) was inoculated in trypticase soy broth (TSB, BD Biosciences, San Jose, CA), which was supplied as growth medium. The cathode chamber was filled with ferricyanide phosphate buffer solution (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). The rGO-X-Ni foams with projected areas between 7 and 10 cm², and thickness of 0.1 cm were used as anodes. Carbon cloth substrates (the area of carbon cloth was about 70 cm², CC6 Plain, Fuel cell Earth LLC, Stoneham, MA) were used as cathode. An external resistor was connected to the anode and the cathode to complete the circuit, and the voltage generated in the MFC was monitored as a function of time. All rGO-X-Ni electrodes were measured using the same MFC device to eliminate the possible discrepancy due to device assembly. The MFCs were operated in batch mode at room temperature (~25 °C). SEM images collected for the bioanode after a few days operation revealed the colonization of MR-1 cells on the rGO sheets and formed a biofilm (Figure 3.6b). The magnified SEM image showed

that the rod-shaped bacteria have a typical diameter of 0.4-0.9 μm and length of 2-3 μm , which are consistent with previously reported values for MR-1.

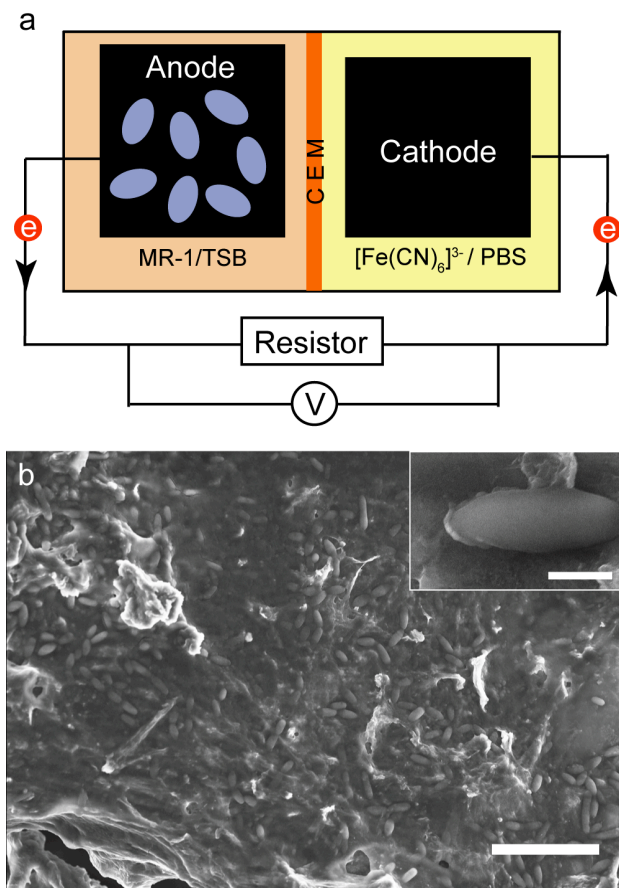


Figure 3.6 (a) A schematic diagram illustrating the configuration of dual-chamber MFC device with MR-1 colonized bioanode and carbon cloth cathode. The anode and cathode chamber was separated by a CEM. MR-1/TSB solution was used as anolyte and ferricyanide/PBS solution was used as catholyte. (b) SEM image of an rGO-Ni anode colonized by rod-shaped *S. oneidensis* MR-1. Scale bar is 20 μm . Inset: Magnified SEM image of a MR-1 bacterium. Scale bar is 1 μm .

The properties of rGO-X-Ni electrodes were investigated through constructing polarization and power curves by varying external resistors between 1 $\text{M}\Omega$ and 50 Ω . These results were compared to the device using plain nickel foam, and conventional anode materials, including carbon felt (GF-S6, Electrolytica, Inc., Amherst, NY),

carbon paper (SGL Group, Germany) and carbon cloth (CC6 Plain, Fuel Cell Earth LLC, Stoneham, MA) (Figure 3.7, Supporting Information). Volumetric power densities were calculated based on the volume of anode electrode when the device established a steady state.

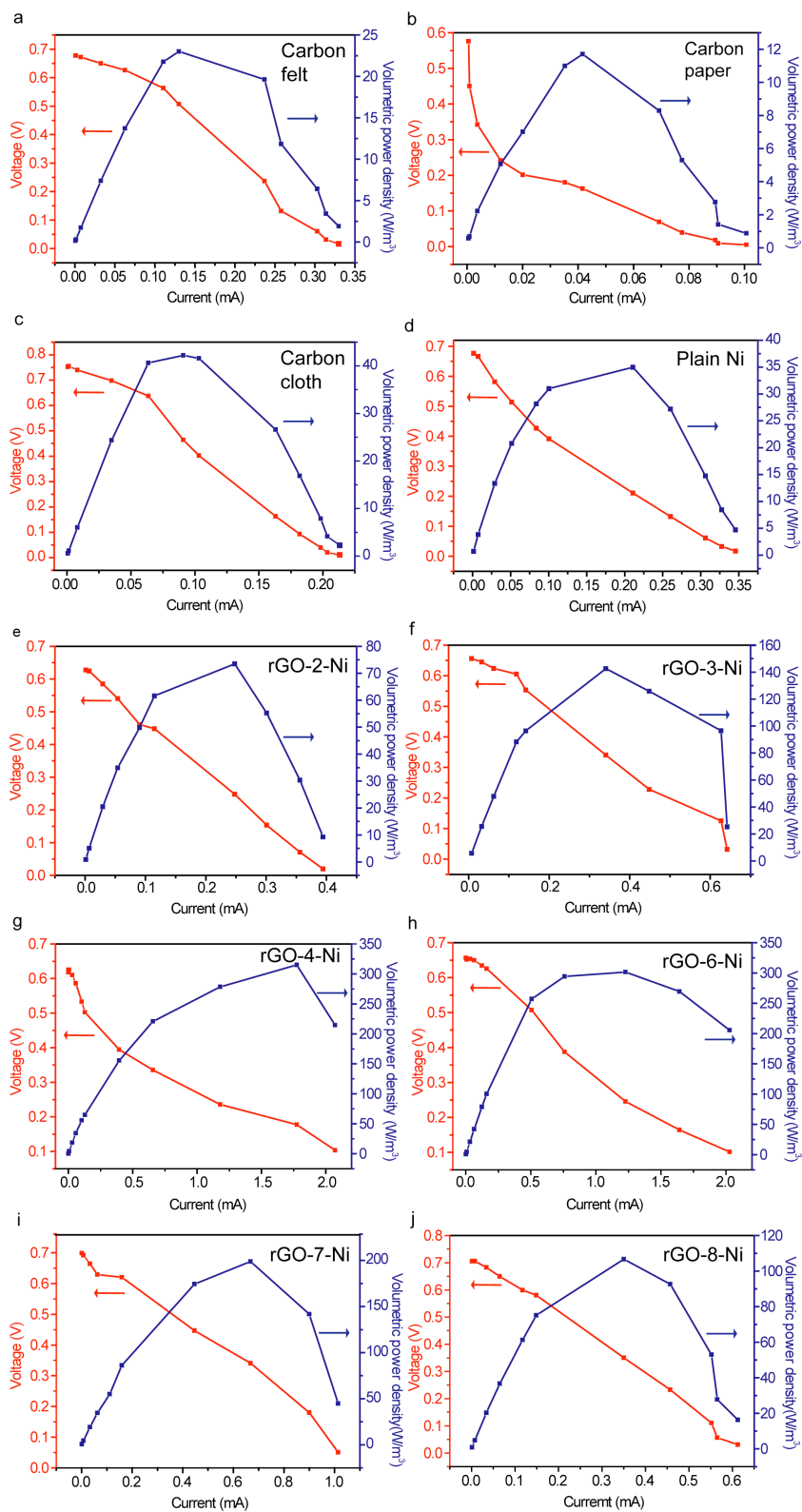


Figure 3.7 Polarization (red symbol) and power (blue symbol) curves collected for MFC device operated with different anode materials. (a) Carbon felt. (b) Carbon paper. (c) Carbon cloth. (d) Plain nickel foam and (e-j) rGO-X-Ni composite structures prepared under different number of rGO loading cycles ($X = 2, 3, 4, 6, 7, 8$).

Figure 3.8a compares the maximum volumetric power densities of MFC devices with different type of anodes. The maximum volumetric power densities of plain nickel foam, carbon felt, carbon paper, and carbon cloth anodes were measured to be 35 W/m^3 , 23 W/m^3 , 12 W/m^3 and 42 W/m^3 , respectively. Significantly, MFC devices employing rGO-X-Ni composite electrodes as anodes showed substantially higher power densities than the values obtained for these conventional electrodes (Figure 3.8a). With the number of rGO loading cycles increased from 2 cycles to 5 cycles, the maximum power densities of MFC devices were gradually increased from 73 W/m^3 to 661 W/m^3 . Figure 3.8b shows the polarization curve of rGO-5-Ni device. It exhibits an open circuit voltage (OCV) of 0.62 V, comparable to the values reported for other MFC devices with MR-1 colonized as anode.³⁸ The short-circuit current (2.7 mA) of this device is substantially higher than the values obtained for other anode electrodes we studied. Significantly, the rGO-5-Ni achieved a remarkable volumetric power density of 661 W/m^3 , which is almost two times higher than the value of a recently reported MFC device with 3D graphene-sponge anode.³⁰ Moreover, this value is almost 29-fold higher than that of carbon felt, which is a conventional anode material with porous 3D structure. The superior performance of the rGO-5-Ni anode is believed to be due to the increased effective surface area for bacteria and electron mediators, as well as the porous Ni foam scaffold that is highly

conductive and allows efficient mass transport of bacterial culture medium. The maximum power densities of devices decrease with further increase of the number of loading cycles. One of the possible reasons is the chemical dissolution of nickel results in the structural collapse of nickel skeleton after prolong treatment in acidic GO solution during the repeated rGO loading processes. Moreover, rGO sheets tend to form aggregates as the increase of rGO loading cycles (Figure 3.3), which could cause the decrease of accessible surface area for bacteria colonization. Notably that the MB absorption measurement indicates the surface area increased continuously with the number of rGO loading cycles, the interior surface in the rGO aggregates may not be accessible for bacteria colonization.

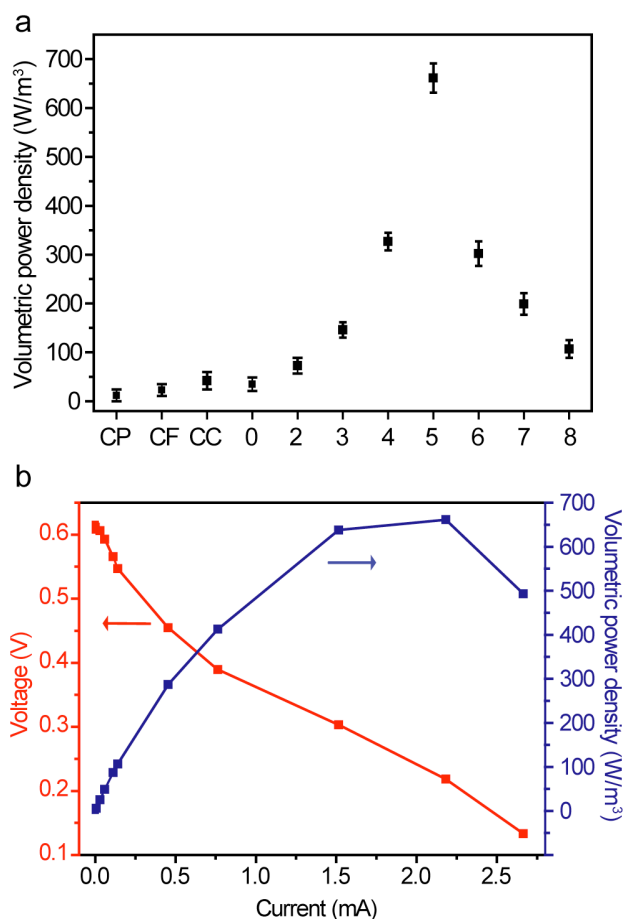


Figure 3.8 (a) Maximum volumetric power densities collected for MFC devices with rGO-X-Ni electrodes as anodes. Maximum volumetric power densities of MFC devices with plain nickel foam, carbon paper (CP), carbon felt (CF), and carbon cloth (CC) electrodes as anodes are also added for comparison. The error bars show the deviation of maximum power densities for at least three devices. (b) Polarization and power curves collected for a MFC device with rGO-5-Ni anode.

Moreover, we also calculate the gravimetric power density of the electrode materials. Since the nickel foam is a 3D structure with large open space, the gravimetric density of nickel foam ($\sim 0.32 \text{ g/cm}^3$) used this study is indeed comparable to that of carbon cloth ($\sim 0.27 \text{ g/cm}^3$), which is another advantage of using 3D electrode structure for MFC application. In Figure 3.9, we compare the maximum

gravimetric power density of different electrode materials. Again the gravimetric power densities of nickel foam electrodes are substantially higher than the other carbon materials, and the rGO-5-Ni electrode achieved the highest gravimetric power density. Importantly, these results also indicate that the gravimetric power density of MFC device could be further improved by replacing the nickel framework with other 3D conductive network with lower gravimetric density.

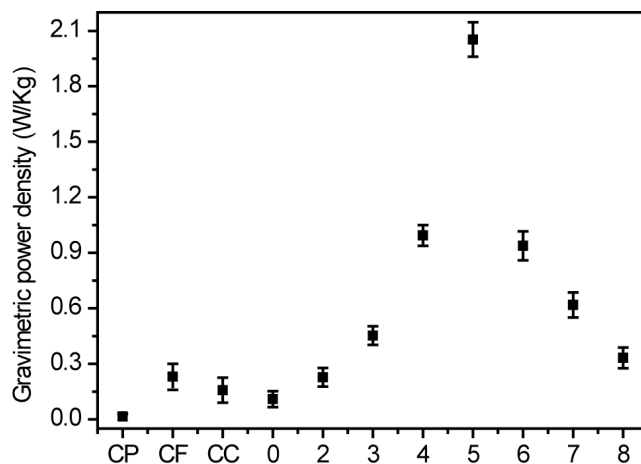


Figure 3.9 Maximum gravimetric power densities calculated for MFC devices with rGO-X-Ni electrodes as anodes. Maximum gravimetric power densities of MFC devices with plain nickel foam, carbon paper (CP), carbon felt (CF), and carbon cloth (CC) electrodes as anodes are also added for comparison. The error bars show the deviation of maximum power densities for at least three devices.

To prove the hypothesis that the 3D conductive scaffold benefits the charge and mass transport, the electrochemical impedance spectroscopy (EIS) spectra were also collected and analyzed for conventional carbon cloth anode and rGO-5-Ni anode (Figure 3.10). By fitting the data of the Nyquist plots with an equivalent circuit, we derived the solution resistance (R_s), charge transfer resistance (R_{p1}) and diffusion resistance (R_{p2}) (Figure 3.10b and Table 3.1). As shown in Table 3.1, the rGO-5-Ni

electrode exhibits considerably smaller resistances than the values obtained on carbon cloth electrode, especially the diffusion resistance. The rGO-5-Ni anode shows a diffusion resistance of 207 Ω , which is an order of magnitude less than that of carbon cloth electrode (2211 Ω). Since both rGO-5-Ni and carbon cloth anode were measured in the same electrochemical cell and electrolyte, the substantial reduction of resistances can possibly be attributed to the 3D conductive structure that allows efficient electron/mass transport. This study suggests the potential advantage of 3D conductive porous scaffold as electrode for MFC devices.

Table 3.1 The fitting parameters of EIS data for the MFCs with rGO-5-Ni and carbon cloth electrode.

	rGO-5-Ni (Ω)	Carbon cloth (Ω)
R_s (solution resistance)	21.9	35.6
R_{p1} (charge transfer resistance)	66	113
R_{p2} (diffusion resistance)	207	2211

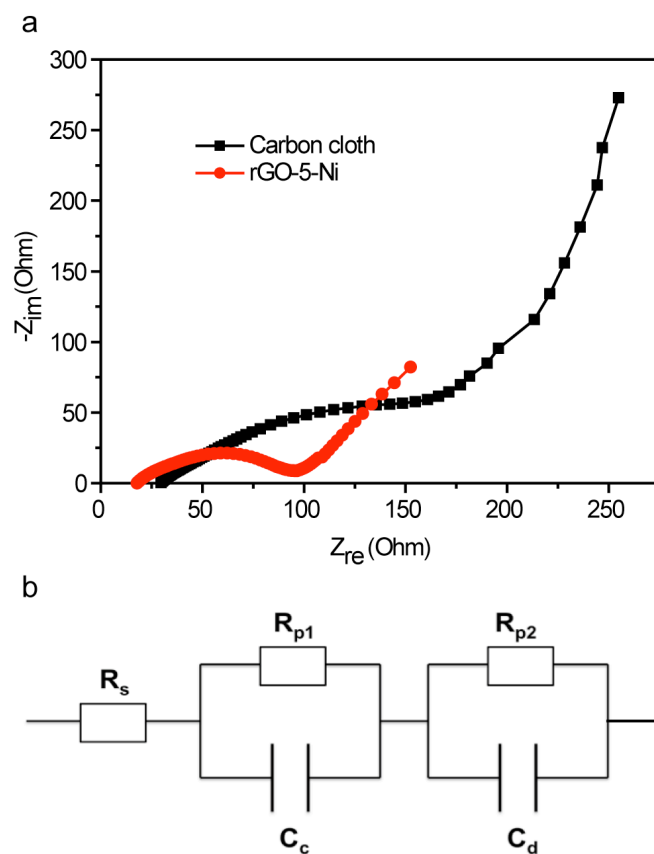


Figure 3.10 (a) Nyquist curves of the EIS tests for traditional carbon cloth electrode and rGO-5-Ni electrode. (b) Equivalent circuit for EIS data fitting.

In previous studies, the volumetric power densities were also calculated based on the volume of anode chamber.⁴⁰ To compare the performance of rGO-X-Ni electrodes with these previous results, we fabricated a roll-up rGO-5-Ni electrode (Figure 3.1d, inset) that can fit in the 25 mL anode chamber, and measured power and polarization curves for the MFC device (Figure 3.11).

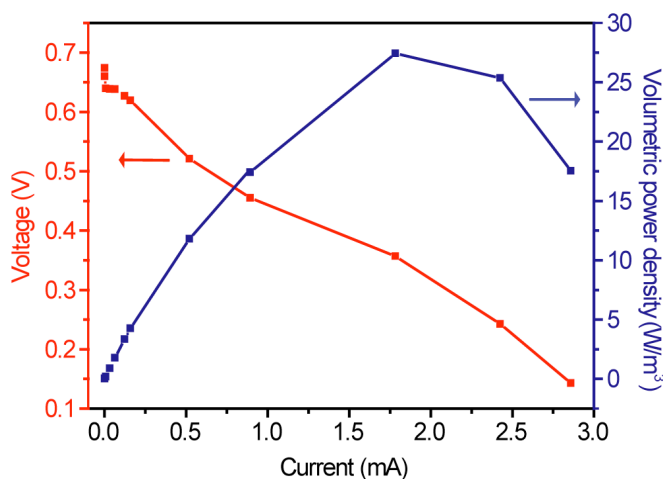


Figure 3.11 Polarization (red) and power (blue) curves collected for MFC with rGO-5-Ni anode. The volumetric power densities were calculated based on the volume of anode chamber (~25 mL).

Moreover, for comparison, power and polarization curves were also collected for MFC devices when the anode chamber was filled with carbon felt or carbon cloth electrodes. Significantly, the maximum volumetric power density of the rGO-5-Ni device was calculated to be 27 W/m^3 , which is substantially larger than the values obtained for carbon felt (1.03 W/m^3) and carbon cloth (1.62 W/m^3) anodes (Figure 3.12) measured with the same MFC device. The power density of 27 W/m^3 is two orders of magnitude larger than the values reported for other milliliter scale H-shaped MFC devices using graphite sticks as electrodes, and MR-1/lactate-Fe(III) citrate medium (0.25 W/m^3) as electrolytes.^{41, 42} It is 135-fold higher than that of mL-MFC device with using carbon cloth as anode and MR-1/TSB as anolyte (0.2 W/m^3).⁴³ And it is also almost 6 times higher than that obtained for mL-MFC device with crumpled graphene particles modified carbon cloth anodes (4.8 W/m^3) and wastewater as

anolyte.²³ To our knowledge, this is the highest volumetric power density obtained for mL-MFC device using pure strain of MR-1.

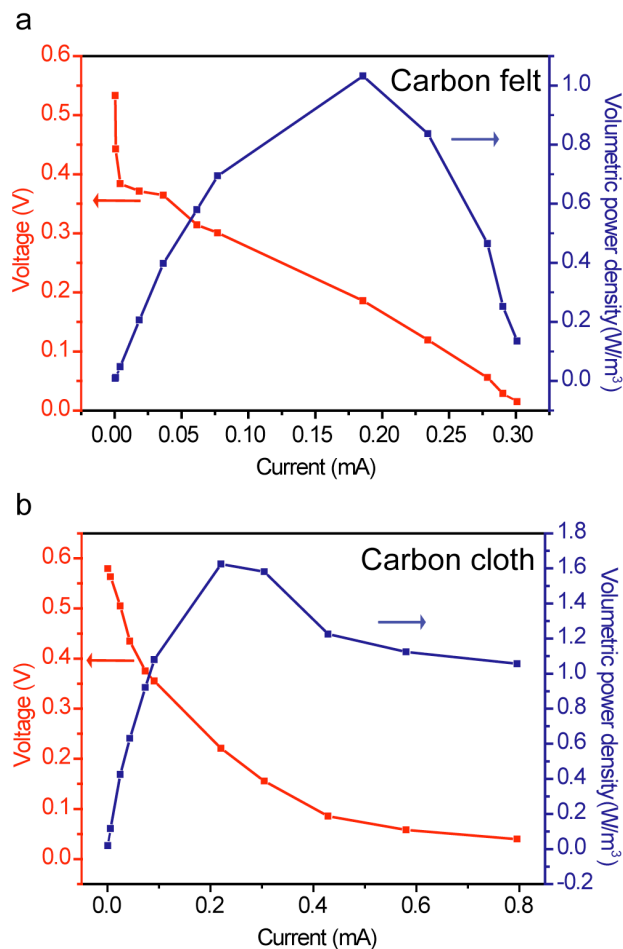


Figure 3.12 Polarization (red symbol) and power (blue symbol) curves collected for MFC with carbon felt anode and carbon cloth anode. The volumetric power densities were calculated based on the volume of anode chamber (~25 mL).

To evaluate the stability of rGO-5-Ni anode, the MFC device was operated in a batch mode. Figure 3.13 shows the continuous current generation from the MFC device in four consecutive feeding cycles, which lasted for almost a week. In each feeding cycle, a current of 0.1 - 0.5 mA was generated, which lasted for ca. 40 hrs

before decreasing to the baseline due to the depletion of nutrient in the MFC device. The slow decay of current suggests effective removal of most of the organic matter in electrolyte. Replenishment of fresh TSB medium into the anode chamber led to a drastic current restoration, and bioelectricity generation sustained for another 40 hrs. After the device operated for ~40 hours, the device yielded a coulombic efficiency of 19 %, indicating the device efficiently converting organic matter to electricity.⁴⁴ The results proved that the MFC device with rGO-5-Ni anode can be operated for at least a week, which is important for practical application.

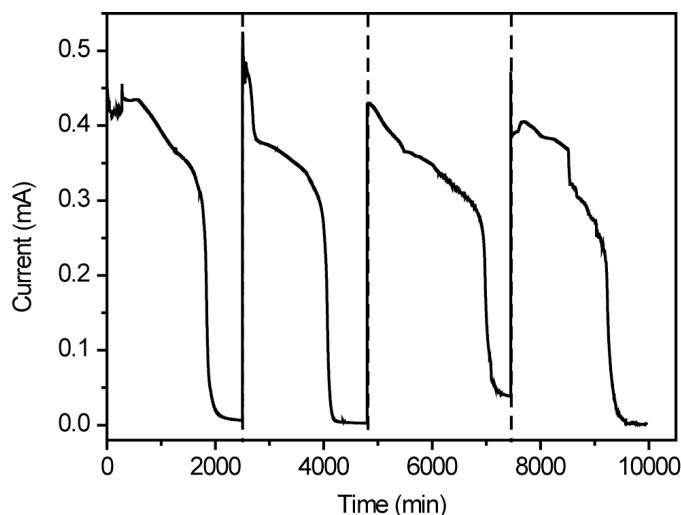


Figure 3.13 The current vs. time plot collected for a MFC device with rGO-5-Ni anode, operated in a batch-fed mode with an external resistor of 1000 Ω .

3.4 Conclusion

In summary, we have successfully developed a 3D electrode by coating rGO sheets onto Ni foam for MFC device. The deposition of rGO sheets on highly conductive Ni foam considerably increased the effective surface area for microbial colonization. The 3D porous nickel scaffold allows efficient electron transfer and

mass transport of bacterial culture medium. MFC devices with rGO-Ni electrodes showed substantially higher power density output compared to the device with plain nickel foam and other conventional carbon-based electrodes. In particular, MFC device with rGO-5-Ni electrode achieved a remarkable volumetric power density of 661 W/m^3 (based on the volume of anode) or 28 W/m^3 (based on the volume of anode chamber), which are the highest values ever obtained for mL-MFCs with pure strain of *S. oneidensis* MR-1. More importantly, 3D electrode is believed to be a general strategy to improve the power output of MFC devices. The maximum power output reported in this study was still limited by the electron producing capability of pure strain MR-1, and it is relatively low compared to that of other optimized MFC devices with mixed bacteria culture inoculated in wastewater.^{45, 46} However, we believe similar enhancement in power output should be expected for those MFC devices with mixed bacteria culture by using the 3D Ni/rGO anode electrode developed in this study. The demonstration of this new 3D electrode could further push the performance of MFC devices and strongly impact the microbial technology.

Reference

1. Yuan, S. J.; Sheng, G. P.; Li, W. W.; Lin, Z. Q.; Zeng, R. J.; Tong, Z. H.; Yu, H. Q., Degradation of Organic Pollutants in a Photoelectrocatalytic System Enhanced by a Microbial Fuel Cell. *Environ. Sci. Technol.* **2010**, *44*, 5575-5580.
2. Logan, B. E.; Hamelers, B.; Rozendal, R.; Schroder, U.; Keller, J.; Freguia, S.; Aelterman, P.; Verstraete, W.; Rabaey, K., Microbial Fuel Cells: Methodology and Technology. *Environ. Sci. Technol.* **2006**, *40*, 5181-5192.
3. Berk, R. S.; Canfield, J. H., Bioelectrochemical Energy Conversion. *Appl. Microbiol.* **1964**, *12*, 10-12.
4. Davis, J. B.; Yarbrough, H. F., Preliminary Experiments on a Microbial Fuel Cell. *Science* **1962**, *137*, 615-616.
5. Qian, F.; Morse, D. E., Miniaturizing Microbial Fuel Cells. *Trends in Biotechnology* **2010**, *29*, 62-69.
6. Liu, H.; Cheng, S.; Logan, B. E., Power Generation in Fed-Batch Microbial Fuel Cells as a Function of Ionic Strength, Temperature, and Reactor Configuration. *Environ. Sci. Technol.* **2005**, *39*, 5488-5493.
7. Kim, J. R.; Min, B.; Logan, B. E., Evaluation of Procedures to Acclimate a Microbial Fuel Cell for Electricity Production. *Appl. Microbiol. Biotechnol.* **2005**, *68*, 23-30.
8. Zhang, X.; Sun, H.; Liang, P.; Huang, X.; Chen, X.; Logan, B. E., Air-Cathode Structure Optimization in Separator-Coupled Microbial Fuel Cell. *Biosens. Bioelectron.* **2011**, *30*, 267-271.
9. Hu, H.; Fan, Y.; Liu, H., Hydrogen Production Using Single-Chamber Membrane-Free Microbial Electrolysis Cells. *Water Res.* **2008**, *42*, 4172-4178.
10. Qian, F.; Baum, M.; Gu, Q.; Morse, D. E., A 1.5 μ L Microbial Fuel Cell for On-Chip Bioelectricity Generation. *Lab Chip* **2009**, *9*, 3076-3081.
11. Zhang, F.; Ge, Z.; Grimaud, J.; He, Z., Improving Electricity Production in Tubular Microbial Fuel Cell through Optimizing the Anolyte Flow with Spiral Spacers. *Bioresour. Technol.* **2013**, *134*, 251-256.
12. Wei, J.; Liang, P.; Huang, X., Recent Progress in Electrodes for Microbial Fuel Cells. *Bioresour. Technol.* **2011**, *102*, 9335-9344.

13. Brondani, D.; Zapp, E.; Vieira, I. C.; Dupont, J.; Scheeren, C. W., Gold Nanoparticles in an Ionic Liquid Phase Supported in a Biopolymeric Matrix Applied in the Development of a Rosmarinic Acid Biosensor. *Analyst* **2011**, *136*, 2495-2505.
14. Chen, D.; Wang, G.; Li, J., Interfacial Bioelectrochemistry: Fabrication, Properties and Applications of Functional Nanostructured Biointerfaces. *J. Phys. Chem. C* **2007**, *111*, 2351-2367.
15. Thiagarajan, S.; Yang, R. F.; Chen, S. M., Palladium Nanoparticles Modified Electrode for the Selective Detection of Catecholamine Neurotransmitters in Presence of Ascorbic Acid. *Bioelectrochemistry* **2009**, *75*, 163-169.
16. Wu, X.; Zhao, F.; Rahunen, N.; Varcoe, J. R.; Avignone-Rossa, C.; Thumser, A. E.; Slade, R. C., A Role for Microbial Palladium Nanoparticles in Extracellular Electron Transfer. *Angew. Chem. Int. Ed.* **2011**, *50*, 427-430.
17. Ganesana, M.; Istarnboulie, G.; Marty, J. L.; Noguer, T.; Andreescu, S., Site-Specific Immobilization of a (His)6-Tagged Acetylcholinesterase on Nickel Nanoparticles for Highly Sensitive Toxicity Biosensors. *Biosens. Bioelectron.* **2011**, *30*, 43-48.
18. Welch, C. W.; Compton, R. G., The Use of Nanoparticles in Electroanalysis: A Review. *Anal. Bioanal. Chem.* **2006**, *384*, 601-619.
19. Yong, Y.-C.; Dong, X.-C.; Chan-Park, M. B.; Song, H.; Chen, P., Macroporous and Monolithic Anode Based on Polyaniline Hybridized Three-Dimensional Graphene for High-Performance Microbial Fuel Cells. *ACS Nano* **2012**, *6*, 2394-2400.
20. Qiao, Y.; Bao, S.-J.; Li, C. M.; Cui, X.-Q.; Lu, Z.-S.; Guo, J., Nanostructured Polyaniline/Titanium Dioxide Composite Anode for Microbial Fuel Cells. *ACS Nano* **2008**, *2*, 113-119.
21. Ci, S.; Wen, Z.; Chen, J.; He, Z., Decorating Anode with Bamboo-Like Nitrogen-Doped Carbon Nanotubes for Microbial Fuel Cells. *Electrochem. Commun.* **2012**, *14*, 71-74.
22. Zhang, T.; Nie, H.; Bain, T. S.; Lu, H.; Cui, M.; Snoeyenbos-West, O. L.; E., F. A.; Nevin, K. P.; Russell, T. P.; Lovley, D. R., Improved Cathode Materials for Microbial Electrosynthesis. *Energy Environ. Sci.* **2013**, *6*, 217-224.
23. Xiao, L.; Damien, J.; Luo, J.; Jang, H. D.; Huang, J.; He, Z., Crumpled Graphene Particles for Microbial Fuel Cell Electrodes. *J. Power Sources* **2012**, *208*, 187-192.

24. Ci, S.-Q.; Wu, N.; Wen, Z.-H.; Li, J.-H., An Overview of Electrode Materials in Microbial Fuel Cells. *Journal of Electrochemistry* **2012**, *18*, 243-251.
25. Fan, Y.; Xu, S.; Schaller, R.; Jiao, J.; Chaplen, F.; Liu, H., Nanoparticle Decorated Anodes for Enhanced Current Generation in Microbial Electrochemical Cells. *Biosens. Bioelectron.* **2011**, *26*, 1908-1912.
26. Kim, S.-I.; Roh, S.-H., Multiwalled Carbon Nanotube/Polyacrylonitrile Composite as Anode Material for Microbial Fuel Cells Application. *J. Nanosci. Nanotechnol.* **2010**, *10*, 3271-3274.
27. Higgins, S. R.; Foerster, D.; Cheung, A.; Lau, C.; Bretschger, O.; Minteer, S. D.; Nealson, K.; Atanassov, P.; Cooney, M. J., Fabrication of Macroporous Chitosan Scaffolds Doped with Carbon Nanotubes and Their Characterization in Microbial Fuel Cell Operation. *Enzyme and Microbial Technology* **2011**, *48*, 458-465.
28. Xie, X.; Hu, L.; Pasta, M.; Wells, G. F.; Kong, D.; Criddle, C. S.; Cui, Y., Three-Dimensional Carbon Nanotube-Textile Anode for High-Performance Microbial Fuel Cells. *Nano Lett.* **2011**, *11*, 291-296.
29. Xie, X.; Ye, M.; Hu, L.; Liu, N.; McDonough, J. R.; Chen, W.; Alshareef, H. N.; Criddle, C. S.; Cui, Y., Carbon Nanotube-Coated Macroporous Sponge for Microbial Fuel Cell Electrodes. *Energy Environ. Sci.* **2012**, *5*, 5265-5270.
30. Xie, X.; Yu, G.; Liu, N.; Bao, Z.; Criddle, C. S.; Cui, Y., Graphene-Sponges as High-Performance Low-Cost Anodes for Microbial Fuel Cells. *Energy Environ. Sci.* **2012**, *5*, 6862-6866.
31. Yuan, Y.; Zhou, S.; Zhao, B.; Zhuang, L.; Wang, Y., Microbially-Reduced Graphene Scaffolds to Facilitate Extracellular Electron Transfer in Microbial Fuel Cells. *Bioresour. Technol.* **2012**, *116*, 453-458.
32. Huang, Y.-X.; Liu, X.-W.; Xie, J.-F.; Sheng, G.-P.; Wang, G.-Y.; Zhang, Y.-Y.; Xu, A.-W.; Yu, H.-Q., Graphene Oxide Nanoribbons Greatly Enhance Extracellular Electron Transfer in Bio-Electrochemical Systems. *Chem. Commun.* **2011**, *47*, 5795-5795.
33. Kemp, K. C.; Seema, H.; Saleh, M.; Le, N. H.; Mahesh, K.; Chandra, V.; Kim, K. S., Environmental Applications Using Graphene Composites: Water Remediation and Gas Adsorption. *Nanoscale* **2013**, *5*, 3149-3171.
34. Zhu, C.; Dong, S., Recent Progress in Graphene-Based Nanomaterials as Advanced Electrocatalysts Towards Oxygen Reduction Reaction. *Nanoscale* **2013**, *5*, 1753-1767.

35. Zangmeister, C. D., Preparation and Evaluation of Graphite Oxide Reduced at 220C. *Chem. Mater.* **2010**, *22*, 5625-5629.
36. Lv, R.; Li, Q.; Botello-Mendez, A. R.; Hayashi, T.; Wang, B.; Berkdemir, A.; Hao, Q.; Elias, A. L.; Cruz-Silva, R.; Gutierrez, H. R.; Kim, Y. A.; Muramatsu, H.; Zhu, J.; Endo, M.; Terrones, H.; Charlier, J.-C.; Pan, M.; Terrones, M., Nitrogen-Doped Graphene: Beyond Single Substitution and Enhanced Molecular Sensing. *Sci. Rep.* **2012**, *2*, 586-573.
37. Jerng, S.-K.; Yu, D. S.; Lee, J. H.; Kim, C.; Yoon, S.; Chun, S.-H., Graphitic Carbon Growth on Crystalline and Amorphous Oxide Substrates Using Molecular Beam Epitaxy. *Nanoscale Research Letters* **2011**, *6*, 565-570.
38. Jo, G.; Choe, M.; Cho, C.-Y.; Kim, J. H.; Park, W.; Lee, S.; Hong, W.-K.; Kim, T.-W.; Park, S.-J.; Hong, B. H.; Kahng, Y. H.; Lee, T., Large-Scale Patterned Multi-Layer Graphene Films as Transparent Conducting Electrodes for GaN Light-Emitting Diodes. *Nanotechnology* **2010**, *21*, 175201-175206.
39. Kaewprasit, C.; Hequet, E.; Abidi, N.; Gurlot, J. P., Application of Methylene Blue Adsorption to Cotton Fiber Specific Surface Area Measurement. *J. Cotton Sci.* **1998**, *2*, 164-173.
40. Fan, Y.; Hu, H.; Liu, H., Enhanced Coulombic Efficiency and Power Density of Air-Cathode Microbial Fuel Cells with an Improved Cell Configuration. *J. Power Sour.* **2007**, *171*, 348-354.
41. Nevin, K. P.; Richter, H.; Covalla, S. F.; Johnson, J. P.; Woodard, T. L.; Orloff, A. L.; Jia, H.; Zhang, M.; Lovley, D. R., Power Output and Columbic Efficiencies from Biofilms of *Geobacter sulfurreducens* Comparable to Mixed Community Microbial Fuel Cells. *Environ. Microbiol.* **2008**, *10*, 2505-2514.
42. Lanthier, M.; Gregory, K. B.; Lovley, D. R., Growth with High Planktonic Biomass in *Shewanella Oneidensis* Fuel Cells. *FEMS Microbiol Lett.* **2008**, *278*, 29-35.
43. Qian, F.; He, Z.; Thelen, M. P.; Li, Y., A Microfluidic Microbial Fuel Cell Fabricated by Soft Lithography. *Bioresour. Technol.* **2011**, *102*, 5836-5840.
44. Newton, G. J.; Mori, S.; Nakamura, R.; Hashimoto, K.; Watanabe, K., Analysis of Current-Generating Mechanisms of *Shewanella loihica* PV-4 and *Shewanella oneidensis* MR-1 in Microbial Fuel Cell. *Appl. Environ. Microbiol.* **2009**, *75*, 7674-7681.
45. Fan, Y.; Han, S.-K.; Liu, H., Improved Performance of CEA Microbial Fuel Cells with Increased Reactor Size. *Energy Environ. Sci.* **2012**, *5*, 8273-8280.

46. Fan, Y.; Hu, H.; Liu, H., Sustainable Power Generation in Microbial Fuel Cells Using Bicarbonate Buffer and Proton Transfer Mechanisms. *Environ. Sci. Technol.* **2007**, *41*, 8154-8158.

Chapter 4

Photoelectrochemical Investigation of Oxygen Deficient TiO₂ Nanowire Arrays and CdS Quantum Dot Sensitization

Abstract

Oxygen-deficient TiO_2 nanowires show substantially increased donor density due to an increase in oxygen vacancies introduced intentionally by thermal treatment in ammonia, vacuum, or hydrogen. By coupling oxygen-deficient TiO_2 nanowires with CdS quantum dots, they show significant enhancement in photoactivities was observed in the entire wavelength region from 350 to 550 nm. These new nanocomposites hold great promise for solar hydrogen generation.

4.1 Introduction

Titanium dioxide (TiO_2) nanostructures have been extensively studied as photoanodes for water oxidation,¹⁻⁵ due to their high chemical stability, low cost, abundance as well as the favorable band-edge alignment with water redox potentials. However, the relatively large bandgap (3.0 eV for rutile and 3.2 eV for anatase TiO_2) and low electrical conductivity limit its wide spread. Recently, we demonstrated that hydrogen-treated TiO_2 nanomaterials (denoted as H: TiO_2) fundamentally improve the photoelectrochemical (PEC) performance for water oxidation.⁶ The improvement of photoactivity was attributed to the increased donor density of TiO_2 nanowires, as a result of increased oxygen vacancies (O_{vac} , shallow donor for TiO_2) upon hydrogen treatment. The introduction of O_{vac} in a controlled manner is critical for improving the photoactivity of TiO_2 materials.

In this work, we further explore the generation of O_{vac} by annealing TiO_2 nanowires under vacuum (oxygen deficient environment) or in ammonia atmosphere (via nitrogen doping). Oxygen deficient TiO_2 nanowires prepared by these new

methods also showed pronounced photoactivities, comparable to the reported hydrogen-treated TiO_2 . The capability of introducing O_{vac} without involving hydrogen or other impurities provides a unique platform to study effect of O_{vac} on photoelectrochemical properties of TiO_2 . Furthermore, we couple the oxygen-deficient TiO_2 nanowires with CdS quantum dots (QDs) (denoted as CdS-H: TiO_2) for enhancing visible light absorption. We found that thermal treatment is critical for improving the crystallinity of CdS QDs, and thereby the electron separation and transfer at the interface of CdS/ TiO_2 . CdS-H: TiO_2 samples show substantially enhanced incident-photon-to-electron conversion efficiency (IPCE) in the UV and visible region.

4.2 Experimental Section

4.2.1 Synthesis

1. Rutile TiO_2 nanowires. The synthesis of rutile TiO_2 nanowire arrays was based on a reported hydrothermal method with slight modification.⁷ 15 mL concentrated hydrochloric acid (36.5-38% by weight) was mixed with 15 mL deionized water under stirring, follow by the addition of 0.475 mL titanium n-butoxide. This precursor solution was poured into a 40 mL autoclave with a Teflon liner. A fluorine-doped tin oxide (FTO) glass substrate was cleaned and transferred into the autoclave with conducting side facing down. The autoclave was then heated at 150 °C for 5 h. After cool down to room temperature, the substrate was covered with a white film of TiO_2 nanowire arrays. The substrate was washed with deionized

water, and then air dried. To obtain crystalline TiO₂, the substrate was calcined at 550 °C for 3 h in the air.

2. CdS QD sensitized TiO₂ nanowires. CdS quantum dots were deposited on TiO₂ nanowire arrays by a chemical bath deposition method.⁸ 5 mL of 40 mM Cd(acetate)₂ dihydrate aqueous solution, 5 mL of 40 mM thiourea aqueous solution and 10 mL deionized water were mixed in a 25 mL vial. Then 0.1 mL of concentrated ammonium hydroxide was added into the solution mixture. TiO₂ sample was submerged in the solution at 55 °C for 20 min.

4.2.2 Photoelectrochemical Measurements

Linear sweep voltammograms were measured in a three-electrode electrochemical cell with an Ag/AgCl reference electrode and a platinum wire as counter electrode, and TiO₂ nanowire samples as working electrode, at a scan rate of 20 mV/s. 0.5 M Na₂SO₄ aqueous solution (pH = 7) was used as electrolyte. For CdS QDs sensitized TiO₂ nanowires (CdS-TiO₂, CdS-H:TiO₂, H:CdS-TiO₂), linear sweep voltammograms measurements were made in a two-electrode electrochemical cell with a platinum wire as counter electrode and nanowire sample as working electrode at a scan rate of 20 mV/s. The electrolyte used was a mixture of 0.25 M Na₂S and 0.35 M Na₂SO₃ aqueous solution (pH = 11.5). All the TiO₂ photoanodes were fabricated by attaching a copper wire onto the bare edge of FTO glass substrate via soldering a small piece of indium metal, and then sealing the FTO glass substrate and metal contact region with insulating epoxy resin. The exposed effective area for the TiO₂ working electrode is around 0.15-0.2 cm². 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 . Incident-photon-to-current-conversion-efficiencies (IPCE) measurements were collected by a CHI 660D electrochemical station with a simulated solar light source (Newport 69920, 1000 W xenon lamp), coupled with an infrared water filter (Oriel 6127) and aligned with a monochromator (Oriel Cornerstone 130 1/8 m). All PEC measurements were carried out with front side illumination. Electrochemical impedance was measured on CHI 660D using Impedance-potential technique at a frequency of 10000 Hz in 0.5 M Na_2SO_4 solution under dark. Mott-Schottky plots were generated from capacitances of TiO_2 in a potential range of -0.2 V to 0.5 V vs. RHE.

4.2.3 Material Characterization

X-ray diffraction (XRD) spectra were measured at room temperature on a Rigaku Americas Miniflex Plus powder diffractometer from a 2θ angle of 20 to 70 degree with a step size of 0.04 degree at a rate of 1 degree/min. Scanning electron microscopy (SEM) images were collected by a field-emission SEM (Hitachi S-4800 II). X-ray Photoelectron Spectroscopy (XPS) analysis was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) using Mg-monochromatic X-ray at a power of 25 W with an X-ray-beam diameter of 10 mm, and a pass energy of 29.35 eV. The pressure of analyzer chamber was maintained below 5×10^{-8} Pa during the measurement. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference.

4.3 Results and Discussion

Rutile TiO_2 nanowire arrays were prepared on a fluorine-doped tin oxide (FTO) glass substrate based on a previously reported method⁷ (Experimental Section). Scanning electron microscopy (SEM) image reveals that FTO substrate is covered with dense and vertically aligned nanowire arrays (Figure 4.1a). The diameters of nanowire are in a range of 100-200 nm with a typical length of 2-3 μm . XRD patterns (Figure 4.1b) collected from the film can be indexed as rutile TiO_2 (JCPDS, No. 88-1175).

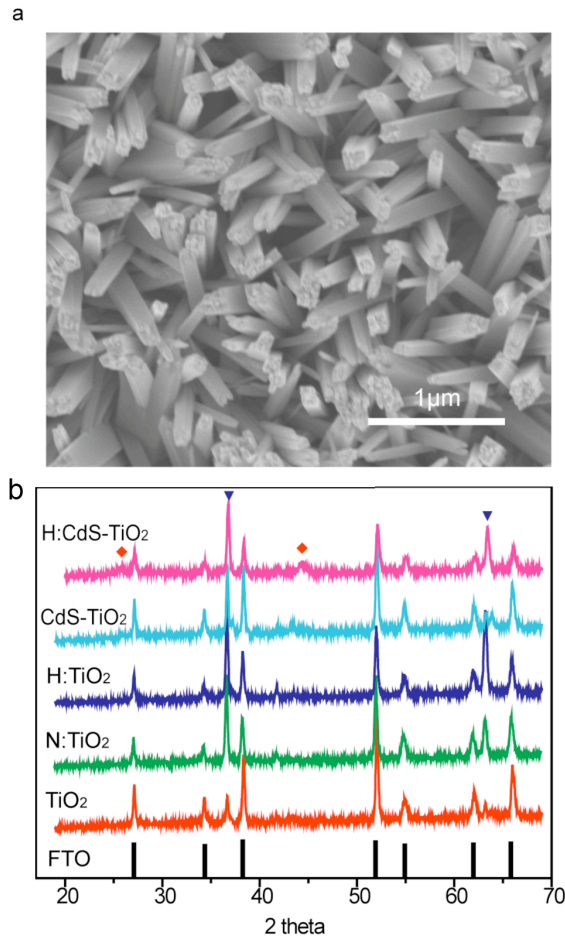


Figure 4.1 (a) SEM image of TiO₂. (b) XRD spectra collected from pristine TiO₂, N-doped TiO₂ (N:TiO₂), hydrogen-treated TiO₂ (H:TiO₂), and CdS QD sensitized TiO₂ (CdS-TiO₂) nanowires. XRD peak positions of FTO substrate are provided as reference (black lines). The two diffraction peaks centered at 2 θ angles of 36.5° and 63.2° (marked by ▼), are identified in the XRD spectra of all TiO₂ samples, which can be indexed as tetragonal rutile TiO₂ (JCPDS, No. 88-1175). Two diffraction peaks centered at 2 θ angles of 26.4° and 44° (marked by ◆), are indexed as hexagonal CdS (JCPDS, No. 41-1049). The diffraction peaks of CdS are missing for CdS-TiO₂ nanowire sample possibly due to the poor crystallinity of CdS QDs on TiO₂ nanowires before thermal annealing.

We managed to create O_{vac} through two different approaches of doping TiO₂ with aliovalent impurities and anneal TiO₂ in oxygen deficient environment. Theoretical studies have suggested that N doping could facilitate the formation of O_{vac} in TiO₂ lattice, and the created O_{vac} mid-gap states locates below the conduction band by 0.7-1.18 eV.^{9, 10} The introduction of N into TiO₂ nanowires (denoted as N:TiO₂) was carried out in a home-built quartz tube furnace by annealing TiO₂ samples in ammonia at 510 °C for different lengths of time. The same method has previously been used for the preparation of N-doped ZnO¹¹ and TiO₂¹² nanowires. To confirm the successful incorporation of N and the chemical states of N in TiO₂, we collected X-ray photoelectron spectroscopy (XPS) for N:TiO₂ nanowires (Figure 4.2a). The N 1s XPS spectrum exhibits a broad peak centered at 399.3 eV with full-width-half-maximum (FWHM) ~4 eV, indicating more than one chemical states of N. This broad peak can be deconvoluted into three peaks. The synthetic peak centered at 397.2 eV is consistent with the typical binding energy reported for N in oxynitride (O-Ti-N) bonding.¹² The peaks centered at 400 eV and 399 eV can be ascribed to

adsorbed N_2 or amines (NH_x) respectively.^{12, 13} The data confirm that N was incorporated substitutionally at O sites in TiO_2 .

Linear sweep voltammograms were collected for TiO_2 and N: TiO_2 samples in a three-electrode PEC cell (Experimental section). Both TiO_2 and N: TiO_2 nanowires showed increased photocurrent densities with ammonia annealing time from 0 to 50 min. The N: TiO_2 nanowire annealed for 50 min achieves an optimal photocurrent density of $\sim 1.9 \text{ mA/cm}^2$ at 1.23 V vs. RHE (Figure 4.2b). The photocurrent enhancement can be due to two factors. First, the ammonia treatment creates O_{vac} in TiO_2 either through aliovalent substitution of N impurities or reduction by H_2 generated in ammonia dissociation, as previously demonstrated in hydrogen-treated TiO_2 .^{11, 14} Second, N-doping creates mid-gap density of states that narrows the band gap of TiO_2 and increase visible light absorption.¹⁵ Nevertheless, the extended annealing in ammonia (100 min) leads to a decrease of photocurrent density from $\sim 1.9 \text{ mA/cm}^2$ to $\sim 0.9 \text{ mA/cm}^2$. It is attributed to the increased resistance of FTO substrate from 20 to 195 Ω after ammonia treatment.

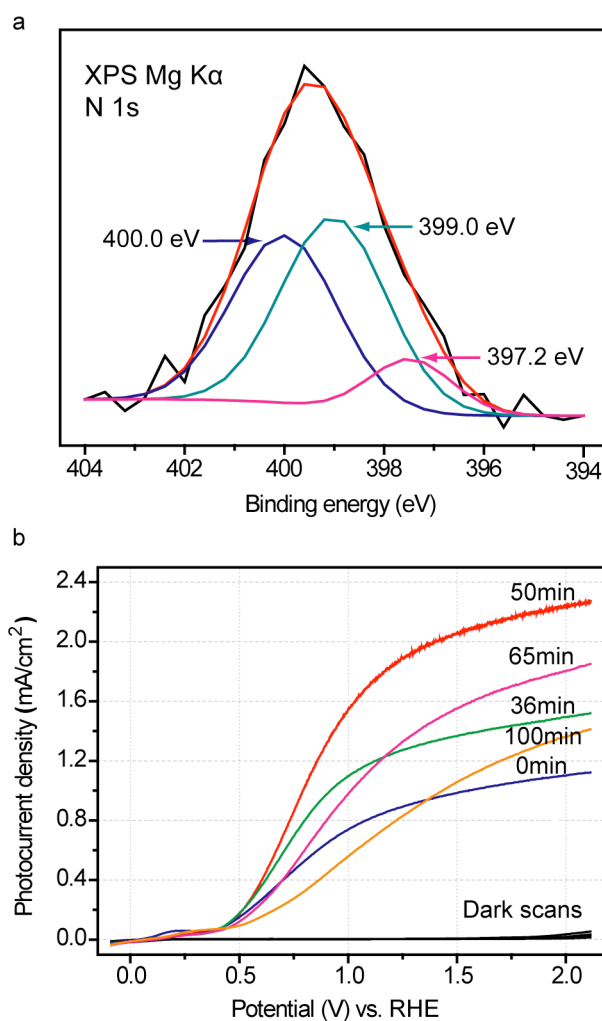


Figure 4.2 (a) XPS N 1s spectrum of N:TiO₂ nanowires. The black curve is the experimental result. The red curve is the summation of the synthetic peaks centered at 397.2 eV (pink curve), 399 eV (green curve) and 400 eV (blue curve). (b) Linear sweeps voltammograms collected from pristine TiO₂ and N:TiO₂ samples annealed at 510 °C for 0, 36, 50, 65 and 100 min, respectively.

To investigate the effect of N-doping, we compared the PEC performance of optimized N:TiO₂ (50 min) with H:TiO₂ samples. H:TiO₂ nanowire samples were prepared by annealing pristine TiO₂ nanowires in hydrogen atmosphere at 320 °C for 3 h. Figure 4.3a shows that H:TiO₂ sample yield a photocurrent density of approx.

1.86 mA/cm² at 1.23 V vs. RHE, which indeed is comparable with the value obtained for the optimized N:TiO₂ sample (annealed in ammonia for 50 min). Furthermore, we investigated the effect of ammonia treatment on H:TiO₂ nanowires. Surprisingly, there is no enhancement in photocurrent densities by further annealing of H:TiO₂ nanowire sample in ammonia. In contrast, the photocurrent of H:TiO₂ samples decreases slowly with the increase of ammonia annealing time (Figure 4.3b). The data indicate that the introduction of N-doping in H:TiO₂ does not improve the photocurrent.

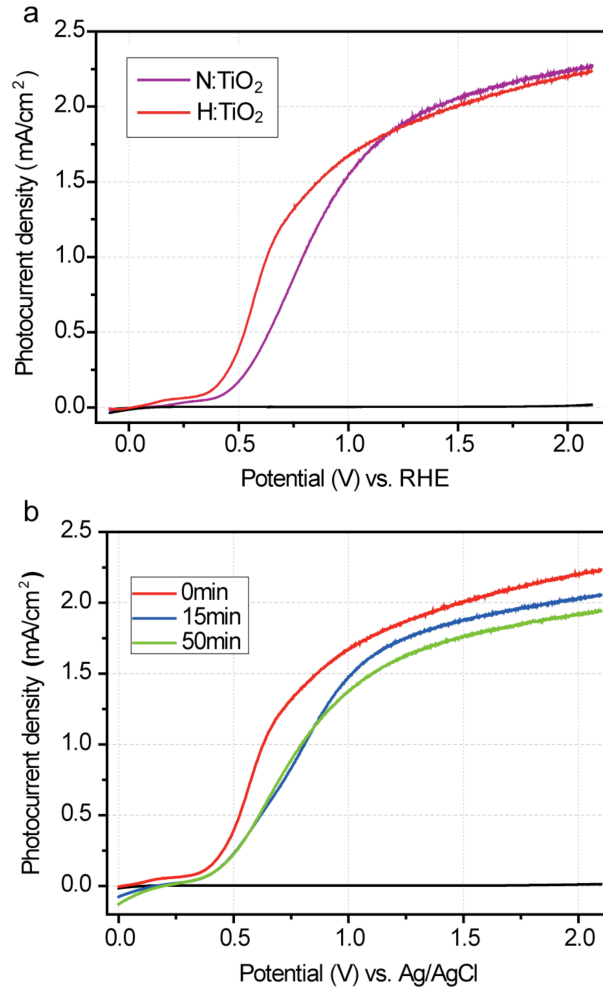


Figure 4.3 (a) Comparison of linear sweep voltammograms of optimized N:TiO₂ (annealed in ammonia for 50 min) and H:TiO₂ nanowires. (b) Linear sweep voltammograms of H:TiO₂ nanowires annealed in ammonia atmosphere for 0, 15 and 50 min, respectively. All linear sweeps were measured at a scan rate of 20 mV/s under 100 mW/cm² white light illumination.

We further performed electrochemical impedance measurements on pristine TiO₂, H:TiO₂, and N:TiO₂ nanowire samples at a frequency of 10 kHz in the dark to determine the capacitance of TiO₂. Carrier density can be quantified from the slope of Mott-Schottky analysis by using the equation¹⁶

$$N_d = (2/e_0\epsilon\epsilon_0)[d(1/C^2)/dV]^{-1}$$

where e_0 is the electron charge, ϵ the dielectric constant, ϵ_0 permittivity of vacuum, V the electrode applied potential, and N_d the donor density. As shown in Figure 4.4a, all the TiO₂ samples exhibit positive slopes as expected for n-type semiconductor.¹⁷ Apparently, N:TiO₂ sample exhibit a similar slope of Mott-Schottky plot with H:TiO₂ sample, and they are substantially smaller than that of pristine TiO₂ (Figure 4.4a, inset). With an ϵ value of 170 for TiO₂,¹⁸ electron densities of TiO₂, N:TiO₂ and H:TiO₂ samples were calculated to be $1.4 \times 10^{18} \text{ cm}^{-3}$, $1.7 \times 10^{22} \text{ cm}^{-3}$ and $1.4 \times 10^{22} \text{ cm}^{-3}$, respectively. Clearly, ammonia and hydrogen treatment led to an increased donor density of TiO₂, which could be attributed to the improved photocurrent densities in N:TiO₂ and H:TiO₂. N-doping in TiO₂ is known to be a shallow acceptor that creates impurity states at 0.04 eV above TiO₂ valence band.¹⁵ Theoretically, nitrogen doped TiO₂ should exhibit p-type property and decrease donor density (increase acceptor density). The enhanced donor density of nitrogen doping is due to the created oxygen vacancies acting as shallow donor, during nitrogen doping.

The incorporation of nitrogen dopant state and oxygen vacancies states may narrow the optical bandgap of TiO₂. To investigate the effect of N-doping on bandgap modulation, we compared the IPCE spectra of pristine TiO₂, N:TiO₂ and H:TiO₂ nanowires measured at 1.2 V vs. RHE using a 1000 W Xe lamp coupled with a monochromator. IPCE can be expressed by the following equation

$$\text{IPCE} = (1240I) / (\lambda J_{\text{light}})$$

where, I is the measured photocurrent density, as well as J_{light} is the measured irradiance at a specific wavelength, and is λ the wavelength of incident light. Compared to pristine TiO₂ nanowires, H:TiO₂ and N:TiO₂ show significantly enhanced photoactivity in UV region with IPCE higher than 90 % at 350 nm, as a result of improved donor densities (Figure 4.4b). IPCE values decrease gradually from approx. 98% at 350 nm to approx. 1% at 420 nm, which is consistent with bandgap energy of rutile TiO₂ (3.0 eV). N:TiO₂ and H:TiO₂ samples showed limited photoactivity in the wavelength range from 600 to 650 nm, as the IPCE values increase slightly from almost zero to ~0.2 %. Similar visible light photoactivity has previously been observed in H-treated TiO₂, which was attributed to the transition between oxygen vacancy states to the conduction band of TiO₂. However, the IPCE values obtained for the visible region are significantly smaller than that in the UV region.

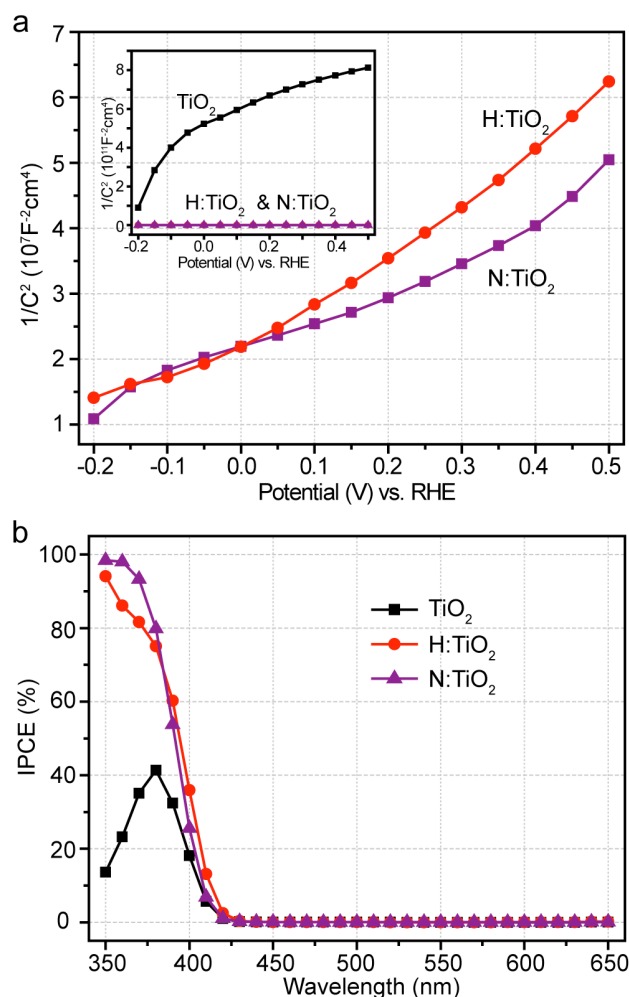


Figure 4.4 (a) Mott-Schottky plots generated at a frequency of 10 kHz in the dark for H:TiO₂ (red curve) and N:TiO₂ nanowires (purple curve). Inset: Comparison of Mott-Schottky plots of pristine TiO₂ (black curve) with H:TiO₂ (red curve) and N:TiO₂ (purple curve) nanowires. (b) IPCE spectra of pristine TiO₂, N:TiO₂ and H:TiO₂ nanowires, measured at a potential of 1.2 V vs. RHE.

Furthermore, we managed to create O_{vac} in TiO₂ under vacuum (oxygen deficient environment), to investigate effect of O_{vac} on the photoactivity of TiO₂. This approach can eliminate the potential effects of N-doping and hydrogen incorporation. It has been reported that O_{vac} can be generated in TiO₂ by annealing in vacuum.^{19, 20} We annealed the as-prepared TiO₂ nanowires at ~ 13 mtorr (denoted as V:TiO₂) in a

home-built tube furnace at 550 °C for 3 hours. As shown in Figure 4.5a inset, the photocurrent density of V:TiO₂ nanowire is at least two times enhanced compared to the pristine TiO₂ that annealed in air and atmospheric pressure, at the same temperature and time. Amperometric *I-t* curves (Figure 4.5b and c) collected from N:TiO₂ and V:TiO₂ samples showed that the photocurrents slightly dropped by ~15% in the first half hour and then became stable for at least for 2 h. This results support that the N:TiO₂ and V:TiO₂ nanowire photoanodes are stable for water oxidation. IPCE spectra of TiO₂ and V:TiO₂ measured at an applied voltage of 1.2 V vs. RHE show similar profiles, with IPCE values increased gradually from 350 nm to 370 nm, then decreased gradually from 370 nm to 420 nm (Figure 4.5a). Significantly, the IPCE values of V:TiO₂ sample are uniformly higher than that of pristine TiO₂ nanowires in the entire wavelengths from 350 to 420 nm.

As expected, V:TiO₂ sample obtains a substantially smaller slope of Mott-Schottky plot compared to pristine TiO₂, with a carrier density of $1.7 \times 10^{20} \text{ cm}^{-3}$ (Figure 4.6, inset). The results support the hypothesis that annealing under vacuum at high temperature could facilitate the creation of O_{vac} and thereby increase the donor density. Nevertheless, the carrier density and IPCE values of V:TiO₂ are still lower than that of N:TiO₂ and H:TiO₂ samples (Figure 4.6). It indicates that the vacuum treatment may be not as efficient as ammonia and hydrogen treatment in creating O_{vac} and/or the incorporated hydrogen impurities also serve as electron donor in TiO₂.

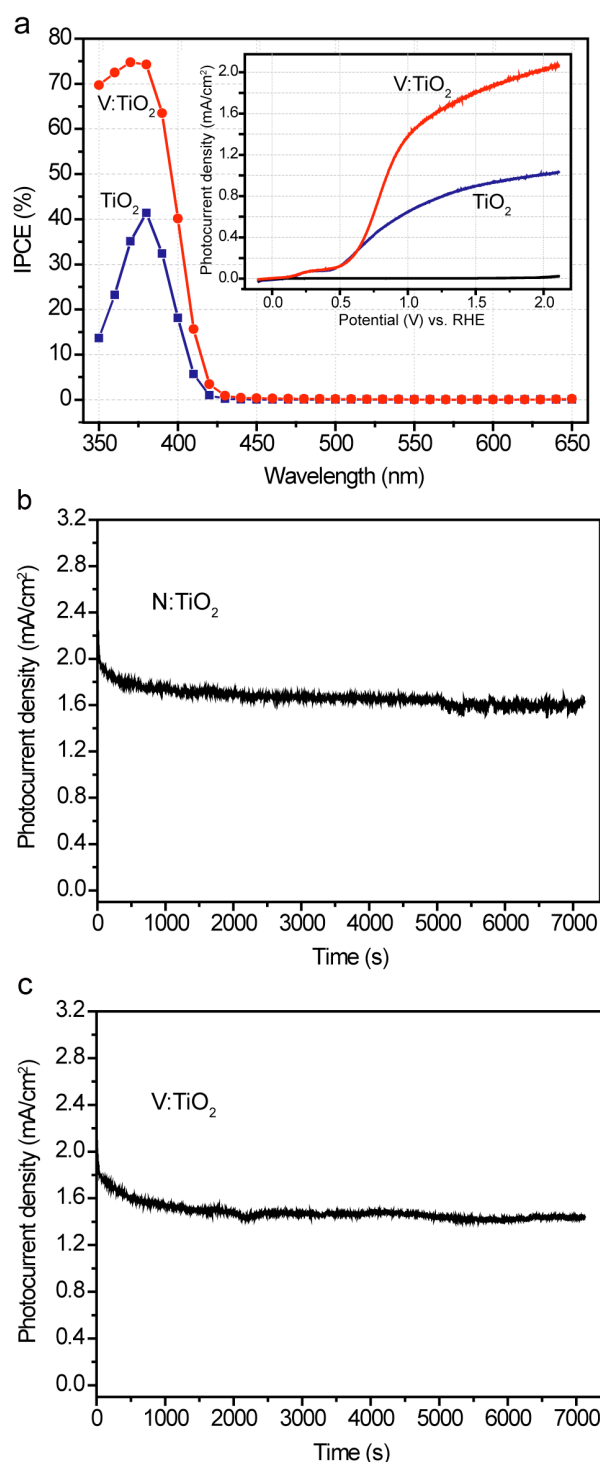


Figure 4.5 (a) IPCE spectra of pristine TiO₂ and V:TiO₂ nanowires measured at a potential of 1.2 V vs. RHE. Inset: Linear sweeps voltammograms of TiO₂ and V:TiO₂ nanowires, measured at a scan

rate of 20 mV/s under 100 mW/cm² white light illumination. The photocurrent-time profiles of (b) N:TiO₂ and (c) V:TiO₂ nanowire samples, measured at a potential of 1.23 V vs. RHE under 100 mW/cm² white light illumination.

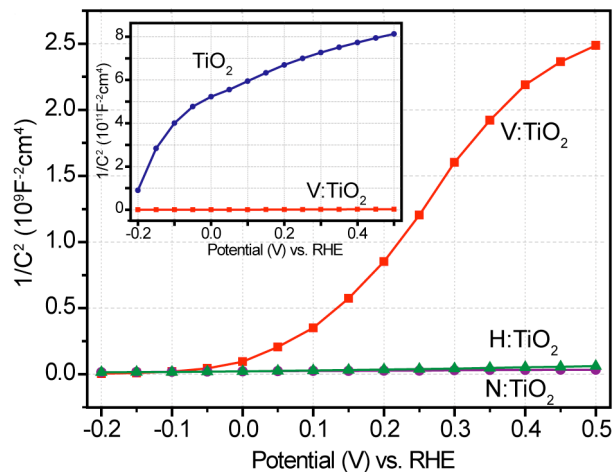


Figure 4.6 Mott-Schottky plots collected at a frequency of 10 kHz in the dark for V:TiO₂ (red curve), H:TiO₂ (green curve) and N:TiO₂ (purple curve) nanowire samples. Inset: Mott-Schottky plots of V:TiO₂ (red curve) and pristine TiO₂ (blue curve) nanowire samples.

XPS spectra collected from pristine TiO₂ nanowire and TiO₂ nanowire samples annealed in H₂, ammonia and under vacuum show identical Ti 2p XPS spectra with Ti 2p_{3/2} and 2p_{1/2} peaks centered at 458.8 eV and 464.4 eV respectively (Figure 4.7).²¹ The two peaks are consistent with the typical binding energies reported for TiO₂, indicating that these treatments do not change significantly the bonding environment of Ti atoms in TiO₂.

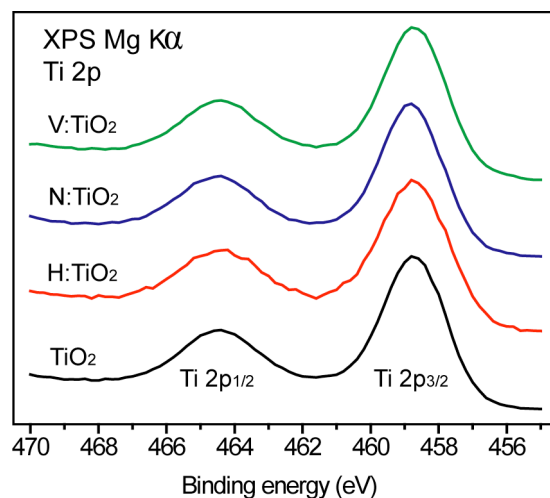


Figure 4.7 Ti 2p XPS spectra of pristine TiO_2 , H:TiO_2 , N:TiO_2 and V:TiO_2 nanowires.

The overlapped O 1s spectra of these samples are displayed in Figure 4.8a. All samples exhibit an asymmetric broad O 1s peak, which suggests more than one chemical states of O are present. Among these samples, the O 1s peak of H:TiO_2 sample significantly shifted to higher binding energy with a full-width-half-maximum of ~ 4 eV. This broad peak can be deconvoluted into three peaks centered at 530.3, 532.0 and 533.4 eV, respectively (Figure 4.8b). 530.3 eV is a characteristic binding energy reported for O_2^- in TiO_2 . 532.0 eV peak can be attributed to be binding energy of Ti-OH, which has been reported to be centered at ~ 1.5 - 1.8 eV higher binding energy than the value for O_2^- . Finally, the 533.4 eV peak can be assigned to adsorbed H_2O ,^{6, 21, 22} due to residual water moisture in the tube furnace. As expected, H:TiO_2 and N:TiO_2 nanowire samples have higher intensity of 532.0 eV peak (-OH group on surface) compared to pristine TiO_2 , which explains the peak shift to higher binding energy (Figure 4.8c). Surprisingly, the O1s XPS fitting curves of V:TiO_2 sample (Figure 4.8d) indicates the presence of OH group even though the

532.0 eV peak is smaller than that observed in H:TiO₂ and N:TiO₂ samples. It is believed that O_{vac} form and exist as active sites during thermal annealing, and water molecules that reside in the vicinity of these O_{vac} dissociate to hydrogen atoms and hydroxyl groups, which has been reported in a previous study on thermal annealed TiO₂ under ultrahigh vacuum.²³ The O 2p energy levels for Ti-OH-Ti and Ti-OH were reported to be located at 2.6 and 0.7 eV below the valence band edge of rutile TiO₂, respectively.^{24, 25} Therefore, the presence of these impurity states should not lead to band gap narrowing of TiO₂.

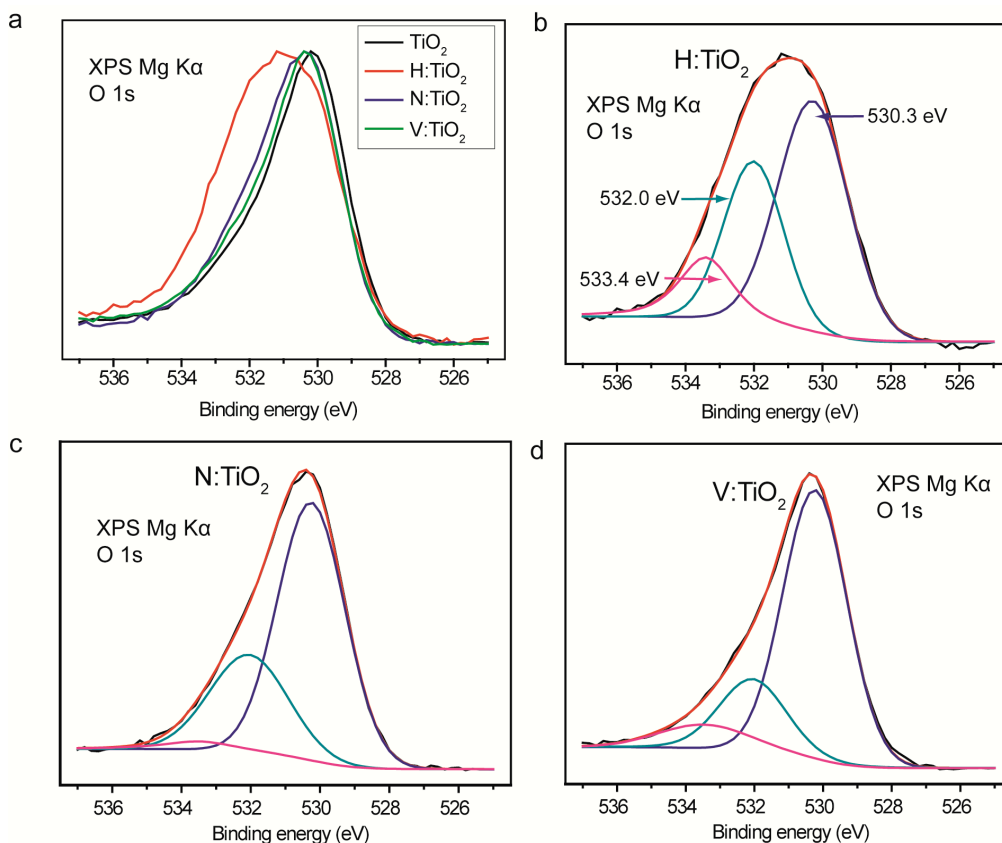


Figure 4.8 (a) Normalized O 1s XPS spectra of the pristine TiO₂, H:TiO₂, N:TiO₂ and V:TiO₂ nanowires. O 1s XPS spectra of (b) H:TiO₂ nanowires, (c) N:TiO₂ nanowires, and (d) V:TiO₂ nanowires. (b-d) The broad peaks are deconvoluted into three peaks. The black

curve is the experimental result. The red curve is the summation of the synthetic peaks centered at 530.3 (blue curve), 532.0 (green curve) and 533.4 eV (purple curve).

Even though creation of O_{vac} in TiO_2 nanowires substantially increases their photoactivities in UV region, absorption of visible light is still very weak. To improve the PEC performance in the visible, we couple CdS QDs as sensitizers for $H:TiO_2$ to enhance visible light absorption. The conduction band edge potentials of TiO_2 and CdS have been reported to be located at -0.5 V^{26} and -0.9 V^{27} vs. normal hydrogen electrode, respectively. This band alignment allows efficient injection of photo-generated electrons from CdS to TiO_2 . We assembled CdS QDs onto TiO_2 nanowire sample by chemical bath deposition as reported elsewhere.⁸ As shown in Figure 4.9a, CdS QDs are uniformly deposited on TiO_2 nanowire surface. Energy dispersive X-ray spectroscopy spectrum confirms the deposited nanoparticles have Cd and S signals (Figure 4.9b).

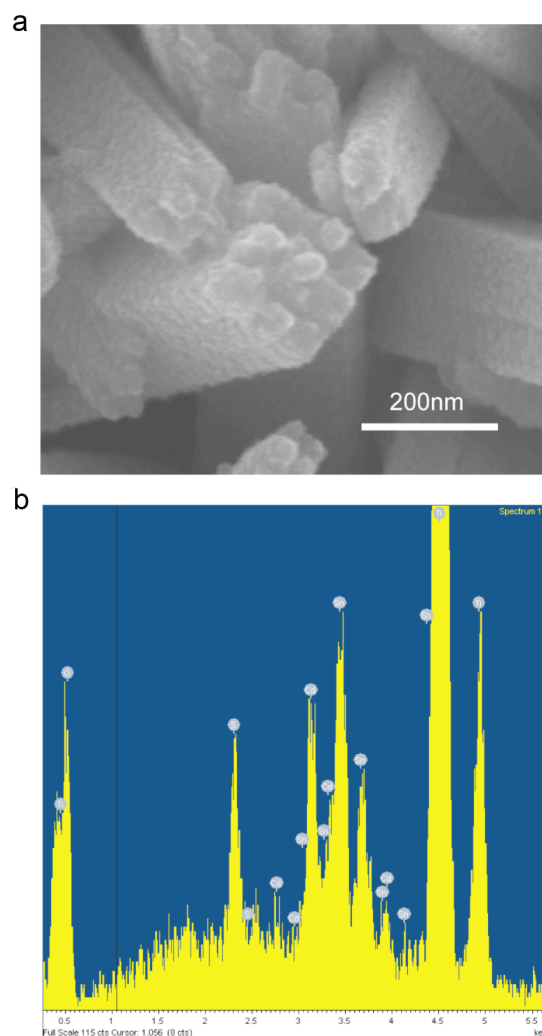


Figure 4.9 (a) SEM images of CdS QD sensitized TiO₂ nanowire arrays prepared on a FTO substrate. (b) EDX spectrum of CdS QD sensitized TiO₂ nanowire arrays.

Linear sweep voltammograms of CdS QD-sensitized TiO₂ (denoted as CdS-TiO₂) and H-doped TiO₂ (denoted as CdS-H:TiO₂) films were measured in a two-electrode electrochemical cell with a platinum wire as counter electrode and nanowire sample as working electrode (Figure 4.10). Note that 0.25 M of Na₂S and 0.35 M of Na₂SO₃ aqueous solution (pH=11.5) was used as electrolyte and hole scavenger. CdS QD-sensitized TiO₂ samples show dramatic increase in photocurrent density due to

the improved visible light absorption. Importantly, the photocurrent density of CdS-H:TiO₂ is slightly higher than that of CdS-TiO₂, and the results are reproducible for all the samples we studied. The enhancement is attributed to the improved charge transport in H:TiO₂ nanowire with higher donor density. IPCE collected from these four samples at 0.5 V vs. RHE show that all CdS QD sensitized TiO₂ samples have notable increased IPCE over the visible light region (> 400 nm), compared to TiO₂. The absorption region of CdS QD sensitized TiO₂ samples are extended to about 550 nm that is agreed with the bandgap of CdS (~2.3 eV).²⁸ More importantly, CdS-H:TiO₂ exhibits enhanced IPCE over the entire UV and visible region compared to CdS-TiO₂, which supports the formation of O_{vac} in H:TiO₂ facilitate the transportation of photoexcited charge carriers from CdS QDs. In comparison to H:TiO₂, the IPCE values of CdS-H:TiO₂ in UV region (< 400 nm) are surprisingly decreased. A possible reason is that a significant portion of UV light was absorbed by CdS QDs on H:TiO₂ nanowires (front side illumination), and severe electron-hole recombination occurs at the interfaces between CdS QDs and CdS/TiO₂ due to the poor crystallinity of CdS prepared by low-temperature chemical bath deposition method. The poor crystallinity of CdS is supported by the absence of CdS diffraction peak in XRD spectrum of CdS-TiO₂ sample (Figure 4.1b). To address this limitation, we performed the hydrogen annealing and QD sensitization in an opposite order. We anticipate that the crystallinity of CdS and the interfacial charge transfer between CdS and TiO₂ will be improved by annealing CdS QDs at elevated temperature. Thermal annealing is a renowned method to increase crystallinity and reduce structural defects in bulk

materials, which has been widely applied to enhance the performance thin film solar cells.²⁹ Indeed, we observed the XRD diffraction peaks for CdS after annealing (Figure 4.1b), suggesting the crystallinity of CdS QD improved. Significantly, CdS QD sensitized TiO₂ sample annealed in H₂ at 320 °C for 3 h (denoted as H:CdS-TiO₂) resulted in a dramatic increase of photocurrent. This sample yields a photocurrent density of 7.2 mA/cm² at 0.5 V *vs.* RHE, which is almost two times higher than that of CdS-H:TiO₂ at the same bias. Apparently, the IPCE values of H:CdS-TiO₂ sample are uniformly higher than the values obtained from a recently reported thermally-treated CdS sensitized mesoporous TiO₂ film over the entire UV-visible region, measured in the same electrolyte at the same bias.³⁰

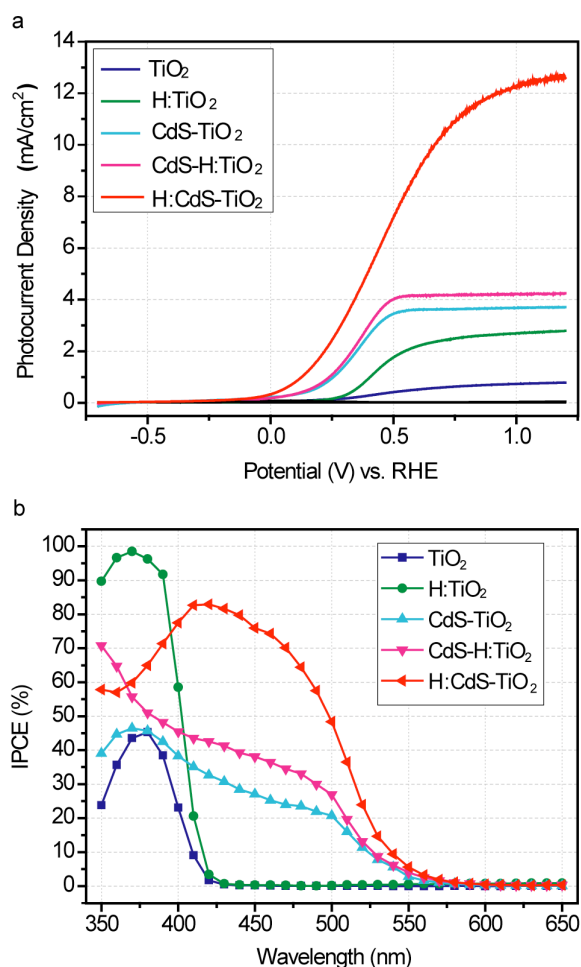


Figure 4.10 (a) Linear sweep voltammograms of the pristine TiO₂, H:TiO₂, CdS-TiO₂, CdS-H:TiO₂ and H:CdS-TiO₂ nanowires, measured at a scan rate of 20 mV/s under 100 mW/cm² white light illumination. (b) Corresponding IPCE spectra collected at a potential of 0.5 V vs. RHE.

A similar enhancement in photocurrent and IPCE was also observed in annealed CdS-TiO₂ nanowires under vacuum and in argon (Figure 4.11). The data suggest that the enhancement achieved by switching the order of QD sensitization and thermal annealing is due to the improved crystallinity of CdS QD and possibly better connection between QDs and TiO₂ nanowires.

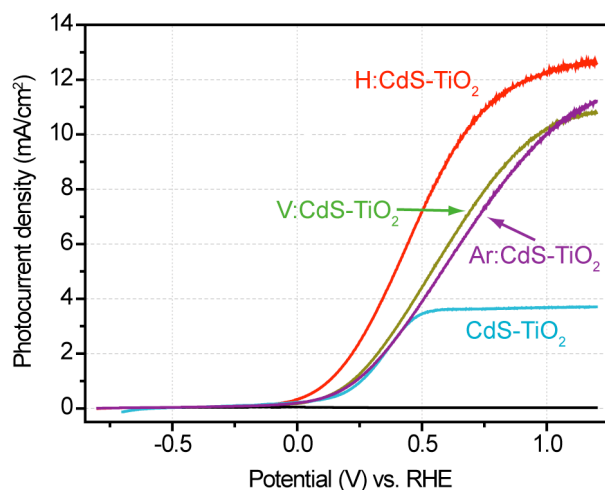


Figure 4.11 Linear sweep voltammograms of the pristine CdS-TiO₂, V:CdS-TiO₂, Ar:CdS-TiO₂, and H:CdS-TiO₂ nanowires, measured at a scan rate of 20 mV/s under 100 mW/cm² white light illumination.

4.4 Conclusion

In summary, we demonstrated that the PEC performance of TiO₂ nanowires as photoanodes for PEC hydrogen generation can be improved through thermal treatment in ammonia or under vacuum. The enhancement is attributed to the improved donor density mediated by the formation of O_{vac}, which can be controlled by tuning the annealing conditions and methods. Furthermore, we investigated the CdS QD sensitized TiO₂ nanowire structures to improve visible light absorption and found that by simply switching the order of sensitization and thermal annealing processes, the CdS QD sensitized TiO₂ samples resulted in a drastic increase of photocurrent density and IPCE. The photocurrent increase is attributed to improved CdS QD crystallinity and possibly the interaction between CdS QDs as well as the interface of CdS and TiO₂. This work presents a simple and general strategy to

improve the photoactivity of TiO_2 nanowires and CdS QD sensitized TiO_2 nanowire composites, which could be extended to other metal oxide based photoelectrodes.

Reference

1. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, 238, 37-38.
2. Khan, S. U. M.; Al-shahry, M.; Ingler Jr., W. B., Efficient Photochemical Water Splitting by a Chemically Modified n-TiO₂. *Science* **2002**, 297, 2243-2245.
3. Lin, Y.; Zhou, S.; Liu, X.; Sheehan, S.; Wang, D., TiO₂/TiSi₂ Heterostructures for High-Efficiency Photoelectrochemical H₂O Splitting. *J. Am. Chem. Soc.* **2009**, 2772-2773.
4. Mor, G. K.; Varghese, O. K.; Wilke, R. H. T.; Sharma, S.; Shankar, K.; Latempa, T. J.; Choi, K.-S.; Grimes, C. A., p-Type Cu-Ti-O Nanotube Arrays and Their Use in Self-Biased Heterojunction Photoelectrochemical Diodes for Hydrogen Generation. *Nano Lett.* **2008**, 8, 1906-1911.
5. Li, Y.; Zhang, J. Z., Hydrogen Generation from Photoelectrochemical Water Splitting Based on Nanomaterials. *Laser Photonics Rev.* **2009**, 4, 517-528.
6. Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y., Hydrogen-Treated TiO₂ Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, 11, 3026-3033.
7. Liu, B.; Aydil, E. S., Growth of Oriented Single-Crystalline Rutile TiO₂ Nanorods on Transparent Conducting Substrates for Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2009**, 131, 3985-3990.
8. Kale, R. B.; Lokhande, C. D., Systematic Study on Structural Phase Behavior of CdSe Thin Films. *J. Phys. Chem. B* **2005**, 109, 20288-20294.
9. Livraghi, S.; Paganini, M. C.; Giamello, E.; Selloni, A.; Valentin, C. D.; Pacchioni, G., Origin of Photoactivity of Nitrogen-Doped Titanium Dioxide under Visible Light. *J. Am. Chem. Soc.* **2006**, 128, 15666-15671.
10. Nambu, A.; Graciani, J.; Rodriguez, J. A.; Wu, Q.; Fujita, E.; Fdez Sanz, J., N doping of TiO₂(110): Photoemission and density-functional studies. *J. Chem. Phys.* **2006**, 125, 094706.
11. Yang, X.; Wolcott, A.; Wang, G.; Sobo, A.; Fitzmorris, R. C.; Qian, F.; Zhang, J. Z.; Li, Y., Nitrogen-Doped ZnO Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2009**, 9, 2331-2336.

12. Hensel, J.; Wang, G.; Li, Y.; Zhang, J. Z., Synergistic Effect of CdSe Quantum Dot Sensitization and Nitrogen Doping of TiO₂ Nanostructures for Photoelectrochemical Solar Hydrogen Generation. *Nano Lett.* **2010**, *10*, 478-483.
13. Asahi, R., Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *Science* **2001**, *293*, 269-271.
14. Bruno, G.; Giangregorio, M. M.; Malandrino, G.; Capezzuto, P.; Fragalà, I. L.; Losurdo, M., Is There a ZnO Face Stable to Atomic Hydrogen? *Adv. Mater.* **2009**, *21*, 1700-1706.
15. Mi, L.; Xu, P.; Shen, H.; Wang, P.-N.; Shen, W., First-Principles Calculation of N:H Codoping Effect on Energy Gap Narrowing of TiO₂. *Appl. Phys. Lett.* **2007**, *90*, 171909.
16. Wang, G.; Ling, Y.; Wheeler, D. A.; George, K. E. N.; Horsley, K.; Heske, C.; Zhang, J. Z.; Li, Y., Facile Synthesis of Highly Photoactive α -Fe₂O₃-Based Films for Water Oxidation. *Nano Lett.* **2011**, *11*, 3503-3509.
17. Bott, A. W., Electrochemistry of Semiconductors. *Curr. Sep.* **1998**, *17*, 88-91.
18. Parker, R. A., Static Dielectric Constant of Rutile (TiO₂), 1.6-1060°K. *Phys. Rev.* **1961**, *124*, 1719-1722.
19. Kim, D.; Hong, J.; Park, Y. R.; Kim, K. J., The Origin of Oxygen Vacancy Induced Ferromagnetism in Undoped TiO₂. *J. Phys. Condens. Matter.* **2009**, *21*, 195405.
20. Diebold, U.; Lehman, J.; Mahmoud, T.; Kuhn, M.; Leonardelli, G.; Hebenstreit, W.; Schmid, M.; Varga, P., Intrinsic Defects on a TiO₂(110)(1×1) Surface and Their Reaction with Oxygen: a Scanning Tunneling Microscopy study. *Surf. Sci.* **1998**, *411*, 137-153.
21. Chen, X.; Liu, L.; Yu, P. Y.; Mao, S. S., Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* **2011**, *331*, 746-750.
22. McCafferty, E.; Wightman, J. P., Determination of the Concentration of Surface Hydroxyl Groups on Metal Oxide Films by a Quantitative XPS Method. *Surf. Interface Anal.* **1998**, *26*, 549-564.
23. Fujino, T.; Katayama, M.; Inudzuka, K.; Okuno, T.; Oura, K.; Hirao, T., Surface Hydroxyl Formation on Vacuum-Annealed TiO₂(110). *Appl. Phys. Lett.* **2001**, *79*, 2716.

24. Imanishi, A.; Okamura, T.; Ohashi, N.; Nakamura, R.; Nakato, Y., Mechanism of Water Photooxidation Reaction at Atomically Flat TiO₂ (Rutile) (110) and (100) Surfaces: Dependence on Solution pH. *J. Am. Chem. Soc.* **2007**, *129*, 11569-11578.
25. Nakamura, R.; Nakato, Y., Primary Intermediates of Oxygen Photoevolution Reaction on TiO₂ (Rutile) Particles, Revealed by in Situ FTIR Absorption and Photoluminescence Measurements. *J. Am. Chem. Soc.* **2004**, *126*, 1290-1298.
26. Grätzel, M., Photoelectrochemical Cells. *Nature* **2001**, *414*, 338-344.
27. Kalyanasundaram, K.; Borgarello, E.; Gratzel, M., Visible Light Induced Water Cleavage in CdS Dispersions Loaded with Pt and RuO₂, Hole Scavenging by RuO₂. *Helv. Chim. Acta* **1981**, *64*, 362-366.
28. Wang, G.; Yang, X.; Qian, F.; Zhang, J. Z.; Li, Y., Double-Sided CdS and CdSe Quantum Dot Co-Sensitized ZnO Nanowire Arrays for Photoelectrochemical Hydrogen Generation. *Nano Lett.* **2010**, *10*, 1088-1092.
29. Rincon, M. E.; Sanchez, M.; Olea, A.; Ayala, I.; Nair, P. K., Photoelectrochemical Behavior of Chemically Deposited CdSe and Coupled CdS/CdSe Semiconductor Films. *Sol. Energ. Mat. Sol. C.* **1998**, *52*, 399-411.
30. Chi, C.-F.; Liao, S.-Y.; Lee, Y.-L., The Heat Annealing Effect on the Performance of CdS/CdSe-Sensitized TiO₂ Photoelectrodes in Photochemical Hydrogen Generation. *Nanotechnology* **2010**, *21*, 025202.

Chapter 5

Photoenhanced Electrochemical Interaction between *Shewanella* and a Hematite Nanowire Photoanode

Abstract

Here we report the investigation of interplay between light, a hematite nanowire-arrayed electrode and *Shewanella oneidensis* MR-1 in a solar-assisted microbial photoelectrochemical system (solar MPS). Whole cell electrochemistry and microbial fuel cell (MFC) characterization of *Shewanella oneidensis* strain MR-1 showed these cells cultured under (semi)anaerobic conditions expressed substantial c-type cytochrome outer membrane proteins, exhibited well-defined redox peaks and generated bioelectricity in a MFC device. Cyclic voltammogram studies of hydrothermally-prepared hematite nanowire electrodes revealed active electron transfer at the hematite/cell interface. Notably, under a positive bias and light illumination, the hematite electrode immersed in a live cell culture was able to produce 150% more photocurrent than that in the abiotic control of medium or dead culture, suggesting a photo-enhanced electrochemical interaction between hematite and *Shewanella*. The enhanced photocurrent was attributed to the additional redox species associated with MR-1 cells that are more thermodynamically favorable to be oxidized than water. Long-term operation of the hematite solar MPS with light on/off cycles showed stable current generation up to two weeks. Fluorescent optical microscope and scanning electron microscope imaging revealed that the top of the hematite nanowire arrays were covered by a biofilm, and iron determination colorimetric assay revealed 11% iron loss after a 10-day operation. To our knowledge, this is the first report on interfacing a photoanode directly with electricigens in a microbial fuel cell system. Such a system could open up new

possibilities in solar-microbial device that can harvest solar energy and recycle biomass simultaneously to treat wastewater, produce electricity and chemical fuels in a self-sustained manner.

5.1 Introduction

Over the past few decades, enormous research efforts have been focused on the conversion of energy from renewable sources into electricity and chemical fuels that are readily usable by human beings. Microbial fuel cells (MFCs) represent a promising technology to directly convert biomass into electricity, hydrogen gas (H_2) or liquid fuels within one step.¹⁻⁵ Recently, MFC technology has received increasing attention due to its potential to be integrated with existing wastewater treatment facilities to recover the chemical energy in the wastewater and convert it into gas- or liquid-phase fuels.⁶⁻⁸ Yet, one issue limiting the practical application of MFC as power generator is their relatively low power density compared to other energy conversion devices. Typical liter-scale MFC reactors generate electrical power densities on the order of mW to W/m^3 .⁹⁻¹¹ In order to generate alternative fuels (e.g. H_2) instead of electricity, an additional electrical energy must be added to overcome the thermodynamic barrier, which would reduce the cost-effectiveness of the method.³

5.2 Experimental Section

5.2.1 Materials

Fluorine-doped tin oxide ($SnO_2:F$) glass substrates were purchased from Wuhan Geao Company. Ferric chloride ($FeCl_3 \cdot 6H_2O$, 99%) was purchased from

Acros Organics. HCl (36.5%–38% by weight), sodium chloride (NaCl, >99.5%), MOPS (>99.5%, cell culture tested), HEPES sodium salt (98%, cell culture reagent grade) and sodium nitrate (NaNO₃, 99.4%) were purchased from Fisher Scientific Company. Sodium DL-lactate solution (syrup, 60 % w/w, cell culture reagent grade), sodium fumarate (>99%), hydroxylamine hydrochloride (>99.999%) and Ferrozine (3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine-4,4-disulfonic acid sodium salt) were purchased from Sigma Aldrich. SYTO® 16 Green fluorescent nucleic acid stain (1 mM in DMSO) was purchased from Life Technologies.

5.2.2 *Synthesis of Hematite (α -Fe₂O₃) Nanostructures*

The hematite nanowire arrays were prepared by previously reported hydrothermal method.^{12, 13} 20 ml aqueous solution containing 0.15 M of ferric chloride and 1 M sodium nitrate at pH 1.5 (adjusted by HCl) was added into a 30 mL stainless steel autoclave with a Teflon liner. A cleaned FTO glass substrate was put into the autoclave, and then heated at 95 °C for 4 hrs. The autoclave was cooled down at room temperature. The substrate was covered with a uniform layer of iron oxyhydroxide nanowire (β -FeOOH) film (yellow color). The β -FeOOH coated substrate was washed with deionized water, and then air dried. To obtain crystalline hematite, the β -FeOOH nanowire arrays were calcined in a horizontal quartz-tube furnace. The tube furnace was first vacuumed to a pressure of 15 Torr, and then filled with ultrahigh purity N₂ at 550 °C for 2 hr (99.998%, Praxair) at 740 Torr pressure with a N₂ flow rate of 50 sccm. Herein, the initial oxygen content is estimated to be 0.43% (O₂/(O₂ + N₂), volume%).¹⁴ The color of the film changed from yellow to red.

For those to be used in control experiment in Fig 5.6, the β -FeOOH nanowire arrays was first calcined in air at 550 °C for 2 hr, then subsequently was annealed at 800 °C for additional 20 min. The β -FeOOH nanowires were converted into hematite nanowires.¹³

5.2.3 Photoelectrochemical (PEC) Measurements

Linear sweep voltammograms were measured in a three-electrode configuration with a platinum wire as counter electrode, Ag/AgCl (in 1 M KCl) as reference electrode, and hematite nanowire-arrayed substrate as working electrode, at a scan rate of 10 mV/s. Hematite photoanode was fabricated by soldering a Ti wire onto the bare edge of FTO glass substrate, and then sealing the FTO glass substrate and metal contact region with insulating epoxy resin. The exposed effective area for the hematite working electrode is 1.0-1.5 cm². All I - V measurements were recorded by an electrochemical workstation (Model CHI 660D, CH Instruments, Inc., Austin, TX); 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/cm². Amperometric I - t curves were collected with the same setup as linear sweep voltammograms, and recorded by an electrochemical workstation (Model CHI 1040B, CH instruments, Inc., Austin, TX) with a light intensity of ca. 45 mW/cm². Cyclic voltammogram studies of the whole cell suspension were carried out under an anaerobic condition where the chamber was pre-purged and continuously purged with nitrogen gas during the measurement.

5.2.4 Bacterial Strain and Culture Conditions

All glassware, solutions and media were autoclaved for sterilization prior to use. *Shewanella oneidensis* strain MR-1 (ATCC 700550) was purchased from American Type Culture Collection (ATCC, Manassas, VA), and cell cultures were started from replicate frozen stocks. For conventional (an)aerobic culture, cells were incubated in *Shewanella* basal medium with sodium lactate (15 mM) as the electron donor.¹⁵ Sodium fumarate (40 mM) was added as the electron acceptors for anaerobic culture. Cells were grown at 30°C and with shaking at 220 rpm for 12-24 h (aerobic) or 24-48 h (anaerobic). For semi-anaerobic culture, cells were cultured in trypticase soy broth (TSB, B.D. Biosciences, Inc., San Jose, CA) at either room temperature or 30°C for 12-24 h with shaking at 100 rpm. For MFC and MPS studies, the cell culture was transferred into the anode chamber of either device. For electrochemical studies, the cell culture was first centrifuged to obtain a cell pellet, which was subsequently re-suspended in 10 mM MOPS (pH=7) and 8.5 mM NaCl solution.¹⁶

5.2.5 Bacterial Fixation and Imaging

For fluorescent imaging, the bacteria-colonizing electrode was rinsed gently with PBS buffer, and then immersed with 1 μ M SYTO stain in PSB buffer solution for 30 min. The sample was rinsed with PBS and mili-Q water again to remove extra dyes, dried at room temperature and imaged with a fluorescent optical microscope (Olympus BX51). For SEM imaging, the photoelectrode was treated using standard glutaraldehyde and osmium tetroxide fixatives before electron microscopic studies.¹⁷ In short, the photoanode was first rinsed with mili-Q water to remove non-adherent

cells, then fixed in 2% glutaraldehyde solution overnight at 4 °C, rinsed with water again, and finally stained with 1% osmium tetroxide solution for 2 hrs. After a final rinsing with water, the samples were dehydrated by serial, 10 min transfers through 50, 70, 90 and 100% ethanol. As-fixed samples were investigated under a field-emission SEM (Hitachi S-4800 II).

5.2.6 Colorimetric Iron Determination Assay

The iron retention was determined by a modified Ferrozine method.¹⁸ First, working curve was obtained by using a series of standard FeSO_4 aqueous solutions from 0.1 to 5 mM. 0.5 mL of each FeSO_4 standard solution was added to 0.5 mL hydroxylamine/1 M HCl solution (saturated hydroxylamine hydrochloride in 1 M HCl aqueous solution), vortex for 10 s and incubated at room temperature for 1 h. Subsequently, a 20 μL of this solution was added to 200 μL of ferrozine (0.05 %) in 50 mM HEPES buffer at pH 7.0, followed by adding 1 mL of mili-Q water. The absorbance at 563 nm was measured and correlated with the known Fe(II) concentration to plot a working curve.

To determine the possible iron dissolution from the photoanode during the long-term culture, all the hematite substrates used were cut into halves, for quantifying the iron mole on the substrate before and after the long-term solar MPS operation. Two different hematite substrates (annealed at 550°C or at 800°C) were tested either without a bias or with an applied bias of 0.8 V vs. Ag/AgCl. For each condition, the experiment was run in triplicate. The substrate was incubated with 2 ml hydroxylamine/ HCl solution until the iron on the substrate was dissolved and

reduced completed, which was then treated as described above and compared with the working curve to determine the iron mole on the substrate.

5.3 Results and Discussion

In order to increase MFCs' power output without increasing operational cost, researchers have attempted to couple solar energy harness with MFC technologies to enable efficient utilization of multiple energy sources.¹⁹⁻²⁷ To date, several types of solar-assisted MFC device prototypes have been reported. For example, photosynthetic strains used as MFC inocula for bioelectricity generation by harvesting sunlight,^{22, 23, 26, 27} a microbial electrolysis cell powered by a solar cell to produce H₂,¹⁹ a semiconductor photocathode employed to drive a microbial anode in a microbial photoelectrochemical cell.²¹ More recently, a photoelectrochemical cell and MFC hybrid device has been demonstrated for producing H₂ using wastewater and sunlight as the only energy inputs.²⁵ However, to our best knowledge, no research attempts have yet been reported of a single solar MFC device that employs a photoanode to interface microbial systems. Indeed, as made of n-type semiconductors, a photoanode may present a few technical challenges to be used in a MFC, including high electrical resistance and poor chemical stability compared to conventional carbon-based anodes. However, we believe it is possible to interface a photoanode with electricigens within a single functional device for synergistic energy conversion, by selecting carefully the semiconductor/microbe system to enable efficient electrical communication between the two distinct systems in a predictable way. Figure 5.1 shows the device configuration and the corresponding band diagram

of our proposed photoanode-based solar microbial photoelectrochemical system (MPS). Such a solar MPS is configured as a three-electrode electrochemical device consisting of an n-type semiconductor photoanode, a Pt cathode and a reference electrode. Cell culture of electrogenic bacteria fills the chamber as the electrolyte. Figure 5.1a highlights the hybrid bio/semiconductor interface. While the photoanode absorbs light to generate electron-hole pairs, the bacterial cells convert organic matter into electricity via bio-catalysis. The harvested electrons are then delivered to the cathode via an external circuit for cathodic reduction. For practical applications such as H₂ production, an external bias may be needed to overcome the cathodic reaction barrier. As a proof-of-concept, we constructed such a device employing a hematite nanowire-arrayed electrode and *Shewanella oneidensis* MR-1, as the photoanode and the microbial system, respectively. Among a wide variety of semiconductors, hematite (α -Fe₂O₃) is chosen due to its favorable band gap for solar light absorption, chemical stability under neutral pH and oxidative environments, wide availability, low-cost, and more importantly, biocompatibility with most bacterial communities. *Shewanella* system is chosen because it represents a model electrogenic microbial system for efficient bioelectricity generation, a facultative strain that can thrive under various oxygen concentration conditions, a dissimilatory metal-reducing bacterium that can live with iron (III) species or even make use them as electron acceptors under anaerobic conditions. An energy diagram (Figure 5.1b) illustrates the band-edge positions of hematite with three dominant reducing species in a *Shewanella* culture. At the neutral pH, the band-edge positions of hematite straddles a range of 2.2 eV

from -0.1 eV (the edge of conduction band, CB) to 2.1 eV (the edge of valence band, VB) vs. normal hydrogen electrode (NHE), and the water oxidation potential is 0.8 V vs. NHE.²⁸ *Shewanella* culture provides a reductive atmosphere with a redox potential window between ca. -0.3 to 0 V vs. NHE.^{2,29} It is reported that *Shewanella* transfers metabolically-generated electrons to external electron acceptors either through direct contact with outer-membrane c-type cytochromes or via the mediation of self-secreted electron shuttles (e.g., riboflavin), whose redox potentials lies ca. -0.21 V vs. NHE.³⁰ In the dark, the device is in an “off” state as the CB edge was not able to receive electrons effectively from any of the above-mentioned reducing species in the electrolyte due to the large overpotential present at the solid/liquid interface, leading to a high anodic resistivity. Under light illumination, the hematite electrode generates photo-excited electron-hole pairs which are subsequently separated by the interfacial electric field at the electrode/electrolyte interface. As shown in Figure 5.1b, the photo-generated holes in the VB accept electrons from cytochrome, electron shuttles or water, while the photo-generated electrons flow through an external circuit to for cathodic reduction at the cathode. Given the continuous supply of sunlight and organic matter, the system is expected to run in a self-sustained manner.

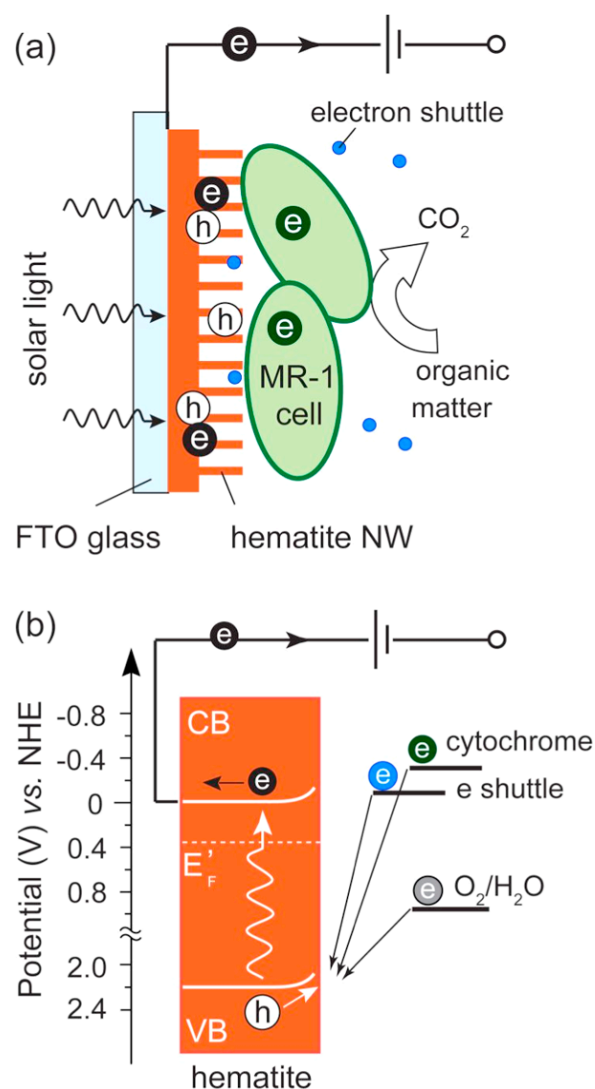


Figure 5.1 Schematic (a) and corresponding energy diagram (b) of the hybrid interface of the hematite photoanode in a solar MPS. The CB, VB and E_F represent for conduction band, valence band and Fermi level, respectively. Solid and empty circles represent electrons and holes, respectively.

To test the overall performance of the proposed solar MPS, we characterized and optimized separately the electrical/electrochemical properties of the microbial and semiconductor systems. MR-1 cells were purchased from ATCC and cultured under three distinct conditions: strictly aerobic, strictly anaerobic, and semi-anaerobic

(for detailed culture conditions see Experimental Section). The aerobic and anaerobic cultures were performed in a lactate-based minimal media, using O_2 and fumarate as electron acceptors, respectively. The semi-anaerobic condition was effectively achieved by using trypticase soy broth (TSB) medium with a moderate shaking speed, where a high cell density is achieved and the oxygen diffusion rate into the medium was far slower than that of the oxygen consumption, leading to an oxygen-deficient atmosphere.³¹ Figure 5.2a compares the cell pellets harvested by centrifugation from these three culture methods. In contrast to the aerobically cultured cells, the (semi)anaerobic cultures appeared bright orange in color, due to the suppressed protein expression of the key c-type cytochrome proteins involved in the Mtr pathway.^{32, 33}

The extracellular electron transfer capability of the MR-1 cells was further examined using electrochemical methods. Figure 5.2b shows the whole-cell cyclic voltammogram (CV) recorded from a glassy carbon electrode (GCE) immersed in a cell suspension in an anaerobic buffer. In comparison to an abiotic control or an aerobic culture, the CV data of strictly or semi-anaerobically culture cells show a pair of well-defined redox peaks in the potential range between -0.9 and 0.5 V vs. Ag/AgCl. After linear background subtraction, a cathodic peak position (E^{pc}) = -329 mV vs. Ag/AgCl and an anodic peak position (E^{pa}) = -25 mV vs. Ag/AgCl can be identified, which a midpoint potential (E^0) = -177 mV vs. Ag/AgCl can be calculated according to $E^0 = (E^{pc} + E^{pa})/2$ (Figure 5.2b, inset). These values were consistent with the redox potentials of the c-type cytochrome of MR-1 cells in either whole-cell

suspension or protein film voltammetry of MtrC and OmcA films.^{17, 34} Therefore, these experiments showed that under anaerobic conditions, MR-1 cells expressed c-type cytochromes that are essential to the extracellular electron transfer, and could electrochemically interact with an external electrode.

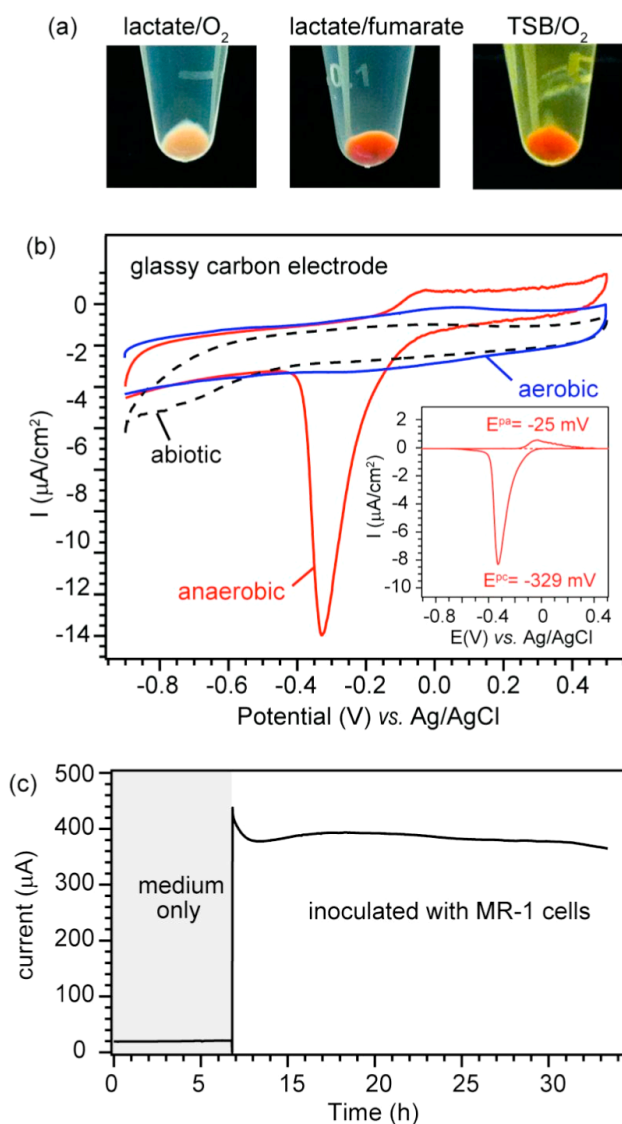


Figure 5.2 MR-1 cell culture and electrochemical characterization. (a) Pictures of cell pellets harvested from aerobic culture (left), anaerobic culture (middle) and semi-anaerobic culture (right). (b) Cyclic

voltammogram data collected using a glassy carbon electrode in an abiotic control of TSB medium (black dashed), aerobic culture (blue solid) and anaerobic culture (red solid), at a scan rate of 50 mV/s. Inset: the same CV data of the anaerobic culture after background subtraction. (c) Current vs. time plot of a ferricyanide-cathode MFC device using MR-1 culture as inocula.

The MR-1 cells were also used to inoculate a MFC to test their substrate-to-electricity conversion capability in a longer run. Figure 5.2c shows the electricity generation by MR-1 cells in a ferricyanide-cathode MFC configuration. Details about the MFC structures and operation conditions can be found in Figure 5.3. Prior to the introduction of the cell culture, the MFC was measured in the sterile growth medium of TSB. Although TSB contain a variety of chemical nutrient with low reduction potentials, the reduction kinetics of these chemicals at the carbon cloth electrode was slow without microbial catalysis, therefore generating a negligible current baseline of less than 20 μA . Following the cell inoculation, the MFC generated an instantaneous current of 450 μA then maintained to a stable output of ca. 380 μA in the next 20 hrs. The output power density was calculated to be 4.8 $\mu\text{W}/\text{cm}^2$. The MFC results show that the cells are able to use organic nutrient to generate electricity and produce sustainable energy on a long-time scale.

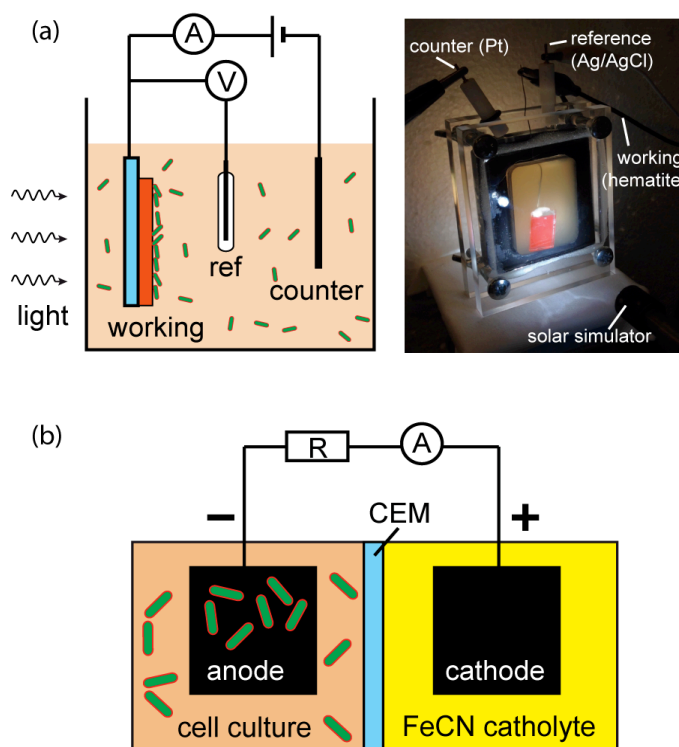


Figure 5.3 (a) Scheme and device picture of the solar microbial photoelectrochemical system (solar MPS), configured as a three-electrode photoelectrochemical cell. (b) Scheme of the microbial fuel cell (MFC) device. CEM represents cation exchange membrane.

Hematite nanowires were used as photoanode material in the solar MPS. Dense and vertically aligned hematite nanowire arrays were grown on a fluorine-doped tin oxide (FTO)-coated glass substrate using hydrothermal method as previously reported (Experimental Method).^{13, 14} Scanning electron microscopy (SEM) images collected from the growth substrate revealed a high-density growth of hematite nanowires (Figure 5.4a, inset). The nanowires have an average diameter of 120 nm and an average length of 700 nm. The photoelectrochemical measurements of hematite photoanode were first performed in a three-electrode electrochemical cell. Linear sweep voltammogram (LSV) were performed in TSB electrolyte, using a

hematite nanowire-arrayed photoelectrode as the working electrode, a platinum wire as the counter electrode, and a reference electrode of Ag/AgCl (1M KCl) at the scan rates of 10 mV (Figure 5.4a). Under one-sun illumination (AM 1.5G, 100 mW/cm²), the hematite photoanode showed a turn-on voltage around 0.05 V, while a pronounced photocurrent density of 0.1 mA/cm² was obtained at 0.7 V *vs.* Ag/AgCl. Subsequently, CV studies of a hematite nanowire electrode were carried out. As a negative control, a CV scan was first carried out in TSB within a potential window ranging from -0.8 to 0.5 V *vs.* Ag/AgCl in the dark (Figure 5.4b, dashed black curve). In this potential range, there is a cathodic peak at -260 mV *vs.* Ag/AgCl. Similar voltammetric profiles have been observed for electrodes coated by hematite nanoparticles or nanorods, and it was attributed to the formation of a thin layer of Fe(III) (hydro)oxide intermediate adsorbed on the hematite surface according to the following reactions:



Reaction (1) represents a slow elemental step that occur more easily in basic solution.¹⁷ It suggests that a hematite electrode could be reduced at a potential more negative than ca. -0.2 V *vs.* Ag/AgCl, especially in a basic solution. On the other hand, CV scan of the same hematite electrode immersed in the live cell culture yielded distinctive redox peaks (Figure 5.4b, solid red curve). A pronounced sharp cathodic and a flatter anodic peak was observed at -290 and -140 mV *vs.* Ag/AgCl, respectively, yielding an E⁰ of -215 mV *vs.* Ag/AgCl. After linear background

subtraction, it can be clearly seen that both the position and amplitude of the redox peaks differ largely from those of the abiotic control while consistent with the c-type cytochromes, suggesting that active electron transfer between the cells and the hematite anode (Figure 5.4b, inset).^{17, 34} On the basis of these results, our hematite nanowire arrays are demonstrated to interact electrochemically with live *Shewanella*.

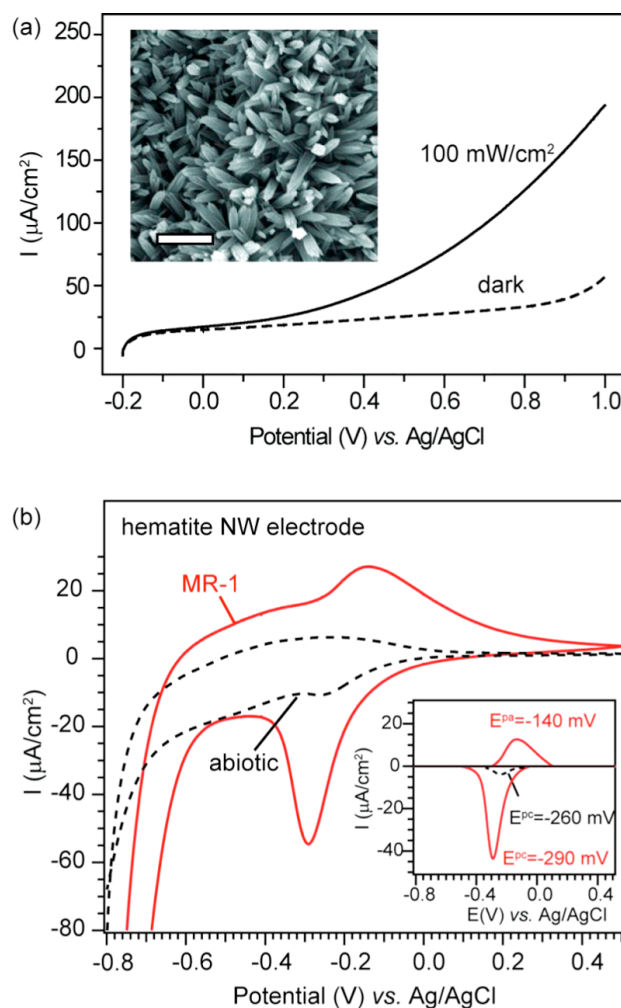


Figure 5.4 (a) Linear scan voltammogram of a hematite nanowire-arrayed electrode in TSB electrolyte at a scan rate of 10 mV/s, in the dark (dashed) and under a one-sun illumination (solid). Inset: a SEM image of the hematite nanowires on the FTO substrate. Scale bar is 1 μm . (b) Cyclic voltammogram data recorded in the dark from a hematite NW electrode, using either a sterile TSB medium (black

dashed) or a MR-1 culture in TSB (red solid). Scan rates are 50 mV/s. Inset: the same CV data of the cell culture after background subtraction.

The effect of light illumination on the hematite/bacteria electrochemical interaction was further investigated. We focused on a potential window between -0.2 and 1.0 V *vs.* Ag/AgCl, in which the hematite is electrochemically stable. LSV in this potential range was first carried out in an abiotic control of TSB medium. As shown in Figure 5.5a, while the dark scan led to a small current density of 20 $\mu\text{A}/\text{cm}^2$, the light curve started to turn on around 0.25 V and reached 0.1 mA/cm^2 at 0.8V *vs.* Ag/AgCl (black curves). In comparison, photoelectrochemical studies carried out on the same photoanode immersed in a MR-1 cell culture showed current onset at a much lower potential (0V *vs.* Ag/AgCl) and significantly increased current density across the entire investigated potential range. For example, the live cell MPS achieved a photocurrent density of 0.25 mA/cm^2 at 0.8 V *vs.* Ag/AgCl, which is 150% more than that from the abiotic control at the same voltage (Figure 5.5a, highlighted by the dashed line). We attribute the extra gain of the photocurrent to the contribution from the microbial system, including the electron transfer from the cell membranes and the oxidation of soluble electron shuttles (Figure 5.1). To prove this hypothesis, the live cell culture was taken out, autoclaved to kill the cells and deactivate most electron shuttles, and then injected back into the device to measure again the PEC performance. In this case, the photocurrent generation was decreased to a similar level with the abiotic control. These measurements confirmed that a rationally-designed photoanode was able to harvest bioelectrons from the

microorganisms in addition to solar energy, and therefore boost the overall energy recovery from multiple renewable energy sources.

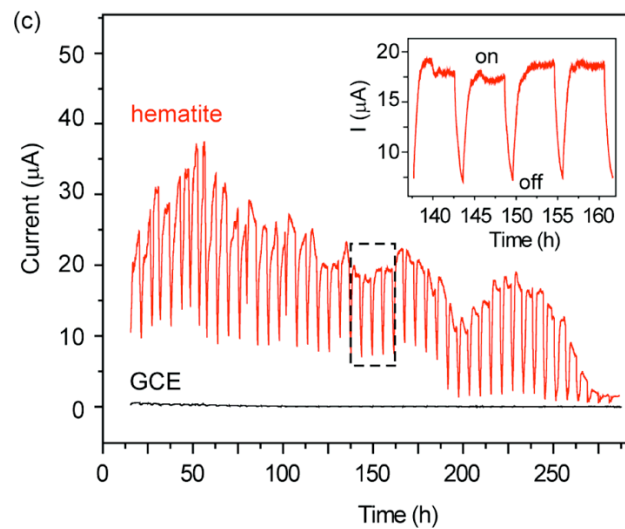
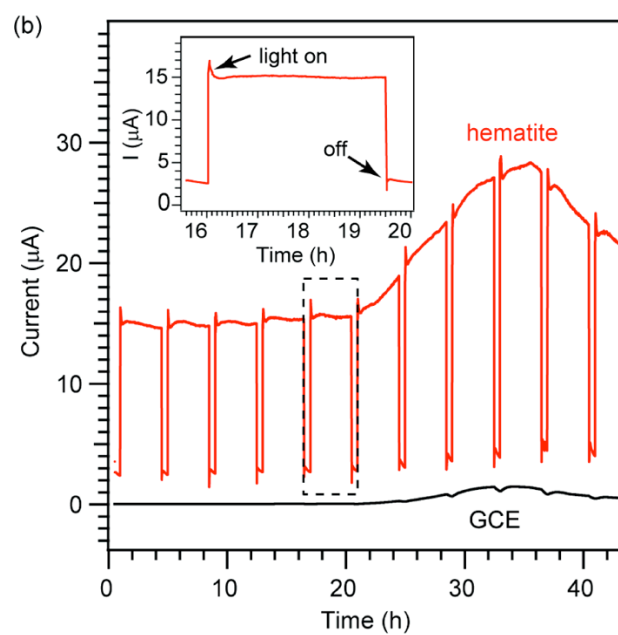
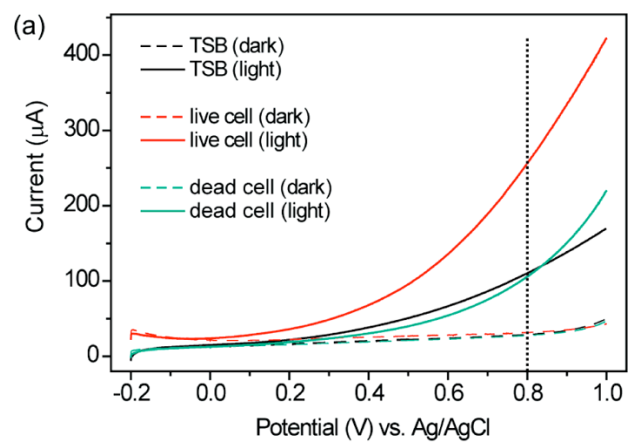
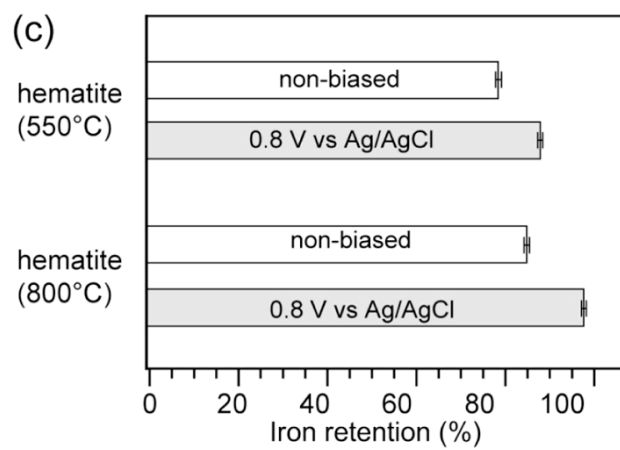
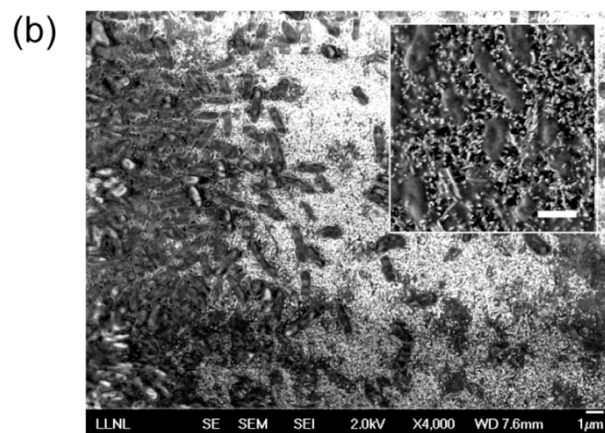
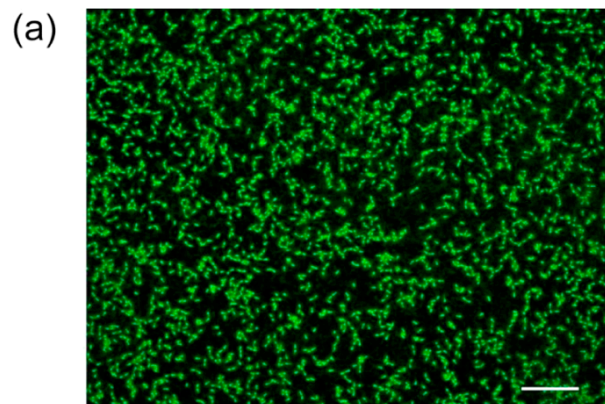


Figure 5.5 Photo-enhanced electrochemical interactions between a hematite electrode and the MR-1 cells. (a) Linear scan voltammogram data recorded from a hematite NW electrode, soaked in TSB medium (black), live MR-1 cell culture (red) and autoclaved MR-1 cell culture (cyan). Scan rates are 10 mV/s. A dotted line indicates the value of photocurrents at 0.8V vs. Ag/AgCl. (b) Amperometric *I-t* curves recorded from a hematite electrode (red) and a GCE (black) immersed in live MR-1 culture, at 0.8V vs. Ag/AgCl, with light on/off cycles at light intensity of 40 mW/cm². Inset: Magnified view of the spectrum highlighted in the dashed box. (c) Long-term *I-t* measurements from a hematite electrode (red) and a GCE (black) for ca. 300 h at 0.8V vs. Ag/AgCl, with light on/off cycles at light intensity of 40 mW/cm². Inset: Magnified view of the spectrum highlighted in the dashed box.

Amperometric *I-t* measurements were performed on the solar MPS to evaluate the long-term chemical stability of hematite photoanode and the overall device lifetime. Figure 5.5b shows the *I-t* curve recorded simultaneously from a hematite photoanode and a glassy carbon electrode (GCE), both sharing an Ag/AgCl reference and Pt counter electrode in a single-chamber device. A positive bias of 0.8 V (vs. Ag/AgCl) as applied to anodes and the light illumination was controlled with a 3.5/0.5 hr light/dark cycle. In the first 20 hrs following cell inoculation, the dark and photo current showed stable respective baselines of 3 and 15 $\mu\text{A}/\text{cm}^2$, while the GCE did not show any light responses, as expected. In the next 20 hrs, a steady increase in the photocurrent up to was observed up to 30 $\mu\text{A}/\text{cm}^2$, while the dark current of the hematite and GCE still maintained at a low level below 5 $\mu\text{A}/\text{cm}^2$. Within one light on/off cycle (Figure 5.5b, inset), the photocurrent generation was stable for a couple of hours without any indication of decay. We also characterized the device performance in 300 hrs, as shown in Figure 5.5c. The device was biased at 0.8 V vs. Ag/AgCl, at 40 mW/cm² solar illumination, 5.5/0.5 hr light on/off cycle. With regular

supplement of new medium and inocula, this device produced electricity for more than 250 hrs, before it eventually decayed to baseline, possibly due to the gradual deactivation of the strain and/or microbial corrosion of hematite electrodes.

The hematite based solar MEC devices were disassembled after operation for post analysis of bacterial growth and electrode integrity. Fluorescent optical images taken from the bacteria-thriving electrode after SYTO-staining showed that the surface of hematite electrode was covered by a uniform layer of bacterial cells (Figure 5.6a). SEM image of the electrode surface revealed that these cells had a rod-shaped morphology and were partially embedded in extracellular protein matrix-like structures, consistent with a MR-1 biofilm (Figure 5.6b). We did not observe other cell shapes indicative of contamination. Due to the tiny gap between individual wires (< 500 nm) that is smaller than the average cell dimensions (~ 2 μm), the MR-1 cells were not able to penetrate the semi-film of nanowire arrays, but rather grew on the top. We did not observe significant morphology change of the nanowires before and after cell inoculation.



Iron retention (%)	Hematite (550°C)		Hematite (800°C)	
	non-biased	0.8 V	non-biased	0.8 V
AVE	79.42	88.93	84.92	97.03
SD	0.20	0.88	1.14	0.74

Figure 5.6 (a) A fluorescent optical image of the MR-1 cell biofilm (stained with SYTO®16) on the hematite electrodes after a 10-day operation. Scale bar is 10 μm . (b) A SEM image taken from a bacteria-colonizing hematite electrode. Inset: a magnified view of the cell/nanowire interface. Scale bars are 1 μm . (c) Data of iron retention percentage of 550°C and 800°C-annealed hematite electrodes operated at either non-bias or 0.8V *vs.* Ag/AgCl in solar MPS for 10 days.

Last, we quantified the possible degradation of hematite anodes during the long-term culture, and investigated the impact of annealing conditions on the material stability. Briefly, the iron moles on the FTO electrodes were quantitatively measured before and after microbial incubation, using a standard ferrozine-based colorimetric assay (see Experimental Section).¹⁸ We defined the ratio of the remaining iron mass (after cell culture) relative to the total iron mass (before cell culture) as the iron retention percentage, as a parameter to reflect the stability of the hematite nanomaterials under long-term cell culture conditions. Hematite nanowires annealed at two different temperatures, namely 550 and 800 °C, both deposited on FTO electrodes, were assembled in individual devices and operated with continuous light illumination, either with or without a + 0.8V *vs.* Ag/AgCl. For each condition, the experiment was run in triplicate. Figure 5.6c compared the results of iron retention after a 10-day-long culture at room temperature. The non-biased 550 °C-annealed hematite (used in this work) showed an apparent dissolution rate of 0.025 $\mu\text{mol/day}$, as a result of bacterial reduction. In comparison, a 0.8 V-biased 550 °C-annealed hematite electrode showed much reduced iron loss of 0.015 $\mu\text{mol/day}$. We believe this is because without a bias, *Shewanella* can use solid iron (III) species as external electron acceptors, leading to a slow reductive dissolution of hematite. However, with

a positive bias, the extra electrons generated in the photoanode are efficiently swept from the hematite surface to the cathode, protecting the photoanode against microbial degradation. We also tested 800°C-annealed hematite nanowire photoanode, which, according to our previous results, exhibited enhanced crystallinity and chemical stability.¹⁴ As the 800 °C-annealed hematite electrodes operated under a bias of 0.8 V in the solar MPS showed a minimal iron loss of $2.97 \pm 0.74\%$ in 10 days, we believe that a high-temperature annealing step helps promote the chemical stability of hematite against the reduction by MR-1 cells, and suggests a promising electrode material candidate for long-term device operation.

5.4 Conclusion

We investigated the photo-enhanced electrochemical interaction between a hematite electrode and electrogenic bacterial strain *Shewanella* species in a single MPS device, as evidenced by drastically increased photocurrent generation in the presence of live cells. Cyclic voltammogram of whole cell suspension of (semi)anaerobically cultured MR-1 cells exhibited distinct redox peaks consistent with the protein film voltammetry of OmcA and MtrC. Using a hematite nanowire-arrayed FTO substrate as the anode and the MR-1 cell culture as the electrolyte, linear sweep scan showed 150% more photocurrent generation at +0.8 V vs. Ag/AgCl than those of abiotic control of medium or dead culture. Long-term *I-t* measurement of the device with light on/off cycles exhibited stable bio/photocurrent generation up to two weeks. This work opens up possibilities in a new category of photo-anode based solar microbial energy conversion system, which could harvest energy from sunlight and

multiple renewable energy sources for producing electricity or chemical fuels in a single device. To achieve this goal, future studies should focus on the development of semiconductor photoanode materials that can enable non-biased, self-sustained operation, the use of wastewater or other recyclable biomass as the bioenergy source, and the reductive cathodic synthesis of liquid fuels of other valuable products using the generated electricity.

Reference

1. Lovley, D. R., Bug Juice: Harvesting Electricity with Microorganisms. *Nat. Rev. Microbiol.* **2006**, *4*, 497-508.
2. Bretschger, O.; Obraztsova, A.; Sturm, C. A.; Chang, I. S.; Gorby, Y. A.; Reed, S. B.; Culley, D. E.; Reardon, C. L.; Barua, S.; Romine, M. F.; Zhou, J.; Beliaev, A. S.; Bouhenni, R.; Saffarini, D.; Mansfeld, F.; Kim, B.-H.; Fredrickson, J. K.; Nealson, K. H., Current Production and Metal Oxide Reduction by *Shewanella oneidensis* MR-1 Wild Type and Mutants. *Appl. Environ. Microbiol.* **2007**, *73*, 7003-7012.
3. Cheng, S.; Logan, B. E., Sustainable and Efficient Biohydrogen Production via Electrohydrogenesis. *Proc. Natl. Acad. Sci.* **2007**, *104*, 18871-18873.
4. Call, D.; Logan, B. E., Hydrogen Production in a Single Chamber Microbial Electrolysis Cell Lacking a Membrane. *Environ. Sci. Technol.* **2008**, *42*, 3401-3406.
5. Logan, B. E.; Call, D.; Cheng, S.; Hamelers, H. V. M.; Sleutels, T. H. J. A.; Jeremiasse, A. W.; Rozendal, R. A., Microbial Electrolysis Cells for High Yield Hydrogen Gas Production from Organic Matter. *Environ. Sci. Technol.* **2008**, *42*, 8630-8640.
6. Du, Z.; Li, H.; Gu, T., A state of the Art Review on Microbial Fuel Cells: A Promising Technology for Wastewater Treatment and Bioenergy. *Biotechnol. Adv.* **2007**, *25*, 464-482.
7. Fornero, J. J.; Rosenbaum, M.; Angenent, L. T., Electric Power Generation from Municipal, Food, and Animal Wastewaters Using Microbial Fuel Cell. *Electroanalysis* **2010**, *22*, 832-843.
8. Li, W.-W.; Yu, H.-Q.; He, Z., Towards Sustainable Wastewater Treatment by Using Microbial Fuel Cells-Centered Technologies. *Energy Environ. Sci.* **2014**, *7*, 911-924.
9. Logan, B. E., Exoelectrogenic Bacteria that Power Microbial Fuel Cells. *Nat. Rev. Microbiol.* **2009**, *7*, 375-381.
10. Ringeisen, B. R.; Henderson, E.; Wu, P. K.; Pleiron, J.; Ray, R.; Little, B.; Biffinger, J. C.; Jones-Meehan, J. M., High Power Density from a Miniature Microbial Fuel Cell Using *Shewanella oneidensis* DSP10. *Environ. Sci. Technol.* **2006**, *40*, 2629-2634.

11. Zhang, F.; Ge, Z.; Grimaud, J.; Hurst, J.; He, Z., Long-Term Performance of Liter-Scale Microbial Fuel Cells Treating Primary Effluent Installed in a Municipal Wastewater Treatment Facility. *Environ. Sci. Technol.* **2013**, *47*, 4941-4948.
12. Vayssieres, L.; Beermann, N.; Lindquist, S.-E.; Hagfeldt, A., Controlled Aqueous Chemical Growth of Oriented Three-Dimensional Crystalline Nanorod Arrays: Application to Iron(III) Oxides. *Chem. Mater.* **2001**, *13*, 233-235.
13. Ling, Y.; Wang, G.; Wheeler, D. A.; Zhang, J. Z.; Li, Y., Sn-Doped Hematite Nanostructures for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, *11*, 2119-2125.
14. Ling, Y.; Wang, G.; Reddy, J.; Wang, C.; Zhang, J. Z.; Li, Y., The Influence of Oxygen Content on the Thermal Activation of Hematite Nanowires. *Angew. Chem. Int. Ed.* **2012**, *51*, 4074-4079.
15. Baron, D.; LaBelle, E.; Coursolle, D.; Gralnick, J. A.; Bond, D. R., Electrochemical Measurement of Electron Transfer Kinetics by *Shewanella oneidensis* MR-1. *J. Biol. Chem.* **2009**, *284*, 28865-28873.
16. Qian, F.; Baum, M.; Gu, Q.; Morse, D. E., A 1.5 μ L Microbial Fuel Cell for On-Chip Bioelectricity Generation. *Lab Chip* **2009**, *9*, 3076-3081.
17. Meitl, L. A.; Eggleston, C. M.; Colberg, P. J. S.; Khare, N.; Reardon, C. L.; Shi, L., Electrochemical Characterization of *Shewanella oneidensis* MR-1 and Its Outer Decaheme Membrane Cytochromes OmcA and mtrC with Hematite Electrodes. *Geochim. Cosmochim. Acta* **2009**, *73*, 5292-5307.
18. Stookey, L. L., Ferrozine-A New Spectrophotometric Reagent for Iron. *Anal. Chem.* **1970**, *42*, 779-781.
19. Chae, K. J.; Choi, M. J.; Kim, K. Y.; Ajayi, F. F.; Chang, I. S.; Kim, I. S., A Solar-Powered Microbial Electrolysis Cell with a Platinum Catalyst-Free Cathode to Produce Hydrogen. *Environ. Sci. Technol.* **2009**, *43*, 9525-9530.
20. Cho, Y. K.; Donohue, T. J.; Tejedor, I.; Anderson, M. A.; McMahon, K. D.; Noguera, D. R., Development of a Solar-Powered Microbial Fuel Cell. *J. Appl. Microbiol.* **2008**, *104*, 640-650.
21. Qian, F.; Wang, G.; Li, Y., Solar-Driven Microbial Photoelectrochemical Cells with a Nanowire Photocathode. *Nano Lett.* **2010**, *10*, 4686-4691.
22. Strik, D. P. B. T. B.; Hamelers, H. V. M.; Buisman, C. J. N., Solar Energy Powered Microbial Fuel Cell with a Reversible Bioelectrode. *Environ. Sci. Technol.* **2010**, *44*, 532-537.

23. Rosenbaum, M.; He, Z.; Angenent, L. T., Light Energy to Bioelectricity: Photosynthetic Microbial Fuel Cells. *Curr. Opin. Biotech.* **2010**, *21*, 259-264.
24. Strik, D. P. B. T. B.; Timmers, R. A.; Helder, M.; Steinbusch, K. J. J.; Hamelers, H. V. M.; Buisman, C. J. N., Microbial Solar Cells: Applying Photosynthetic and Electrochemically Active Organisms. *TRENDS Biotechnol.* **2011**, *29*, 41-49.
25. Wang, H.; Qian, F.; Wang, G.; Jiao, Y.; He, Z.; Li, Y., Self-Biased Solar-Microbial Device for Sustainable Hydrogen Generation. *ACS Nano* **2013**, *7*, 8728-8735.
26. Xing, D.; Zuo, Y.; Cheng, S.; Regan, J. M.; Logan, B. E., Electricity Generation by *Rhodospseudomonas palustris* DX-1. *Environ. Sci. Technol.* **2008**, *42*, 4146-4151.
27. He, Z.; Kan, J.; Mansfeld, F.; Angenent, L. T.; Nealson, K. H., Self-Sustained Phototrophic Microbial Fuel Cells Based on the Synergistic Cooperation between Photosynthetic Microorganisms and Heterotrophic Bacteria. *Environ. Sci. Technol.* **2009**, *43*, 1648-1654.
28. Xu, Y.; Schoonen, M. A. A., The Absolute Energy Positions of Conduction and Valence Bands of Selected Semiconducting Minerals. *Am. Mineral.* **2000**, *85*, 543-556.
29. Firer-Sherwood, M.; Pulcu, G. S.; Elliott, S. J., Electrochemical Interrogations of the Mtr Cytochromes from *Shewanella*: Opening a Potential Window. *J. Biol. Inorg. Chem.* **2008**, *13*, 849-854.
30. Marsili, E.; Baron, D. B.; Shikhare, I. D.; Coursolle, D.; Gralnick, J. A.; Bond, D. R., *Shewanella* Secretes Flavins that Mediate Extracellular Electron Transfer. *Proc. Natl. Acad. Sci.* **2008**, *105*, 3968-3973.
31. Wang, G.; Qian, F.; Saltikov, C. W.; Jiao, Y.; Li, Y., Microbial Reduction of Graphene Oxide by *Shewanella*. *Nano Res.* **2011**, *4*, 563-570.
32. Tsapin, A. I.; Nealson, K. H.; Meyers, T.; Cusanovich, M. A.; Beuumen, J. V.; Crosby, L. D.; Feinberg, B. A.; Zhang, C., Purification and Properties of a Low-Redox-Potential Tetraheme Cytochrome c₃ from *Shewanella Putrefaciens*. *J. Bacteriol.* **1996**, *178*, 6386-6388.
33. Pitts, K. E.; Bobbin, P. S.; Reyes-Ramirez, F.; Thomson, A. J.; Richardson, D. J.; Seward, H. E., Characterization of the *Shewanella oneidensis* MR-1 Decaheme Cytochrome MtrA. *J. Biol. Chem.* **2003**, *278*, 27758-27765.

34. Eggleston, C. M.; Khare, N.; Lovelace, D. M., Cytochrome c Interaction with Hematite (α -Fe₂O₃) Surfaces *J. Electron. Spectrosc.* **2006**, *150*, 220-227.

Chapter 6

Summary and Outlook

Solar-assisted MFC devices hold great promise for recovering energy from wastewater and simultaneously remove the organic wastes. However, there still are several major challenges in the realization of practically useful solar-assisted MFC devices, including energy conversion efficiency, fabrication and operation cost, and the device scalability.

Cost effectiveness is the most important factor for evaluating the practicality of solar-assisted MFCs. Use the PEC-MFC device as an example, the ion exchange membrane, Pt-decorated carbon cloth electrode and Pt electrode are costly. To lower the cost, the device architecture should be further simplified. For example, the demonstration of the MPC device with a photo cathode directly interfacing with bioanode offers important insights in simplifying the device structure. On the same scientific basis, a photoanode could also integrate with a bio-cathode to replace the expensive Pt electrodes. In addition to reduce the material cost, it is equally important to increase the energy conversion efficiency. The previous studies showed that conversion efficiency of solar-assisted MFC device is determined by the interaction between the bio- electrode and photoelectrode, in which the charges generated on both sides need to be matched. Therefore, the relatively slow generation rate of bio-electrons limits the overall efficiency for hydrogen production. To address this issue, a possible direction is the fabrication of electrical conductive three-dimensional (3D) anode electrode with large surface area.¹⁻³ For example, I have developed a 3D flexible, low-cost and conductive reduced graphene oxide-nickel (denoted as rGO-Ni) foam as an anode for MFC by controlled loading rGO sheets on the Ni foam

substrate.¹ In comparison to conventional electrodes, the 3D rGO-Ni electrode provide not only a larger accessible surface area for microbial colonization and electron mediators, but also a uniform macro-porous scaffold for effective mass diffusion of the culture medium. This 3D rGO-Ni foam MFC device achieved an optimal volumetric power density of 661 W/m³, inoculated with pure strain *S. oneidensis* MR-1.

Another challenge is to scale up the solar-MFC technology from the lab scale to industrial scale. Recent advances in the development of new types of electrodes, investigations of the impact of membranes, MFC configurations, and separators are positive indicators that commercialization of the solar-assisted MFC technology is feasible.⁴⁻⁶ To bring the solar-MFC technology to practical applications, it is critical to build the device with low cost and stable materials. All photoelectrodes have to be made by earth abundant and low cost semiconductor materials. To improve the efficiency of utilizing solar energy, the photoelectrodes should have a favorable band-gap. The preparation of these electrodes must be scalable. Moreover, it is critical that the photoelectrodes are chemically stable in the solution with a variety of organic compounds, pH value, and temperature. To date, impressive progress has been accomplished in the development of high performance large scale MFC and MEC devices.⁷ For example, a pilot-scale 1000 L continuous flow MEC device was constructed and tested for current generation of 7.4 A/m³ and chemical oxygen demand (COD) removal of 62 ± 20% with winery wastewater at NAPA, California.⁸

These initial successes of large-scale MFC systems have created a solid foundation for the development of large-scale solar MFC systems.

Reference

1. Wang, H.; Wang, G.; Ling, Y.; Qian, F.; Song, Y.; Lu, X.; Chen, S.; Tong, Y.; Li, Y., High Power Density Microbial Fuel Cell with Flexible 3D Graphene-Nickel Foam as Anode. *Nanoscale* **2013**, 10283-10290.
2. Xie, X.; Ye, M.; Hu, L.; Liu, N.; McDonough, J. R.; Chen, W.; Alshareef, H. N.; Criddle, C. S.; Cui, Y., Carbon Nanotube-Coated Macroporous Sponge for Microbial Fuel Cell Electrodes. *Energy Environ. Sci.* **2012**, 5, 5265-5270.
3. Xie, X.; Yu, G.; Liu, N.; Bao, Z.; Criddle, C. S.; Cui, Y., Graphene-Sponges as High-Performance Low-Cost Anodes for Microbial Fuel Cells. *Energy Environ. Sci.* **2012**, 5, 6862-6866.
4. Tender, L. M.; Gray, S. A.; Grovemanb, E.; Lowy, D. A.; Kauffmand, P.; Melhado, J.; Tycy, R. C.; Flynn, D.; Petrecca, R.; Dobarra, J., The First Demonstration of a Microbial Fuel Cell as a Viable Power Supply: Powering a Meteorological Buoy. *J. Power Sources* **2008**, 179, 571-575.
5. Logan, B. E., Exoelectrogenic Bacteria that Power Microbial Fuel Cells. *Nat. Rev. Microbiol.* **2009**, 7, 375-381.
6. Logan, B. E., Scaling Up Microbial Fuel Cells and Other Bioelectrochemical Systems. *Appl. Microbial Biotechnol.* **2010**, 85, 1665-1671.
7. Cheng, S.; Logan, B. E., Increasing Power Generation for Scaling Up Single-Chamber Air Cathode Microbial Fuel Cells. *Bioresour. Technol.* **2011**, 102, 4468-4473.
8. Cusick, R. D.; Bryan, B.; Parker, D. S.; Merrill, M. D.; Mehanna, M.; Kiely, P. D.; Liu, G.; Logan, B. E., Performance of a Pilot-Scale Continuous Flow Microbial Electrolysis Cell Fed Winery Wastewater. *Appl. Microbiol. Biotechnol.* **2011**, 89, 2053-2063.