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Solar photothermal electrodes for high-efficient microbial energy harvesting at low ambient temperatures

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Abstract: Temperature is an important parameter for the performance of bioelectrochemical systems (BESs). Energy-intensive bulk water heating was usually employed to maintain a desired temperature for the BESs. Herein, we reported a proof-of-concept of light-to-heat photothermal electrode for solar heating the local electroactive biofilm in a BES for efficient microbial energy harvesting at low temperatures, replacing the bulk water heating approaches. The photothermal electrode was prepared by coating Ti₃C₂T_x MXene sunlight absorber onto carbon felt. The as-prepared photothermal electrode could efficiently raise local temperature of the bioelectrode to ca. 30 °C from low bulk water temperatures (i.e. 10, 15, and 20 °C) under simulated sunlight illumination. As a result, high-efficient microbial energy could be harvested from the low temperature BES equipped the photothermal electrode without the bulk water heating. This study represents a new avenue for the design and fabrication of electrodes for temperature-sensitive electrochemical and biological systems.

Introduction

Microbial bioelectrochemical systems (BESs), promising biotechnology platforms that are capable of interconvert electrical and chemical energy with the aid of living microorganisms, have attracted great interest among researchers.^[1] Microbial fuel cell (MFCs) is one of the classic examples of the BESs, which has been intensively studied in recent years because they can generate electricity from a diverse range of environmental fuels such as carbohydrates, protein, biomass and wastewaters.^[2] In the meanwhile, the MFCs also hold great potential for other applications, including wastewater treatment, chemical synthesis, desalination, and remediation.^[3] However, the successful commercialization of MFCs has been strongly hindered because of their low power outputs. One of the significant issues contributing to low performance is inefficiency of the anodic processes that involve the microbial extracellular electron transfer from bacterial cells to electrode.^[4]

Temperature fluctuation is one of the key issues that must be solved in order to achieve high-performance MFCs.^[5] In general, optimal temperatures enable fast start-up and better anode performance for the MFCs because the anodic biofilm formation is faster and enzymes are more active.^[6] Low ambient temperatures lead to a lower microbial bioelectrocatalytic activity and metabolic rates, thus impacting the rate of electric energy conversion of MFCs.^[7] Previous studies found that the MFC performance was linearly correlated with the temperature from 4 to 30 °C with a slope of 33 mW/m²/°C and 4 A/m³/°C for power and current, respectively.^[8] The performance of the MFCs increased along with raising the temperature. Currently, most of MFCs have been operated at controlled and elevated temperatures (typically ca. 30 °C) because the optimal cell growth temperature of those typical exoelectrogens (i.e. *Shewanella* and *Geobacter*) is ca. 30 °C.^[6b, 8a, 9] This temperature is usually held by placing the MFC reactors in an incubator or a temperature-controlled room to heat the entirety of bulk water. Indeed, the MFCs are inevitably operated at low temperatures for practical applications in temperate or subtropical climates.^[1, 10] In this areas, wastewaters are discharged most of the time at low ambient temperatures (4 to 20 °C). However, the conventional bulk heating of water is energy-intensive when the MFCs are practically used to treat wastewaters. One fact that is often overlooked is that reactions catalyzed by the microorganisms is indeed surface processes in the BESs, in which biofilms attached on the electrodes are capable of oxidizing organic matter diffused from bulk water. Thus, an efficient and energy-saving approach to keep local biofilm warm in the MFCs is highly desirable.

Light-to-heat conversion, also known as photothermal conversion, an ancient strategy in which photon energy is converted into heat, has been gained renewable research interest due to its' operation simplicity, wide variety of materials of choice, and extremely high energy conversion efficiency in recent years.^[11] This photothermal process has been applied widely in cancer therapy, steam generation and water desalination.^[12] Of particular note, it has been found that membranes associated with various photothermal materials are extremely efficient for steam generation and water desalination because it localizes the solar heat generation to the evaporation surface of a body of water, instead of wastefully heating the entire body of water.^[12a, 12b, 13] In this regard, 2D materials, such as graphene and transition-metal carbides (MXene), have been used to constructed light-to-heat conversion membranes due to their excellent photothermal conversion capabilities.^[14] For instance, temperatures increased from 20 °C to around 75 °C and 35 °C in air and in air-water interface, respectively, could be achieved from an MXene-based light-to-heat membrane under one sun illumination.^[12a] Inspired by these results, we expect to use solar energy to heat the electrode of a BES by associating an efficient photothermal material with the conventional electrode.

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Herein, we, for the first time, report a proof-concept of photothermal electrode for solar heating an electroactive biofilm in order to efficiently generate microbial electricity in the BES at low operating temperatures. The photothermal electrode was prepared by coating MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) onto carbon felt (CF) electrode (CF/MXene). MXene was rationally chosen as the light absorber because of its broad-spectrum adsorption and high photothermal conversion efficiency.^[15] Our results clearly indicated that the as-prepared photothermal electrode could efficiently raise local temperature of the bioelectrode to ca. 30 °C from low temperatures (i.e. 10, 15, and 20 °C) under simulated sunlight illumination, which enabled the efficient microbial energy harvesting from the BESs at low operating temperatures.

Results and Discussion

The CF/MXene electrode was fabricated by coating one side of CF with MXene suspension that was previously synthesized by HF etching of Ti_3AlC_2 to remove the aluminium layer. Scanning electron microscopy (SEM) images in Figure 1a and 1b observed the presence of accordion-like MXene with opened interspace on the carbon fibers of CF, indicating that the CF was successfully coated with MXene. The chemical structure of MXene was confirmed by X-ray diffraction (XRD) pattern and X-ray photoelectron spectroscopy (XPS). The XRD pattern of MXene displayed the disappearance of the intense peaks at $\sim 39^\circ$ after HF treatment and the remaining of peaks from 20° to 40° , suggesting the successful conversion of MAX (Ti_3AlC_2) to MXene with wider gaps and a good periodicity between the stacked MXene layers (Figure S1).^[12c, 16] The XPS survey spectrum revealed the existence of F and O on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (Figure S2). The high resolution Ti 2p and O 1s spectra showed that the surface of MXene was dominated hydroxyl (Ti–OH), oxygen (Ti–O–Ti) and fluorine (Ti–F) groups.^[17] After the MXene particles were coated on CF, cyclic voltammetric (CV) feature of the electrode was disclosed in the potential range from 0.2 to -0.8 V vs. SCE. As shown in Figure 1c, the MXene coating increased the double layer current, suggesting an increase in the surface area.^[18] Electrochemical impedance spectroscopy (EIS) measurements displayed that the CF/MXene electrode had a smaller charge transfer resistance (R_{ct} , 23.9 Ω) than that of the CF electrode (30.2 Ω) (Figure 1d), also confirming that the improved electrochemical properties by MXene coating.

It is worth noting that MXene was chosen as the light absorber because of its outstanding photothermal conversion efficiency compared to other conventional light absorbers (Table S1). The light-to-heat conversion properties of the electrodes were investigated by placing the electrodes into the cold water (20 °C) (Figure 2a). Under the simulated solar light irradiation with an intensity of 1.0 kW/m^2 , IR thermal images showed that high temperature zones were appeared on the top of the glass bottle in the presence of CF and CF/MXene. As shown in Figure 2b, the temperature of the CF/MXene electrode increased dramatically to 32.3 °C under one sun light irradiation, while the temperature of the CF electrode only increased to 25.6 °C at the electrode surface facing to the light. The UV–vis–NIR absorption

spectra showed the MXene presented a stronger absorption of light irradiation than CF-based powder, rGO and CNT (Figure S3a). Therefore, a more outstanding light-to-heat conversion efficiency can be achieved from the CF/MXene than those from the rGO and CNT coated CF electrodes. As a result, the MXene electrode even produced higher temperature than those electrodes coated by the carbon-based light absorbers such as reduced graphene oxide (rGO) and carbon nanotube (CNT) under one sun light irradiation (Figure S3b). The temperature of the as-prepared electrode was depended on the light intensity (Figure 2c). The water temperature profile as a function of depth

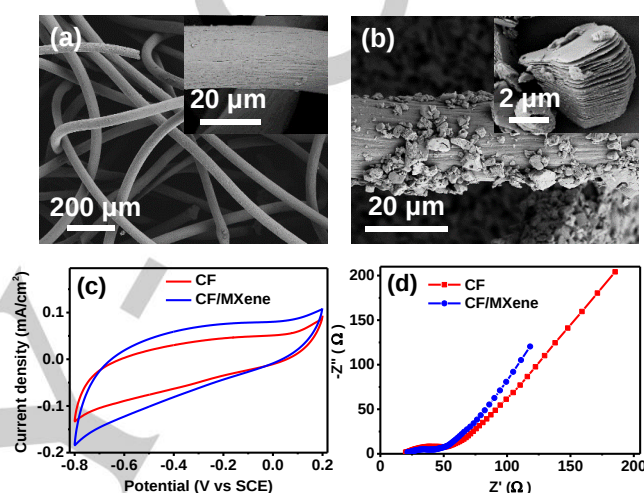


Figure 1. (a) SEM images of original CF (Inset: a single carbon fiber); (b) SEM images of the MXene-coated CF (Inset: a single MXene particle); (c) CV scans of the CF and CF/MXene electrode at scan rate of 5 mV/s; (d) EIS tests for the CF and CF/MXene electrodes.

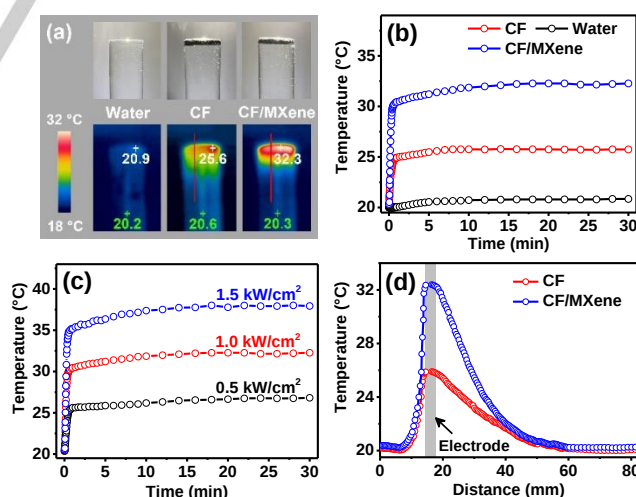


Figure 2. (a) photographic and IR images revealing temperature profiles of the CF and CF/MXene electrodes under one sun illumination; (b) temperature time course of the electrode surface under one sun illumination; (c) dependence of the electrode surface temperature on the light intensity; (d) temperature depth profiles of the CF and CF/MXene electrodes for photothermal heating conversion under one sun illumination.

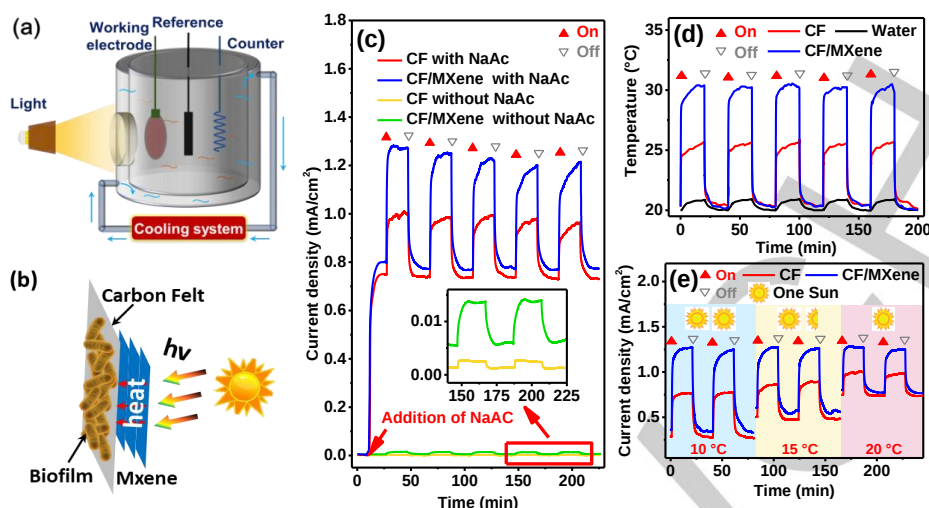


Figure 3 (a) Schematic illumination of the BES with a light window and a water bath cooling system to control the temperature of bulk water (electrolyte); (b) schematic illumination of the CF/MXene bioelectrode heated by sun light irradiation; (c) current generation of the bioelectrode in the presence and absence of sodium acetate (Naica) under one sun light irradiation, in which the bulk water of the BES was controlled at 20 °C; (d) photothermal temperature evolution of CF, CF/MXene, and electrolyte in the BESs; (e) current generation of bioelectrode fed with sodium acetate solution at varied low temperatures (the temperature of bulk water: 10, 15, and 20 °C) and sun light intensities (2.0, 1.5 and 1.0 sun).

with the CF/MXene electrode was showed in Figure 2d, which showed clear high temperature zone around the electrode. It is noticeable that a CF/MXene electrode with 2.5 mm in thickness is cable of producing a high temperature zone around the electrode (above 30 °C) with 1.0 cm in depth.

The as-prepared CF/MXene electrode was examined as a bioelectrode for microbial energy harvesting in a BES in which the temperature of the BES was held by a circulating water bath (Figure S4a). Figure S4b shows the catalytic current development from the time of inoculation under constant polarization at 0.2 V vs. SCE at 30 °C (controlled by water bath) for both CF and CF/MXene electrodes. A slight higher current density could be obtained from the CF/MXene than that from the CF electrode, which could originate from the improved electrochemical properties of the MXene-coated CF. The SEM images confirmed the formation of biofilms on the CF and CF/MXene electrodes, which displayed distribution of rod-shape bacterial cells on these two electrodes (Figure S5). The measured biomass was 1.02 ± 0.07 and 0.99 ± 0.03 mg_{protein}/cm² on the CF and CF/MXene electrode, respectively, demonstrating that the MXene coating did not affect the bacterial growth on the electrode. The current generation from these bioelectrodes was affected by the temperature of the reactor. As the temperature of the whole reactor switched between 20 and 30 °C, the current densities of both the CF and CF/MXene bioelectrodes in the presence sodium acetate were periodically switched as well (Figure S6a). Current densities of 0.73 ± 0.01 and 0.82 ± 0.02 mA/cm² were achieved from the CF and CF/MXene electrodes at 20 °C, respectively, which were obviously lower than those of 1.22 ± 0.01 and 1.30 ± 0.02 mA/cm² at 30 °C. The temperature-sensitive response of the current generation was originated from the biocatalytic reaction of electroactive biofilm because only very small current variations could be achieved from the abiotic electrodes (Figure S6a). Changes in current density in response to temperature were shown in Figure S6b. A slope of 0.0482 and

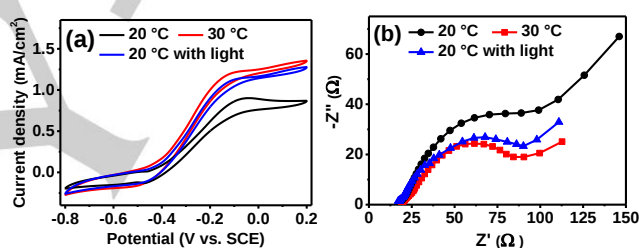


Figure 4. (a) Turnover CV scans of the CF/MXene bioelectrode in the presence of Knaack under various conditions; (b) EIS measurements of the CF/MXene bioelectrode under various conditions.

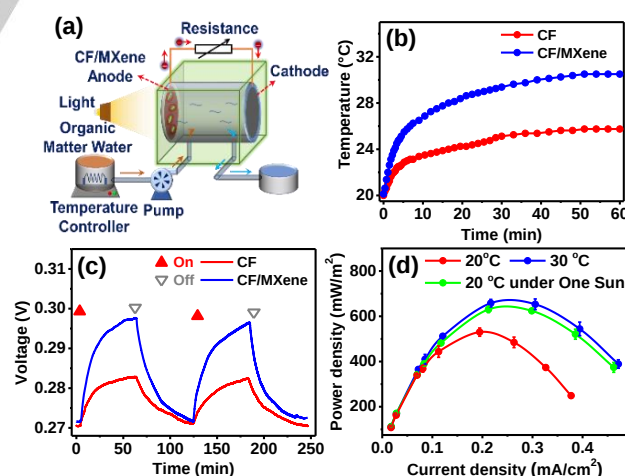


Figure 5. (a) Schematic illumination of the single-chamber air-cathode MFC with a light window at the anode and flowing system to control the temperature of bulk water; (b) photothermal temperature evolution of the wetted CF and CF/MXene anodes in the MFCs under one sun light irradiation; (c) Recycling voltage outputs of the bioanodes under the one sun light irradiation; (d) Power density curves of the MFCs with the CF/MXene anode operated at 20 °C and 30 °C without solar light irradiation, and 20 °C with one sun light irradiation.

0.0478 mA/cm²/°C was obtained from the CF and CF/MXene electrodes, respectively (Figure S6c). Previous studies reported similar changes of the current generation in response to temperature.^[8c]

Having confirmed that current generation from the bioelectrode was temperature-dependent, we tested the CF/MXene electrode as a photothermal bioelectrode for microbial energy harvesting (Figure 3a). The MXene coated side of the electrode was faced to the light window of the reactor and low temperatures of the entire reactor were maintained via a water circulation bath. Figure 3b illustrated the configuration of the CF/MXene electrode in which the MXene was coated on one side of the CF and served as a light absorber to conduct the light-to-heat conversion. The converted heat could be subsequently used to heat the local biofilm attached on the CF/MXene electrode. Figure S4c showed the start-up of the current generation from the CF/MXene electrode at 20 °C, which produced lower current density than that at 30 °C. However, the current density of the CF/MXene electrode at 20 °C with one sun light irradiation was similar to CF/MXene at 30 °C (Figure S4c). This result indicated that the light illumination might favor the current generation of the biofilm at a low temperature. As shown in Figure 3c, the current densities increased to 0.72 ± 0.02 and 0.80 ± 0.02 mA/cm² for the CF and CF/MXene electrode in the controlled-temperature BES at 20.0 ± 0.5 °C, respectively, when sodium acetate was added to the reactors. The current densities increased to 0.98 ± 0.02 and 1.24 ± 0.03 mA/cm² under one sun light illumination. Notably, very small current responses could be observed from the abiotic electrodes (Figure S7a) and bioelectrode in the absence of sodium acetate under the same light on/off conditions (Figure 3c). The results demonstrated that the current responses were mainly attributed to the acetate oxidation rather than the photocurrent generation. The current densities of the bioelectrodes were linearly correlated with the light intensities (Figure S7b and c). The increases in the currents by sun light illumination originated from the increased local temperature of the bioelectrodes. As shown in Figure 3d, the CF/MXene electrode could be heated from 20.0 ± 0.5 to 30.4 ± 0.8 °C under one sun light illumination, while the CF electrode could only be heated to 25.2 ± 0.7 °C. Notably, the bulk water temperature in the BES was almost remained unchanged. The results demonstrated that the MXene was efficient to convert light into heat to maintain a high local temperature for the bioelectrode. Figure 3e showed that the photothermal electrodes also enabled high efficient current generation under other low temperature conditions (i.e. 10 and 15 °C). The CF/MXene electrode operated at 20 °C under light illumination was verified to produce reproducible and similar current generation cycles as the CF electrode operated at 30 °C without light illumination, indicating the stability of the electrode (Figure S8a). The coulombic efficiency (CE) of the CF/MXene electrode was calculated to be 60.2 ± 1.5 % at 20 °C under light illumination, which was similar to that (66.4 ± 2.0 %) of the CF/MXene electrode at 30 °C (Fig. S8b). However, the CE of CF/MXene electrode was only 43.2 ± 1.7 % at 20 °C without sun light illumination. The results indicated that the increased local temperature of the bioelectrode under light illumination could enhance the CE of the low-temperature BES.

Figure 4a showed the turnover CV scans of the bioelectrodes under different temperatures. A significant lower catalytic current was observed from the electrode scanned at 20 °C compared with that at 30 °C, confirmed that the catalytic reaction of the bioelectrodes was affected by temperature of the reactor. The catalytic current of the electrode at 20 °C was recovered due to the light-to-heat effect when it was irradiated by light. The EIS measurements also showed the increase in the R_{ct} when the temperature of the electrolyte decreased from 30 to 20 °C (from 93.6 to 117.8 Ω) (Figure 4b). The R_{ct} decreased to 99.7 Ω as the electrode was illuminated by light, which was only slightly higher than the R_{ct} of the electrode operated at 30 °C. These results indicated that the electron transfer process of the biofilm was facilitated on the solar heated bioelectrode at low ambient temperature due to the increased local temperature of the biofilm.

Finally, the as-prepared photothermal electrode was further tested as the anode in a complete MFC. Figure 5a showed the configuration of an air-cathode single-chamber MFC with a light window at the anode side. To achieve stable and efficient bioanodes, the MFCs with the CF and CF/MXene anodes were firstly started up in a batch mode at 30 °C (Figure S9a). The MFCs with different anodes were inoculated and fed acetate. The cell voltages increased to several hundred millivolts across a 1 k Ω resistor after several cycle operations, indicating a successful start-up (Figure S9b). In order to have a convenient temperature control, the batch mode MFC was switched to a flow mode, in which the temperature of the fuel was controlled with a water bath (Figure S10). In this system, the temperature of the CF/MXene anode also increased from 20.0 ± 0.5 to 30.5 ± 0.6 °C under one sun light irradiation, which was more efficient than that of the CF anode for photothermal conversion (Figure 5b). Notably, the temperature of photothermal electrode was linearly related to both the flow rate (15-90 mL/h) and light intensity (Figure S11). As the flow rate increased, the temperature of the electrode decreased under one sun light irradiation, which could be due to the rapid heat dissipation by the enhanced cold water flow. In this regard, in order to achieve a temperature of near 30 °C under one sun light irradiation, the flow rate of 60 mL/h for the fuel should be controlled. The recycling voltage output could be also achieved from the photothermal electrodes with one sun light on/off cycles (Figure 5c). The power density of the MFC was increased from 530.0 ± 18.2 to 657.9 ± 16.6 mW/m² as the temperature of the feeding solution was increased from 20 to 30.5 °C. As expected, the power density of the MFC fed with a sodium acetate solution of 20 °C could produce 630.1 ± 13.7 mW/m² under one sun light irradiation (Figure 5d), demonstrating that the CF/MXene photothermal anode enabled high-efficient power production at a low temperature by maintain a high local temperature for the bioanode.

Conclusions

In summary, we have demonstrated a photothermal bioelectrode for microbial energy harvesting at low ambient temperatures, using solar energy to heat local biofilms of the

bioelectrodes in the BESs. The concept was embodied for the first time by a rational integration of light-to-heat conversion material and electroactive biofilm onto conventional carbon felt electrodes, which exhibited significantly energy saving feature in comparison to conventional bulk heating approaches. The as-prepared CF/MXene electrode could heat up the bioelectrode from 20 to 30 °C under one sun light irradiation, which enabled the efficient current generation in the BES operated at a low temperature of 20 °C. Solar energy, a renewable and abundant energy source, plays an important role in the future energy sustainable development. The results presented here indicated that solar thermal energy could act as a sustainable technology to potentially address the problem of bioelectrochemical systems for practical applications in temperate or subtropical climates. Furthermore, this concept could be also applied to other temperature-sensitive electrochemical and biological systems for energy and environmental applications. Overall, we believe that this study represents a new avenue for the application of solar energy and inspires new designs for electrochemical and biological systems, and thus in the long term contributes to the effort in addressing energy and environment issues.

Experimental Section

Synthesis of MXene

Ti₃AlC₂ (200 mesh, purity >99%) was purchased from Beijing Forsman Scientific Co., Ltd (China). The MXene powder was produced by HF-etching of Ti₃AlC₂.^[16b] Typically, 1.0 g Ti₃AlC₂ powder was immersed in 20 mL HF (48%, purity >98%) and magnetically stirred for 24 h at 60 °C. The suspension was then washed multiple times with deionized water and anhydrous ethanol, centrifuged (4000 rpm for 5 min) and decanted until the pH of the supernatant reached approximately 6.0. The obtained powder (Ti₃C₂T_x MXene) was dried at 80 °C under vacuum for 24 h.

Characterization of Ti₃C₂T_x MXene

The morphology and microstructure of MXene, CF and CF/MXene were observed by SEM using (Carl Zeiss Gemini 500, Germany), after gold sputter coatings on samples. The XRD analyses were performed on a PANalytical (Netherlands) X'pert PRO MAD diffractometer (40 kV, 40 mA) using CuK_{α1,2} radiation ($\lambda = 0.15406, 0.15444$ nm). XPS spectra studies were performed using an ESCALAB 250 (Thermo Fisher Scientific Inc., Waltham, MA, USA) with a monochromatic Al K α X-ray source (1486.6 eV) operated at 150 W. The absorption performance was measured by an Ultraviolet Visible Near Infrared (UV-vis-NIR) Spectrophotometer (SHIMADZU UV-3600 Plus, Japan) with integrating sphere system (ISR-603, 60 mm).

Preparation and photothermal performance of photothermal electrode

To prepare the photothermal electrode, 25.0 mg MXene powder was dispersed in 0.5 mL anhydrous ethanol and then added 50 μ L Nafion solution. The suspension was vortexed for 30 seconds. The as-prepared Ti₃C₂T_x MXene was coated on one side of CF (4.0 cm²) and then air-dry at least 24 hours. The rGO and CNT coated CF electrodes were also obtained by the same preparation route. Graphene oxide (GO) was prepared from graphite powder according to Hummer's method and reduced by reaction with hydrazine.^[19] CNT was purchased from Shenzhen Nanotech Port Co., Ltd (China). Photothermal performance of photothermal electrode was analyzed by irradiating with sun light simulator (PerfectLight, PLS-SXE300, China). The temperature evolution

of electrode surfaces was recorded on an infrared thermal imaging instrument (FTIR ETS320 camera, USA). The temperature of electrodes surface in the BESs was monitored by TES-1310 digital thermometer with a WRN-01BF thermocouple (TES Electrical Electronic Corp., Taiwan, China).

BES setup and operation

The BES was constructed with a conventional three-electrode system in a double-walled glass container (with inner volume of 180 mL) integrated with temperature control system through external water circulation. Current was record by a multichannel potentiostat (CHI1000C, Chenhua Co. Ltd, Shanghai, China). The CF and CF/MXene electrodes with a size of 2.0 $\times$ 2.0 $\times$ 0.25 cm (length $\times$ width $\times$ thickness) were used as the working electrodes, a saturated calomel electrode (SCE) as the reference electrode, and the Ti wire as the counter electrode, respectively. To start-up the BES, 50 mL of pre-acclimated bacteria from another well-running cell (originally inoculated with aerobic sludge) and 130 mL culture medium solution containing 1.0 g L⁻¹ sodium acetate were added into the BES in a double-walled glass container. The culture medium solution was prepared as previous report.^[20] Biomass attached to the electrodes was extracted and quantified with a bovine serum albumin standard using a SpectraMax Absorbance Reader (CMax Plus, Sunnyvale, CA, USA).

MFC setup and operation

Air-cathode single-chamber MFCs were made of plexiglass with a length of 4.0 cm and a diameter of 3.0 cm (with an inner volume of 28 mL) as previously reported.^[21] The CF and CF/MXene electrodes were used as the anodes with a size of 3.0 $\times$ 0.5 cm (diameter $\times$ thickness). The cathode was prepared from 30% wet-proofed carbon cloth (type B) with four layers of PTFE coating. The other side of the cathode was coated with Pt/C (0.5 mg cm⁻² Pt loading) as an oxygen-reduction catalysis layer. The MFC reactors were inoculated with 10.0 mL pre-acclimated bacteria from other well-operated MFC reactors and fed with 1.0 g/L sodium acetate in culture medium solution at a fixed external resistance of 1000 Ω . For a continuous flow mode, culture medium solution containing 1.0 g L⁻¹ sodium acetate was continuously injected from feed tank to MFC chamber with the flow rate of 60 mL/h controlled by a peristaltic pump. The culture medium solution was phosphate buffer solution (PBS), which had a conductivity of 7.0 mS/cm and contained the following components: NaH₂PO₄·2H₂O (2.78 g/L), Na₂HPO₄·12H₂O (11.40 g/L), NH₄Cl (0.31 g/L), KCl (0.13 g/L), a vitamin stock solution (7.5 mL/L), and a mineral stock solution (7.5 mL/L).^[22]

Electrochemical measurements

Cyclic voltammetry (CV) was measured by electrochemical workstations (CHI660D, Chenhua Co. Ltd, Shanghai, China) in a three-electrode system with the CF or CF/MXene as a working electrode, the Ti wire as a counter electrode, and the SCE as a reference electrode, respectively. CV measurements were performed with a potential range of - 0.8 ~ + 0.2 V at scan rate of 5 mV/s. Electrochemical impedance spectroscopy (EIS) of the abiotic MXene electrode was conducted at 0.2 V vs. SCE potential bias over a frequency range of 1 $\times$ 10⁵ to 0.1 Hz with a sinusoidal perturbation amplitude of 5 mV. The electrolyte for EIS tests composed of 50 mM phosphate buffer (pH 7.0), 2.5 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] and 0.1 M KCl.

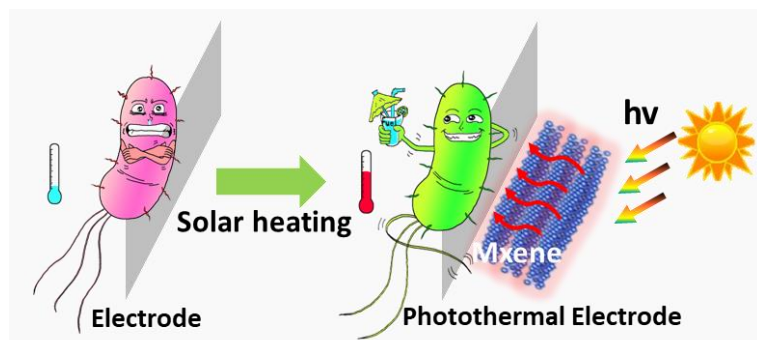
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- [1] B. E. Logan, K. Rabaey, *Science* **2012**, 337, 686-690.
- [2] B. E. Logan, J. M. Regan, *Environ. Sci. technol.* **2006**, 40, 5172-5180.
- [3] a) H. Wang, F. Qian, Y. Li, *Nano Energy* **2014**, 8, 264-273; b) C. Santoro, C. Arbizzani, B. Erable, I. Ieropoulos, *J. Power Sources* **2017**, 356, 225-244; c) S. Gadkari, S. Gu, J. Sadhukhan, *Chem. Eng. J.* **2018**; d) D. Mao, L. Lu, A. Revil, Y. Zuo, J. Hinton, Z. J. Ren, *Environ. Sci. technol.* **2016**, 50, 8205-8213.
- [4] a) R. Kumar, L. Singh, A. Zularisam, *Renewable Sustainable Energy Rev.* **2016**, 56, 1322-1336; b) Y. Wang, H. Huang, B. Li, W. Li, *J. Mater. Chem. A* **2015**, 3, 5110-5118.
- [5] M. Oliot, B. Erable, M.-L. De Solan, A. Bergel, *Electrochim. Acta* **2017**, 258, 134-142.
- [6] a) X. Mei, D. Xing, Y. Yang, Q. Liu, H. Zhou, C. Guo, N. Ren, *Bioelectrochemistry* **2017**, 117, 29-33; b) I. S. Michie, J. R. Kim, R. M. Dinsdale, A. J. Guwy, G. C. Premier, *Energy Environ. Sci.* **2011**, 4, 1011-1019.
- [7] S. A. Patil, F. Harnisch, B. Kapadnis, U. Schröder, *Biosens. Bioelectron.* **2010**, 26, 803-808.
- [8] a) S. Cheng, D. Xing, B. E. Logan, *Biosens. Bioelectron.* **2011**, 26, 1913-1917; b) L. Li, Y. Sun, Z. Yuan, X. Kong, Y. Li, *Environ. Technol.* **2013**, 34, 1929-1934; c) L. Lu, D. Xing, N. Ren, B. E. Logan, *Bioresour. Technol.* **2012**, 124, 68-76.
- [9] a) Y. Yuan, S. Zhou, J. Tang, *Environ. Sci. technol.* **2013**, 47, 4911-4917; b) W. Yang, K. Y. Kim, B. E. Logan, *Bioresour. Technol.* **2015**, 197, 318-322.
- [10] R. J. Ciotola, J. F. Martin, J. M. Castaño, J. Lee, F. Michel, *Energies* **2013**, 6, 5182-5199.
- [11] a) S. Loeb, C. H. Li, J. H. Kim, *Environ. Sci. technol.* **2017**; b) Y. Liu, J. Chen, D. Guo, M. Cao, L. Jiang, *ACS Appl. Mat. Interfaces* **2015**, 7, 13645-13652.
- [12] a) R. Li, L. Zhang, L. Shi, P. Wang, *ACS nano* **2017**, 11, 3752-3759; b) C. Finnerty, L. Zhang, D. L. Sedlak, K. L. Nelson, B. Mi, *Environ. Sci. technol.* **2017**, 51, 11701-11709; c) H. Lin, X. Wang, L. Yu, Y. Chen, J. Shi, *Nano Lett.* **2016**, 17, 384-391; d) H. Lin, S. Gao, C. Dai, Y. Chen, J. Shi, *J. Am. Chem. Soc.* **2017**, 139, 16235-16247; e) X. Han, J. Huang, H. Lin, Z. Wang, P. Li, Y. Chen, *Adv. Healthcare Mater.* **2018**, 1701394.
- [13] a) J. Yao, G. Yang, *J. Mater. Chem. A* **2018**, 6, 3869-3876; b) Y. Ito, Y. Tanabe, J. Han, T. Fujita, K. Tanigaki, M. Chen, *Adv. Mater.* **2015**, 27, 4302-4307.
- [14] a) Y. Li, T. Gao, Z. Yang, C. Chen, Y. Kuang, J. Song, C. Jia, E. M. Hitz, B. Yang, L. Hu, *Nano Energy* **2017**, 41, 201-209; b) J. Xuan, Z. Wang, Y. Chen, D. Liang, L. Cheng, X. Yang, Z. Liu, R. Ma, T. Sasaki, F. Geng, *Angew. Chem.* **2016**, 128, 14789-14794; c) J. Ran, G. Gao, F. T. Li, T. Y. Ma, A. J. Du, S. Z. Qiao, *Nat. Commun.* **2017**, 8, 13907; d) G. Liu, J. Xu, K. Wang, *Nano Energy* **2017**.
- [15] H. Lin, Y. Wang, S. Gao, Y. Chen, J. Shi, *Adv. Mater.* **2018**, 30, 1703284.
- [16] a) M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, *Adv. Mater.* **2011**, 23, 4248-4253; b) M. Alhabeb, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin, Y. Gogotsi, *Chem. Mater.* **2017**, 29, 7633-7644.
- [17] a) J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen, M. W. Barsoum, *Appl. Surf. Sci.* **2016**, 362, 406-417; b) J. Halim, M. R. Lukatskaya, K. M. Cook, J. Lu, C. R. Smith, L.-Å. Näslund, S. J. May, L. Hultman, Y. Gogotsi, P. Eklund, *Chem. Mater.* **2014**, 26, 2374-2381; c) S. Shah, T. Habib, H. Gao, P. Gao, W. Sun, M. Green, M. Radovic, *Chem. Commun.* **2017**, 53, 400-403.
- [18] H. F. Cui, L. Du, P. B. Guo, B. Zhu, J. H. Luong, *J. Power Sources* **2015**, 283, 46-53.
- [19] S. Park, J. An, J. R. Potts, A. Velamakanni, S. Murali, R. S. Ruoff, *Carbon* **2011**, 49, 3019-3023.
- [20] Y. Yuan, S. G. Zhou, N. Xu, L. Zhuang, *Appl. Microbiol. Biotechnol.* **2011**, 89, 1629-1635.
- [21] Y. Yuan, S. Zhou, Y. Liu, J. Tang, *Environ. Sci. technol.* **2013**, 47, 14525-14532.
- [22] D. R. Lovley, E. J. Phillips, *Appl. Environ. Microbiol.* **1988**, 54, 1472-1480.



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Solar photothermal electrodes for high-efficient microbial energy harvesting at low ambient temperatures

Photothermal bioelectrode: The photothermal electrode was prepared by coating $\text{Ti}_3\text{C}_2\text{T}_x$ MXene sunlight absorber onto carbon felt electrode. The photothermal electrode could efficiently raise local temperature of the bioelectrode to ca. 30 °C from low bulk water temperatures (i.e. 10, 15, and 20 °C) under simulated sunlight illumination, leading to efficient microbial energy harvesting from the low temperature microbial fuel cells.