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Photothermal Janus Anode with Photosynthesis-shielding Effect for Activating Low-temperature Biological Wastewater Treatment

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Abstract: Biological wastewater treatment (BWT), which is used to manage global wastewater, suffers from a sharp decrease in microbial activity at low temperature ($<10\text{ }^{\circ}\text{C}$). Photothermal technology with a high energy efficiency theoretically exceeding 80% has the potential to activate low-temperature BWT. However, photothermal BWT is threatened by the propagation of photosynthetic algae in wastewater under irradiation, and these microorganisms can suppress the functional bacteria or even kill anaerobic species by photosynthetically releasing oxygen. Herein, taking microbial fuel cells (MFCs) as a representative biological reactor, we designed a photothermal Janus anode (PTJA) composed of a carbon black/polydimethylsiloxane photothermal nonporous layer and a graphite felt porous layer to promote low-temperature BWT. Unlike

traditional symmetrical porous anodes, the nonporous layer of PTJA can isolate the wastewater in the porous layer from light irradiation during photothermal conversion, thus preventing photosynthetic algae from poisoning anaerobic functional microbes. Under ~ 1 sun illumination, the PTJA MFC exhibits 1.6 and 24.2 times higher organic pollutant removal rate and power density generation, respectively, than MFCs using traditional anodes for low-temperature BWT (7.0 ± 2.0 °C). This development can allow new utilization of solar energy and is a promising resolution for low-temperature BWT.

1. Introduction

Biological wastewater treatment (BWT), working on the basis of microbial metabolism, is used to manage wastewater worldwide.^[1–5] However, low temperature (< 10 °C) is a tough challenge for BWT and causes the suppression of enzymatic activity of microbe metabolism, resulting in a more than 90% decrease in performance or even failed start-up of BWT when below 10 °C.^[6–8] The most common solution to the low-temperature problem is to domesticate psychrophilic bacteria,^[9–13] yet this strategy suffers due to the fragility of bacterial flora, substantial time requirement (domestication period of over 1 year) and operation complexity. Increasing the temperature of wastewater should be a relatively more direct method to improve the microbial activity for enhancing BWT performance.^[8] Additionally, exploring solar energy to produce electricity to meet the energy requirement during water treatment has been proposed.^[14–16] However, the photoelectrical conversion efficiency of commercial solar cells is generally approximately 20%; thus, it is inadvisable to electrically heat wastewater by solar energy (light-to-electricity-to-heat route). Overall, low temperature is still an “Achilles heel” for BWT.

Localized photothermal technology, which directly transfers light energy to heat energy by

utilizing specific light absorbers (light-to-heat pathway), has attracted broad attention in various applications, including biomedical technologies,^[17–21] solar distillation,^[22–28] water sterilization^[29,30] and so on.^[31] Due to the energy conversion efficiency exceeding 80%, localized photothermal technology has the theoretical feasibility of acting as a sustainable means to activate low-temperature BWT. Nevertheless, photothermal BWT is challenged by the propagation of photosynthetic algae in real wastewater during sunlight illumination (photosynthesis), which can suppress the functional bacteria or even kill anaerobic species by photosynthetically releasing oxygen.

Microbial fuel cells (MFCs), as a typical and promising anaerobic wastewater treatment system, can simultaneously purify wastewater and acquire electricity from organic waste degradation.^[32–35] The anode of MFCs provides attachment sites for the cloning of anaerobic functional bacteria and is thus a suitable region for photothermal heating.^[36–40] However, traditional anodes of MFCs are generally symmetrical porous architecture (**Figure 1a**), the wastewater will penetrate the whole anode and come into contact with light during the photothermal process, hence resulting in failure in shielding photosynthesis for photothermal BWT (**Figure 1b**). As the counterpart to symmetrical architecture, Janus construction can expertly regulate asymmetrical transportation,^[41–43] therefore, it is expected to resolve the drawback of traditional symmetrical porous anodes. The asymmetrical photothermal Janus anode (PTJA) is proposed in **Figure 1c**, which is composed of a photothermal and waterproofing nonporous layer and an electroconductive porous layer. **Figure 1d** illustrates the corresponding wastewater transportation and light transmission in the anode. The photothermal nonporous layer with excellent light absorbance can effectively deplete light energy and isolate wastewater in the porous layer (**Figure 1c**) from irradiation. Thus, wastewater transportation and light transmission can be separately performed in

the two asymmetrical layers of PTJA, which will completely eradicate the growth of photosynthetic algae by shielding photosynthesis effect.

Based on the above inspiration, in the present work, a dense film based on a carbon black/polydimethylsiloxane (CB/PDMS) composite was anchored on the upper layer of a porous graphite felt electrode, thus obtaining an integrative Janus anode with photothermal nonporous and conductive porous layers. Under irradiation, anodic functional microbes can be successfully activated to metabolize pollutants due to the photothermally generated heat transfer to the conductive fibers of the porous layer. Our photothermal MFC system achieved excellent pollutant degradation and superior bioelectricity generation (1.6 times and 24.2 times higher organic pollutant removal rate and power density, respectively, than those of the photothermal system with traditional anode). In addition, the system also performed well for organic pollutant degradation when operated during day/night cycles, even for practical brewery wastewater. Most importantly, the energy conversion efficiency of this light-to-heat pathway is approximately 84.0%, which is ~ 4 times the light energy utilization of the light-to-electricity-to-heat route. This development demonstrates a new application route for solar energy and is also quite meaningful for energy-efficient biological wastewater management.

2. Results and Discussion

2.1. Characterization and Photothermal Performance of Photothermal Janus anode

A PTJA with an asymmetrical structure was fabricated to enable wastewater transportation in the porous layer independent of light transmission in the nonporous layer. First, to guarantee the mass transfer of wastewater and microbial growth in MFCs, commercial three-dimensional porous graphite felt (GF) was selected as the PTJA porous layer. The GF was constructed from the random

accumulation of graphite fibers with an average diameter of $\sim 10\ \mu\text{m}$, creating an interconnected porous structure (**Figure 2a**). To achieve the photo-to-heat and waterproofing ability of the PTJA, the nonporous layer was fabricated with a carbon black/polydimethylsiloxane (CB/PDMS) composite by blade coating and subsequent thermal curing, in which CB nanoparticles possessing a high photothermal ability served as the light absorber and hydrophobic PDMS acted as a film-forming component.^[25,26,44–47] Here, the viscosity of the CB/PDMS precursor directly determines the formation of a nonporous layer and the combination of nonporous layer and porous layer. Therefore, we control the precursor viscosity by increasing the CB concentration (Figure S1a, Supporting Information) to enhance the internal friction of the polymeric liquid.^[48,49] The high-fluidity CB/PDMS precursor created defective holes on the nonporous layer when the CB concentration was limited to less than 16 wt% (Figure S1b-e, Supporting Information), and these holes are harmful for preventing the contact of wastewater with light irradiation. The overly viscous CB/PDMS precursor (CB concentration >20 wt%) not only seriously damaged the porous layer during the coating process but also failed to form an intact nonporous layer (Figure S2a, Supporting Information). Only when the CB concentration was controlled at 18 wt% and 20 wt% (Figure 2b; Figure S1f, Figure S2b, Supporting Information) can flawless and dense nonporous layers be obtained on the porous layer. In particular, the nonporous layer with 20 wt% CB exhibited a better light absorbance of $\sim 96.3\%$ (Figure 2c; Figure S3a, Supporting Information), showing its superiority as the optimal nonporous layer. Moreover, the light transmittance of the nonporous layer with 20 wt% CB was nearly zero (Figure S3b, Supporting Information), which would completely eradicate light transmission into the porous layer. The effective integration between the nonporous layer and porous layer determines the fulfillment of the anisotropic function of the Janus anode. As shown in Figure 2d, the PTJA nonporous layer was partly embedded and linked into the porous

layer, forming an effective overlap between the two parts by mechanical pressure during coating; therefore, an asymmetric Janus structure was obtained after thermal curing. The water resistance of the nonporous layer is another key factor aimed at protecting functional microorganisms from photosynthesis poisoning during the photothermal process. The test results show that the nonporous layer could effectively resist water even when the hydrostatic pressure was increased up to the maximum value of the testing equipment of 70 kPa, revealing that the nonporous layer has the potential to create a photosynthesis-shielding region in PTJA (Figure 2e).

The PTJA anode exhibits a remarkable photothermal conversion ability with high energy efficiency. As one of the main components of the PTJA, carbon black is a superior candidate for photothermal applications owing to its outstanding light absorption, low cost and easy availability. It adsorbs light widely in the entire solar spectrum due to the closed spaced energy levels of the loosely-held π electrons and then releases heat by relaxing the photoexcited electrons to their ground state. As shown in Figure 2f, the photothermal heat was generated by CB particles as the energy converter and then transferred to the porous layer through the dispersed CB and graphite fibers bonded in the nonporous layer. The photothermal property of the PTJA electrode (size of 3 cm) was monitored by infrared (IR) thermal imaging under solar simulator (Figure 2g; Figure S4a, Supporting Information). The temperature of the PTJA nonporous layer rapidly increased from a low temperature (7.0 ± 2.0 °C) to the equilibrium temperature (~ 57.0 °C) within 120 s of irradiation (Figure S4b, Supporting Information). It is worth noting that the photothermal ability of the PTJA electrode under LED illumination was almost identical to that under solar simulator irradiation (Figure S5a, Supporting Information). Considering the practical operability of the subsequent multiple sets of parallel experiments and the service life of the solar simulator under long-term irradiation, the LED light was thus chosen as the daylight simulator to substitute for the solar

simulator in this work. The similar surface temperature and slight temperature difference between the two sides of PTJA and GF electrodes indicated the good heat conductivity of the fabricated PTJA photothermal nonporous layer. (Figure S5 and Figure S6, Supporting Information). The contribution of the PTJA electrode to the whole photothermal reactor system was further investigated (Figure 2h). The reactor with PTJA eventually achieved an equilibrium temperature of $\sim 28\text{ }^{\circ}\text{C}$ after approximately 120 min of irradiation while the temperature of the control reactor without the PTJA electrode only increased by $\sim 6.4\text{ }^{\circ}\text{C}$. As shown in Figure 2i and 2j, the LED light illuminated the PTJA electrode through a transparent window of the photothermal reactor system. The local heat generated from the nonporous layer of PTJA was transferred to the porous layer and further to the water via heat conduction. Then the heat in porous layer was transferred to water via heat conduction and the heat is transferred inside water via heat convection, thus improved the temperature of reactor system. Furthermore, the photothermal conversion efficiency η of the PTJA in the photothermal reactor system was estimated to be 84.0% (see Supporting Information in detail).^[27] For the identical photothermal ability of PTJA under LED light and solar simulator (Figure 2g; Figure S5a, Supporting Information), the photothermal efficiency of the light-to-heat pathway could be approximately regarded as the same value. Under the same conditions, assuming the efficiency of the electrical heating is 100%, the energy conversion efficiency of the light-to-electricity-to-heat route is just a quarter of that of our light-to-heat method.

2.2. Solar Photothermally Activated Low-temperature MFCs

Photothermal MFCs using PTJA were applied to treat low-temperature wastewater ($7.0 \pm 2.0\text{ }^{\circ}\text{C}$) and exhibited outstanding biocatalytic activity. To demonstrate the function of PTJA and determine the performances of the photothermal MFCs, the PTJA electrodes were integrated into MFCs under low-temperature conditions ($7.0 \pm 2.0\text{ }^{\circ}\text{C}$) and then activated by light (PTJA-with-light MFCs,

Figure S7a, Supporting Information). Additionally, MFCs using PTJA without light irradiation as well as using traditional graphite felt anode under light (PTJA-without-light MFCs, traditional anode-with-light MFCs) were also investigated as control examples. The MFCs under different conditions were inoculated with domestic wastewater at the start-up stage and fed with acetate (1 g L^{-1}) both in the start-up and operation periods, and the light irradiation was uninterrupted for 24 h. In addition, half of the inoculation medium and nutrients in the bioreactors was replaced every cycle to decrease the solution temperature fluctuation. Under such circumstances, the cell voltage outputs were recorded at the whole stages. The PTJA-with-light MFCs obtained repeatable voltage cycles (maximum voltage value of $515 \pm 15\text{ mV}$) after the start-up period of ~ 7 days (**Figure 3a**), signifying the successful start-up of the photothermal reactors. Moreover, the voltage output of the photothermal MFC reactor without bacterial inoculation was also tested (Figure S7b, Supporting Information). The nearly zero-voltage state indicated that the voltage output of the photothermal MFC system was generated from the electroactive bacteria metabolism, independent of the photovoltaic effect of the PTJA electrode. In contrast, the PTJA-without-light MFCs under low-temperature conditions could not normally start up during continuous inoculation and only exhibited a maximum voltage output of $5 \pm 2\text{ mV}$. In other words, the voltage output of the PTJA-based photothermal MFCs increased by more than 100 times compared to that of the low-temperature controls. However, not every anode with photothermal properties is suitable for photothermal MFCs. The GF electrode is a traditional anode for MFCs and exhibits a comparable photothermal property to that of the PTJA electrode (Figure S6, Supporting Information). The traditional anode-with-light MFCs also presented a periodic voltage output (Figure 3a). The maximum value was only $130 \pm 10\text{ mV}$, which is just 25.5% that of the value the PTJA-with-light MFCs obtained. Afterwards, the polarization curves of the two systems in the steady operation

period were examined (Figure 3b). The maximum power density of the PTJA-with-light MFCs reached 678.3 mW m^{-2} , which was 24.2 times higher than that of the traditional anode-with-light system (28.0 mW m^{-2}). In addition, the maximum open-circuit voltage of the former reactors (773.4 mV) was 1.7 times that of the latter reactors (460.1 mV). As observed from Figure 3c, the larger voltage output of the photothermal system using PTJA should be due to the relatively higher cathode potentials and lower anode potentials. The obvious redox peaks in the CV measurements further evidenced the superior bioelectrochemical activity of the photothermal system (Figure 3d).^[50] Moreover, the chemical oxygen demand (COD) and coulombic efficiency (CE) were used to estimate the organic pollutant removal and energy recovery efficiency of the MFCs (Figure S7c, Supporting Information). The COD removal (82.2%) and CE (31.3%) of the PTJA-based photothermal MFCs increased by 1.6 times and 4.5 times, respectively, compared to those of the photothermal system based on the traditional anode. Compared to the big difference in voltage outputs, the narrowing of difference in the organic degradation rates of the two photothermal systems should be mainly due to the ability of algae species to degrade organic matter.^[51,52] It is supposed that algae could metabolize organic matters to some extent while poisoning electroactive bacteria in the photothermal MFC with traditional anode.

2.3. Enhancement Mechanism for Photothermal MFCs

The PTJA enhancement mechanism for the photothermal MFC can be attributed to the photosynthesis-shielding effect by the Janus anode structure and the local photothermal heating effect. To investigate the importance of the photosynthesis-shielding effect of PTJA on the performance of photothermal MFCs, the anode biofilm morphologies and community structures of the above photothermal systems were characterized and examined. **Figure 4a** and Figure S8a show that dense rod-shaped bacteria covered the graphite fibers of the PTJA porous layer in

PTJA-with-light MFCs, while the PTJA surface was unchanged, as shown in the inset of Figure 4a. In contrast, no biofilm formed on the anode in the low-temperature control MFCs (Figure S8b, Supporting Information). The above great difference in the biofilms reconfirmed the outstanding photothermal effect of PTJA under irradiation. For the traditional anode-with-light MFCs, aside from rod-shaped functional bacteria, many spherical algae cells also grew on the porous anode, and the GF surface also appeared green (Figure 4b; Figure S8c, Supporting Information), which was preliminarily concluded to be due to the occurrence of photosynthesis in the traditional anode.

Furthermore, the anode biofilm community composition of different photothermal MFCs was identified via 16S gene sequence analysis. As displayed in Figure 4c, *Geobacter* species were the main exoelectrogenic microbes in the PTJA-based photothermal MFCs, accounting for a substantial proportion (76.4%) of the biofilm on PTJA. In sharp contrast, as the main electricigens in photothermal MFCs based on traditional anodes, *Alishewanella* species only occupied 26.3% of the biofilm (Figure 4d). Additionally, 18S rRNA gene sequence analysis confirmed the existence of *Chlorella* in the traditional anode biofilm (Figure S8d, Supporting Information). The differences in the main microbial species in the two photothermal systems are compared in Figure 4e. The sole dominant microbe in the PTJA-based photothermal system was the high-proportion strictly anaerobic electricigen, whereas the low-occupancy facultative anaerobic electricigen and photosynthetic algae are the two main microbes in the other photothermal system. Clearly, the photothermal and waterproofing PTJA nonporous layer could stifle the growth of photosynthetic algae and create an advantageous environment for anaerobic electricigens to degrade organic pollutants and generate electricity. On the other hand, the oxygen produced from photosynthetic algae in the traditional porous anodes seriously poisoned the anaerobic bacteria and thus caused the formation of facultative anaerobic functional microbes, eventually leading to an extremely low

electricity output.

To further demonstrate the local thermal contribution of PTJA in the photothermal MFC system, the performances of room-temperature MFCs based on PTJA were also examined as a control. At the same water temperature, the maximum voltage output of room-temperature MFCs was 435 ± 15 mV, which was 15.5% lower than that of the photothermal MFCs (Figure S9a, Supporting Information). The maximum power density (506.6 mW m^{-2}) was reduced by 25.3% compared to that of the photothermal system (Figure S9b, Supporting Information). In addition, the biocatalytic activity of the anodic biofilm in room-temperature MFCs was also weaker than that of the photothermal system, as indicated by the redox peaks in CV curves (the inset of Figure S9b, Supporting Information). The above results are likely because PTJA can act as an effective ‘heating bed’ for bacterial growth in the photothermal MFC system. The periodic instantaneous local thermal heat generated from the PTJA nonporous layer by the photothermal effect is first transferred to the conductive fibers in the porous layer and then locally activates the bacterial catalysts followed by metabolization of the pollutants.

2.4. Feasibility of Photothermal MFCs driven by daylight

Considering that practical wastewater treatment is only performed under alternating solar irradiation conditions, the feasibility of the photothermal MFC system during day/night cycles (10 h/14 h) was investigated with both simulated wastewater and real brewery wastewater (**Figure 5a**). As shown in Figure 5b, after successful start-up under uninterrupted illumination, the PTJA-based photothermal MFCs begin to work under alternating light and dark conditions (light on/off cycles) to simulate the system operation during day/night cycles. During this period, once the light was turned off, the voltage dropped off sharply, indicating that the metabolic activity of the electroactive microorganisms was influenced by the decreasing temperature. The temperature changes and

voltage output curves during the first 3 h operation in the dark are shown in Figure S10a. The system voltage dropped sharply when the wastewater temperature dropped from 20 °C to around 7 °C, further confirming the effect of low temperature on the system performance. Nevertheless, the voltage increased again when the light was periodically turned on, and the maximum voltage output (505 ± 5 mV) barely changed compared with that observed under uninterrupted irradiation. Similarly, the maximum power density obtained during light on/off cycles (Figure 5c) was ~ 646.9 mW m⁻², just 4.6% lower than that of the system operated during continuous illumination. The electrode potentials of the two systems also maintained a high consistency (Figure S10b, Supporting Information). In addition, microbial component analysis shows that the proportion of main functional bacteria was basically unchanged after periodic changes in light and dark (Figure S10c, Supporting Information). Above results indicated that the electroactive bacteria of the photothermal MFC system could effectively withstand the low-temperature conditions and were recoverable during day/night cycles. In addition, real brewery wastewater (COD of ~ 1450 mg L⁻¹) was treated during light on/off cycles to investigate the practical operation stability of the photothermal MFC system (Figure 5d). Once the brewery wastewater was added, the system directly adapted to the real wastewater and maintained a steady state, exhibiting a maximum power density of 256.1 mW m⁻² (Figure S11, Supporting Information). The COD removal rates and corresponding CEs under different conditions are listed in Figure 5e. When the photothermal MFCs treated artificial wastewater, the CE was 20.8% during light on/off cycles, decreasing by 33% relative to that obtained under continuous illumination. This difference was due to the metabolic loss of the electroactive bacteria at low temperature in darkness.^[8] In contrast, the photothermal MFCs during continuous illumination and light on/off cycles achieved outstanding COD removal rates (82.2% and 80.0%, respectively). This result reveals that the organic degradation ability of

electroactive bacteria remained when the photothermal MFCs operated during day/night cycles. This phenomenon may be attributed to the self-protection characteristics of the anodic microorganisms to accumulate more energy in the dark phase.^[53] Notably, when treating real brewery wastewater, the photothermal MFCs also acquired a good organic pollutant removal efficiency (78.7%), indicating the potential application prospect of a photothermal BWT.

3. Conclusion

In conclusion, in face of the low-temperature challenge in biological wastewater treatment, we demonstrated a novel photothermal BWT strategy utilizing solar energy and conducted a proof-of-concept study in MFC systems. A photothermal Janus anode with an asymmetrical nonporous layer and a porous layer was rationally designed for the photothermal MFC system. The remarkable photothermal and heat-conducting PTJA nonporous layer created a superior environment for anaerobic functional bacteria to metabolize and degrade pollutants. At the same time, the biocatalyst poisoning arising from the propagation of photosynthetic algae was completely avoided via isolation of the light and wastewater by the PTJA nonporous layer. The photothermal MFC system achieves appreciable removal of organic pollutants and stable electricity generation, and the performance was tens of times better than that of the low-temperature control system and the poisoned photothermal system. Moreover, the light-to-heat pathway with a high conversion efficiency of 84.0% will utilize ~ 3 times more light energy than the heating route of the light-to-electricity-to-heat path. Significantly, the photothermal MFC system could also operate well during day/night cycles for practical wastewater treatment. This development is meaningful for low-temperature BWT and other biological processes and may provide a new application for solar energy.

4. Experimental section

PTJA electrode fabrication: The PTJA electrode was prepared by simply coating the surface of a graphite felt electrode with the optimal carbon black and PDMS composite. In detail, the graphite felt (thickness of 2 mm, Beijing Jinglongtetan Technology Co., Ltd.) was soaked in 1 M HCl overnight, sonicated for 30 min in ethanol, rinsed with distilled water several times, and dried at 80 °C. The PDMS precursor and corresponding crosslinker (Sylgard 184, Dow Corning Co., America) were mixed at a ratio of 10:1 and stirred for 15 min. Commercial carbon black (particle size of 30 nm, CABOT, VX72R) was mixed with PDMS for approximately 30 min by mechanical mixing to make CB/PDMS composites with a series of concentrations (10, 12, 14, 16, 18, 20 and 22 wt%). The CB/PDMS composites were coated onto the surface of the GF (4.5×4.5 cm) with a hard brush, and the average loading amount was approximately 0.032 g cm⁻². Finally, the CB/PDMS-GF composites were cured at 120 °C for 30 min.

Material characterization: The absorbance spectra were obtained from the reflectance and transmittance spectra measured by UV-Vis absorption spectroscopy (Shimadazu, UV 2550). The surface and cross-sectional morphologies of the samples were observed by scanning electron microscopy (FEI-Quanta 200). The viscosity of the CB/PDMS composite was measured using a rotational viscometer (DV-79, Shanghai Nirun Intelligent Technology Co., Ltd.). The total spectral absorption of the sample was obtained from the reflectance and transmittance spectra measured by UV-Vis-NIR absorption spectroscopy (PerkinElmer Lambda 950). The water resistance trial was performed by a smart vacuum pump (ANJ703.5).

Photothermal experiments: Photothermal images were taken using an IR thermal imager (FLIR T1040). Solar simulator (NBeT Solar-500) and LED light (Foshan Morning Rainbow

Lighting Appliance Co., Ltd) were used for the photothermal characterization of the materials. Considering the practical operability of the following photothermal MFC experiments and the service life of a solar simulator under long-term irradiation, LED light was chosen as the daylight simulator to substitute for the solar simulator in this work. It should be noted that the transparent window of the photothermal MFC reactor allowed only $\sim 92\%$ of visible light to pass onto the anode surface because the light was limited by plexiglass. Hence, an incident power density of $115 \pm 5 \text{ mW cm}^{-2}$ was applied here and in the following experiments by adjusting the distance between the LED light source and the photothermal system.

MFC system tests: All MFC experiments were performed in batch mode using single-chamber air-cathode reactors with $1 \text{ k}\Omega$ resistance loading. Under photothermal conditions, the reactors used light-tight measures to avoid light disturbance except for the transparent window (only an area of 7 cm^2 in the center) on the anode side. A thermal sensor (S305C, Thorlabs Inc.) was used to adjust the incident power. In the start-up phase, domestic wastewater (COD value of $300\text{-}350 \text{ mg L}^{-1}$) was applied as a bacterial source, and a medium containing 1 g L^{-1} sodium acetate, 50 mM PBS and other components (vitamin 5 mL L^{-1} and mineral 12.5 mL L^{-1}) was selected as the nutrient. The MFC system stopped inoculation after the system reached the maximum voltage output for at least two cycles, and the nutrient offered was the same as that described above. Only half of the solution was replaced with fresh inoculation medium and nutrient solution during the start-up and operation phase to prevent temperature shock due to the low temperature of solution, and the concentration of newly added medium was twice that of the original. For the room-temperature MFC system, the average water temperature was set to $28 \text{ }^\circ\text{C}$. In addition, brewery wastewater was acquired from a local Budweiser beer factory with a pH ranging from 6.8 to 7.4 and a COD value of $\sim 1450 \text{ mg L}^{-1}$. The voltage output was measured every 5 min using a data acquisition system (Model 2700,

Keithly). The polarization curve was measured under stable MFC operation conditions for at least 20 min at different external circuit resistances (10000-100 Ω). The electrode potentials were measured using a saturated calomel electrode. Cyclic voltammetry of the MFC system was performed based on an Autolab (CHI660E, Chenhua Co., Ltd., China) with a three-electrode system (scan rate of 5 mV s⁻¹). COD values were evaluated using HACH reagent. The Coulombic efficiency was calculated by dividing the practical coulombs (calculated by integrating the current over time) by the theoretical value of coulombs based on the COD removal in the MFC system.^[54]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Figures:

Figure 1. a) Diagram of the traditional photothermal anode structure. b) Schematic process of light transmission and water transportation in a traditional anode. The occurrence of photosynthesis will poison the photothermal activation of bioelectrocatalysis. c) Diagram of the asymmetrical photothermal Janus anode (PTJA) structure. d) Schematic mechanism of the Janus anode to achieve photothermal bioelectrocatalysis. The wastewater transportation and light transmission are separated in the two asymmetrical layers of PTJA, which will shield the photosynthesis. The decay curves of the light intensity in c) and d) were simulated following the ideal exponential decay of Lambert-Beer's law by assuming electrodes are a uniform medium, in which α and β represents the absorbance coefficients. The water loading rate in the electrode medium was a constant value (k) when the water loading reached equilibrium.

Figure 2. Structure and optical characterization of the PTJA electrode. a) SEM image of a PTJA porous layer composed of disordered porous graphite fibers. b) SEM top view of the PTJA nonporous layer. c) Adsorption spectrum of the PTJA nonporous layer; the inset is the transmittance spectra. d) SEM cross-sectional view of the PTJA electrode (the nonporous layer composed of carbon black/PDMS composite and the porous layer). e) Water resistance test of the PTJA nonporous layer with the water pressure increasing to a maximum value of 70 kPa. f) Heat transfer mechanism of the PTJA electrode. g) IR thermal image of the PTJA electrode was irradiated with simulated solar source (power density of 100 mW m^{-2}) in the low-temperature room ($7.0 \pm 2.0 \text{ }^{\circ}\text{C}$). h) Temperature change of the water in photothermal MFC with PTJA under illumination. i) Schematic of the photothermal MFC system (top view). j) IR thermal image of the photothermal MFC system (top view) when the system reached equilibrium under irradiation (single chamber air-cathode MFC with a volume of 28 mL).

Figure 3. Performance comparison of different MFC systems. a) Voltage outputs versus time of MFCs with $1 \text{ k}\Omega$ resistance loading under different conditions. The arrow symbol signifies the point of the wastewater input. b) Polarization and power density curves, c) Electrode potential curves and d) CV plots (scan rate of 5 mV s^{-1}) of photothermal MFCs based on different anodes.

Figure 4. Mechanism analysis of different photothermal MFC systems. SEM images of an anodic biofilm in a) photothermal MFCs with PTJA (the inset is the photograph of the PTJA nonporous layer after operation) and b) photothermal MFCs with traditional anodes (the inset is the photograph of the illuminated GF anode surface after operation). Microbial community components of the anodic biofilm in c) photothermal MFCs with PTJA and d) photothermal MFCs with traditional anodes (16S gene sequence analysis). e) Ratios of the main microbial species in the different photothermal MFC systems.

Figure 5. Performance of the photothermal MFC system during light on/off cycles (10 h/14 h). a) Photograph of the photothermal bioreactor sets. b) Voltage output curve of the photothermal MFC system when treating artificial wastewater during light on/off cycles (operation of 10 h under illumination followed by 14 h of operation in the dark). c) Polarization and power density curve comparison between the photothermal MFCs with PTJA during light on/off cycles and those under continuous illumination. d) Voltage output curve of the photothermal MFC system when treating real brewery wastewater. e) COD removal rates and corresponding CEs under different operation conditions.

TOC

Solar-activated low-temperature biological wastewater treatment (BWT) is achieved by the design of the photothermal Janus anode composed of a unique photothermal waterproof nonporous layer and a conductive porous layer. The photothermal Janus anode successfully prevents anodic electrochemical microorganism poisoning by shielding photosynthesis and enables the BWT system to achieve appreciable removal of organic pollutants and stable electricity generation.

Keywords

Photothermal technique, Photothermal biological wastewater treatment, Microbial fuel cell, Low-temperature wastewater treatment

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Photothermal Janus Anode with Photosynthesis-shielding Effect for Activating Low-temperature Biological Wastewater Treatment