Efficient CO₂ conversion to formic acid in a novel microbial photoelectrochemical cell using a visible-light responsive Co₃O₄ nanorod-arrayed photocathode

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A B S T R A C T

A microbial photoelectrochemical cell (MPEC) is a self-biased, solar-driven device combining bioenergy with solar energy to produce sustainable electricity and chemicals. Here, an MPEC with a p-type Co₃O₄ nanorod-arrayed photocathode and bio-anode was constructed that matched well the redox potentials of anode microorganisms with the band gap of the Co₃O₄. The yield of formic acid produced by this MPEC under visible light irradiation with an external resistance of 300 Ω was 239 ± 10 μmol in 10 h, which was 1.8 times that produced by a bare Co₃O₄ photocathode under visible light, and 4.9 times that produced by the MPEC operated in dark. The maximum power density was 331 ± 4 mW m⁻² under visible light, compared to 175 ± 25 mW m⁻² in the dark. This study of MPEC with the synergistic effect of light energy and bioenergy opens up new opportunities for applications in environmental treatment of wastewaters and chemicals production.

1. Introduction

The combustion of fossil fuels has led to excessive emissions of CO₂ into the atmosphere, resulting in climate change which is a great threat to the goal of sustainable development [1–3]. Conversion of CO₂ to chemical fuels is a potential way for producing chemicals and reducing CO₂ emissions [4–6]. In general, photocatalysis [7–9], electrocatalysis [10–12] and photoelectrochemical catalysis [13–15] are three commonly used methods for CO₂ conversion in water. Compared with single photocatalytic or electrocatalytic systems, photoelectrochemical CO₂ conversion exhibits more advantages: the assistance of light energy could lower the input electricity in comparison with electrocatalytic CO₂ conversion; the applied external voltage could enhance the photocatalytic charge separation and efficiency of photocathode compared with photocatalytic process [16–18]. In a photoelectrocatalytic CO₂ conversion process, a photocathode with excellent photocatalytic and electrocatalytic properties is of great importance [19]. Among kinds of semiconductor materials, Co₃O₄, as a p-type, visible-light responsive photocatalyst, with remarkable electrochemical performance [20–22], is regarded as one of the most promising candidates to serve as the photocathode that could efficiently realize the photoelectrocatalytic CO₂ conversion. Recent studies have demonstrated that Co₃O₄ has the ability to reduce CO₂ into value-added chemical fuels in the photoelectrocatalytic process [23–25]. Although the photoelectrocatalytic CO₂ conversion shows more advantages, the input of additional electrical energy increases the cost and cannot satisfy the requirement for industrial applications. A microbial fuel cell (MFC) is a bioelectrochemical system that provides an efficient way to oxidize organic matter in wastewaters using electrochemically active microorganisms to remove pollutants and produce electricity at the same time [26–28]. Recently, an MFC with a light-driven semiconductor photocathode (MPEC) was developed that could generate hydrogen gas by combining the energy from the microbial degradation of organic matter with solar energy. Electricity derived from the degradation of organic matter by microorganisms on the anode is used in the MPEC to supply electrons to the photocathode, enhancing charge separation of semiconductor photocatalysis and improving photocatalytic efficiency. A visible-light driven MPEC with a Cu₂O nanowire photocathode was constructed by Qian et al. [29], and substantial current generation was successfully obtained in this MPEC at zero bias by coupling bioenergy produced by the anode with light on the cathode. An MPEC with a CuO nanowire-arrayed photocathode was also fabricated by Sun et al. [30], and a maximum power density of 46 mW m⁻² under light irradiation was generated.

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which was 1.26 times that generated in the dark. Subsequently, an MPEC with a composite CuO2/No3O photocathode for efficient H2 production was constructed by Liang et al. [31], and a H2 production rate of 5 μL·h−1·cm−2 was obtained under continuous light illumination with 0.2 V external bias. However, the visible-light driven copper oxide photocathodes used in these studies were unstable, and most constructed MPECs have been used for H2 production. There have not yet been any studies on CO2 conversion to chemicals in the photocathode chamber of an MPEC.

Here, an MPEC was constructed that used a Co3O4 nanorod-arrayed photocathode for CO2 conversion to formic acid by co-utilization of light energy and bioenergy. Using electrons derived from the anodic conversion of biodegradable organic matter, the Co3O4 nanorod-arrayed photocathode exhibited enhanced photocatalytic activity for CO2 conversion compared with the control (Co3O4 nanorod-arrayed photocatalyst alone) under visible light irradiation. The COD removal efficiency, coulombic efficiency and power density of this MPEC were also examined for the MPEC compared to controls.

2. Experimental methods

2.1. Reagents

The chemical reagents included cobalt chloride hexahydrate (CoCl2·6H2O), urea (CO(NH2)2), nickel foam, sodium sulfate (Na2SO4), sodium acetate (CH3COONa), ammonium chloride (NH4Cl), potassium chloride (KCl), sodium dihydrogen phosphate (NaH2PO4·2H2O), disodium hydrogen phosphate (Na2HPO4·12H2O), vitamins and trace minerals. All the reagents were used as received without further purification. Deionized water was used throughout this study.

2.2. Preparation of Co3O4 nanorod-arrayed photocathode

To prepare the Co3O4 nanorod-arrayed photocathode, nickel foam was washed with ultrasonication in acetone and ethanol for 20 min. Then, CoCl2·6H2O (0.95 g) and CO(NH2)2 (1.20 g) were put into a Teflon-lined stainless steel chamber with 50 mL of deionized water. The mixture was stirred for 0.5 h, and then the pretreated nickel foam was vertically placed into the container, and then sealed and kept at 95 °C for 8 h in an oil bath pan with continuous stirring. After cooling to room temperature, the nickel foam was rinsed with deionized water with ultrasonication for 3 min, dried at 60 °C for 6 h, and then annealed at 250 °C for 1 h, producing the final Co3O4 nanorod-arrayed photocathode.

2.3. Reactor setup and operation

2.3.1. Bio-anode culture

The bio-anode was cultivated in a single-chamber air-cathode microbial fuel cell (MFC) configuration with a volume of 56 mL (diameter of 3 cm, 8 cm long) (Fig. S1). The anode was a carbon fiber brush which was 7 cm long and 3 cm in diameter. The carbon brush was first cleaned by soaking in pure acetone for 12 h, and then heated in a muffle furnace at 450 °C for 0.5 h. The chamber was inoculated with municipal wastewater and a medium containing sodium acetate (1.0 g/L), 50 mM phosphate buffer solution (0.13 g/L of KCl, 0.31 g of NH4Cl, 3.32 g/L of Na2HPO4·2H2O and 10.32 g/L of Na2HPO4·12H2O, 12.5 mL of a trace mineral solution, and 5 mL of a vitamin solution. The air cathode was made by the rolling press method [32]. The external resistance of the MFC was kept at 1000 Ω during acclimation. The chamber was kept anaerobic except when the inoculation medium was refilled every 24 h. The bio-anode was acclimated for 3 weeks until the carbon fiber brush was enriched with electrochemically active microorganisms as shown by a stable output voltage of ~500 mV (Fig. S2).

2.3.2. MPEC construction and operation

The acclimated bio-anode was transferred into the MPEC containing a Co3O4 nanorod-arrayed photocathode in an H-type, two-chamber reactor (Fig. S3). The anode and photocathode chambers each had a volume of 100 mL, with the two chambers separated by proton exchange membrane (PEM, 2.3 cm2; Beijing Anketech Membrane Separation Engineering & Technology Co., Ltd., China) held in a tube with an inner diameter of 1.7 cm and a length of 1.2 cm on each side of the membrane. The anode was inserted vertically into the anode chamber through the small hole in the PTFE cover. The cathode (projected area of 3.8 cm2) was held using an electrode clamp, and inserted vertically into the cathode chamber through the small hole on the PTFE cover. A quartz window was set on the photocathode chamber for transmission of light. The photocatalytic cathode and microbial anode were connected with wires across an external resistance. The light source was a 150 W xenon lamp (GY-10A, Tuopu Co. Ltd., China, 380–780 nm). Na2SO4 (0.1 M) was used as supporting electrolyte in the photocathode chamber.

2.4. Photocathode characterization

X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX III-3B diffractometer with Cu Kα source (40 kV and 30 mA) to investigate the crystal phase structure and composition of the photocathode. Ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS) was conducted using a Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere detector, with BaSO4 as the reflectance sample. The surface morphology was obtained using a field-emission scanning electron microscope (SEM, FEI Quanta 200 F). Transmission electron microscopy (TEM) was obtained using a JEM-3010 electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy was conducted using a PHI-5700 ESCA instrument with Al Kα radiation. N2 adsorption/desorption was tested by Brunauer-Emmett-Teller (BET) with a 3H-2000PS1 surface area analyzer (Beishide, China) at 77 K.

2.5. Photoelectrochemical measurements of the photocathode

Linear sweep voltammetry (LSV) curves and current density-power density (I–P) curves were obtained using an Applied Photocatalysis (PCGM-1256C, China) with a solar simulator, with the optimal conditions obtained for the photocathode. The incident light intensity was 100 mW cm−2. Reaction solutions with pH 2 were obtained by varying the external resistance over a range from 10,000 to 100 Ω. A multimeter was used to record the cell voltage, anode and cathode potentials. The current density was obtained with Pt foil (99.9 %) as a counter electrode, and a saturated calomel electrode (SCE, +0.242 V vs standard hydrogen electrode; SHE) as the reference electrode. The frequency of EIS test was set from 0.01 Hz to 100,000 Hz, with an amplitude of 10 mV (RMS). The light source was a 150 W xenon lamp (GY-10A, Tuopu Co. Ltd., China, 380–780 nm).

2.6. Data collection and analysis of MPEC system

The output voltages (U) of the MPEC system were recorded with a data acquisition board (PISO-813, ICP DAS Co., Ltd.). The polarization curves and power density of MPEC under light and dark conditions were obtained by varying the external resistance over a range from 10,000 to 100 Ω. A multimeter was used to record the cell voltage, anode and cathode potentials. The current density was obtained with the formula of I = U/RA, where U is the cell voltage, R the external resistance, and A the projected surface area of the cathode. The measured anode and cathode potentials, power density were corrected for ohmic drops between the working and reference electrodes, and calculated as previously reported [33,34].

2.7. CO2 conversion in MPEC

CO2 conversion using the single Co3O4 nanorod-arrayed photocathode with light irradiation was first examined in a single
photocathode chamber. Prior to CO₂ conversion tests, high purity CO₂ gas was sparged into the Na₂SO₄ electrolyte (0.1 M, 70 mL) for 0.5 h at a gas flowrate of 20 mL min⁻¹ to remove the residual air. For conversion tests, the gas flowrate of CO₂ was maintained at 10 mL min⁻¹. The light source was same as that used in the photoelectrochemical measurements of photocathode. During irradiation, 1.5 mL of liquid was taken from the cathode chamber every 1 h over the duration of the experiment (10 h) to evaluate chemical production. CO₂ conversion tests were also conducted using only the single Co₃O₄ nanorod-arrayed photocathode without light irradiation.

CO₂ conversion performance of the MPEC system was also tested with and without light irradiation. For light irradiation tests, the reactor was first kept in an open-circuit state and saturated calomel electrodes (SCE, +0.242 V vs standard hydrogen electrode; SHE) were placed into the cathode and anode chambers to monitor the electrode potentials. Before these experiments, high purity CO₂ gas was sparged into the cathode Na₂SO₄ electrolyte (0.1 M, 70 mL) at 20 mL min⁻¹, and the anode chamber was replaced with fresh medium. When the anode potential reached about −500 mV, the cathode and anode were connected with wires across a 300 Ω resistor. After the xenon light was turned on, the gas flowrate of CO₂ in cathode was reduced to 10 mL min⁻¹ and samples were taken of the catholyte as described above. The anode and cathode potentials, and the voltages were recorded using a data acquisition system.

The products of CO₂ conversion were analyzed using an ion chromatograph (IC 6100, Wanyi, AnHui, China). Before analysis, the liquid samples were diluted 10 times and filtered through a 0.22 μm pore diameter syringe filter. The process of CO₂ conversion using this MPEC without light irradiation was the same as the process of CO₂ conversion with light irradiation except for the omission of the light.

The concentration of acetate in the anolyte at the beginning and end of the tests was based on its chemical oxygen demand (COD). The COD removal rate and coulombic efficiency (CE) were calculated as previously reported based on the changes in COD and the measured current [35].

3. Results and discussion

3.1. Characterisation of photocathode

The XRD patterns of the Co₃O₄ nanorod-arrayed powder removed from the Ni foam substrate showed that all the diffraction peaks were derived from Co₃O₄. The peaks and the corresponding crystal planes of the spinel Co₃O₄ phases were at 19.0 (111), 31.2 (220), 36.8 (311), 44.8 (400), 59.4 (511) and 65.2° (440) (JCPDS 09-0418) (Fig. 1A), and no other peaks of impurities were observed. The UV diffraction reflection spectroscopy of the Co₃O₄ nanorod-arrayed photocathode showed obvious optical absorption in both the ultraviolet and visible light wavelengths (Fig. 1B). To calculate the band gap values, the plot of (Ahv)² vs hv (Fig. 1B, inset) was investigated, where A is the absorption and hv is the photon energy (Fig. 1B, inset). A band gap of 1.43 eV calculated from the plot was attributed to the transition from O²⁻ to Co³⁺. Another calculated band gap of 2.39 eV was attributed to the transition of O²⁻ to Co³⁺, which was the “true” energy gap corresponding to inter-band transitions [36]. The results of the calculated band gaps demonstrated that the synthetic Co₃O₄ nanorod-arrayed photocathode could absorb visible light and was a visible light responsive photocatalyst. The conduction band and valence band potentials of this Co₃O₄ photocathode were further calculated with:

\[ E_{VB} = X \cdot E^0 + 0.5Eg \]  
\[ E_{CB} = E_{VB} - Eg \]  

where \( E_{VB} \) and \( E_{CB} \) are the potentials of conduction band edge and valence band edge, respectively, \( X \) and \( Eg \) are the electronegativity and band gap of a semiconductor, respectively, and \( E^0 \) is the energy of free electrons vs. hydrogen (about 4.5 eV/NHE) [37]. The X values of Co₃O₄ is 5.93 eV [38,39]. Thus, the \( E_{VB} \) and \( E_{CB} \) of Co₃O₄ were calculated to be 2.625 eV and 0.235 eV (vs. NHE).

The XPS spectra showed large peaks corresponding to Co and O. Two major peaks were observed with a spin-energy separation of 15 eV in the Co 2p spectra (Fig. 1C). The peak at the binding energy of 779.84 eV corresponded to Co 2p3/2, and a peak at 794.84 eV was attributed to that for expected Co 2p1/2, which were characteristic of the Co₃O₄ phase [40]. In the O 1s spectra (Fig. 1D), the observed peaks at about 531.7 eV and 530.1 eV were derived from the lattice oxygen atom in Co₃O₄ and the −OH species adsorbed on the surface of Co₃O₄ [41,42].

The SEM image of the Co₃O₄ photocathode showed a high density of Co₃O₄ nanorods and were grown uniformly on the Ni foam substrate (Fig. 2A and B). The Co₃O₄ nanorod arrays grew almost vertically on the Ni foam substrate (Fig. 2C). The TEM image (Fig. 2D) of a single Co₃O₄ nanorod scraped off the Ni substrate showed that the diameter of a Co₃O₄ nanorod was around 80 nm, and that there were many meso-pores distributed on the surface. The lattice spacing of 0.47 nm in the HRTEM image (Fig. 2E) corresponded to the (111) crystal planes of spinel Co₃O₄ [43], consistent with the XRD data. The corresponding SAED pattern (Fig. 2F) demonstrated that the Co₃O₄ nanorod had a polycrystalline structure. [44]

N₂ adsorption-desorption isotherm and corresponding Barrett–Joyner–Halenda (BJH) pore size distributions were obtained to further investigate the structure of the mesopores (Fig. 3). The pores of the mesoporous structures were 12.0 nm. Moreover, the Co₃O₄ nanorod exhibited a BET surface area of 40.7 m² g⁻¹ and pore volume of 0.2 cm³ g⁻¹. These structural characteristics would benefit the adsorption of CO₂ on the surface of the Co₃O₄ nanorod-arrayed photocathode during the CO₂ conversion process.

3.2. Photoelectrochemical performance of photocathode

The linear sweep voltammetry (LSV) curves of the Co₃O₄ nanorod-arrayed photocathode in 0.1 M N₂ or CO₂ saturated Na₂SO₄ aqueous solution were performed under visible light irradiation and in the dark (Fig. 4A). In the N₂-saturated electrolyte, the current density curves of Co₃O₄ photocathode were relatively flat whether under irradiation or not. However, a dramatic enhancement in current density with regard to CO₂ reduction in CO₂-saturated electrolyte was observed under both irradiation and in dark. The onset potential of this Co₃O₄ photocathode obtained in dark was approximately −0.85 V, which was more positive than that of a hierarchical Co₃O₄ electrode reported previously [24], indicating that the Co₃O₄ photocathode had a superior electrocatalytic capability for CO₂ reduction. The onset potential moved to a more positive value and the reduction current density was obviously larger with light irradiation than that in dark, confirming a faster CO₂ reduction rate due to the generation of the photogenerated electron-hole pairs under visible light irradiation. The EIS spectra of the Co₃O₄ photocathode were analyzed using an equivalent circuit model (Fig. 4B), where \( R_s \) is the resistance of the electrolyte between two electrodes, \( Cdl \) the double layer capacitance, \( R_t \) the charge transfer resistance, and \( W \) the Warburg impedance [9]. The charge transfer resistance was \( R_t = 0.013 \Omega \) in the light, compared to 0.28 Ω in the dark (Table S1). The decreased charge transfer resistance in the light indicated that the Co₃O₄ photocathode had a better electron transfer ability with light irradiation. The photoelectrochemical performance thus confirmed that the p-type Co₃O₄ could function as an efficient photocathode for effective photoelectrocatalytic CO₂ reduction.

3.3. Evaluation of MPEC performance

The current densities produced by the MPEC were examined with and without visible light irradiation. With an external resistance of 300 Ω, the generated current density in dark was 21.6 μA cm⁻², which gradually increased to 60.2 μA cm⁻² under visible light irradiation.
The current density of the MPEC also showed stable and reproducible cycles over several on-off light irradiation cycles. Polarization and power density curves were also obtained with and without light irradiation. The open circuit voltage under visible light was 608 ± 8 mV, compared to 571 ± 1 mV in the dark. The maximum power densities was 331 ± 4 mW m\(^{-2}\) with light irradiation, and 175 ± 25 mW m\(^{-2}\) without light (Fig. 6A). Based on the electrode potential curves (Fig. 6B), the anode potentials were the same under dark or light conditions, ranging from 0 to 0.98 A m\(^{-2}\) over a range of 0–1 A m\(^{-2}\). However, the cathode potential was substantially improved with light, indicating the improved performance was due to the cathode.

3.4. Conversion of CO\(_2\) into simple organic molecules

The catalytic activities for CO\(_2\) conversion were examined (Fig. 7A).
For a single Co₃O₄ nanorod-arrayed photocathode in dark condition, no production was detected due to the absence of the electrons without irradiation. For the conditions of bare Co₃O₄ photocathode with light irradiation, the MPEC system with and without light irradiation, formic acid was the only product detected, indicating a high selectivity. The yield of formic acid produced by the single Co₃O₄ nanorod-arrayed photocathode under visible light irradiation was 133 ± 14 μmol through analysis of the catholyte after 10 h reaction. For the MPEC system with an external resistance of 300 Ω, the generation rate of formic acid was slow in the initial stage of CO₂ conversion, both under visible light and in dark, demonstrating that the anodic microorganisms needed time to adapt to this process. The yield of formic acid detected when the MPEC was operated under visible light irradiation in 10 h reaction time was 239 ± 10 μmol, which was about 4.9 times that produced by the MPEC operated in dark (49 ± 9 μmol), and 1.8 times that produced by a single Co₃O₄ nanorod-arrayed photocathode under visible light irradiation.

The COD removal efficiency in the anode of the MPEC system was 8.2 ± 0.9 % under visible light, which was 61 % larger than that obtained in dark (5.1 ± 0.4 %). The coulombic efficiency of the MPEC system was 10.5 ± 0.9 % under visible light, which was about 1.4 times that produced in dark (7.5 ± 1.2 %) (Fig. 7B). The enhanced catalytic activity for CO₂ conversion and improved coulombic efficiency were attributed to the Co₃O₄ photocathode, as the cathode potential was improved under light irradiation compared to the cathode in dark, while the anode potentials were essentially unchanged (Fig. 7C). The enhanced cathode potential under light irradiation made more electrons derived from the bio-anode driven to the photocathode through the external circuit, as shown by the higher current densities (Fig. 7D), leading to the enhanced coulombic efficiency and greatly improved separation of photogenerated electrons and holes of the Co₃O₄ photocathode. Thus, the catalytic activity for CO₂ conversion to formic acid was also increased.

3.5. Discussion on the mechanism

A self-biased MPEC with a microbial anode and a Co₃O₄ nanorod-arrayed photocathode for spontaneous electricity generation and CO₂ reduction under visible light irradiation was successfully constructed, with the corresponding schematic diagram shown in Fig. 8. The reactions involved in the process of CO₂ reduction using this MPEC could be summarized as follows:

Anode: CH₃COO⁻ + 2H₂O → 2CO₂ + 7H⁺ + 8e⁻  

(1)
Cathode: $\text{Co}_3\text{O}_4 + hv \rightarrow h_{vb} + e_{cb}$  \hspace{1cm} (2)

$e^- + h_{vb} \rightarrow hv$  \hspace{1cm} (3)

$\text{CO}_2 + 2 \text{H}^+ + 2 e_{cb}^- \rightarrow \text{HCOOH}$  \hspace{1cm} (4)

In the anode of this MPEC, microorganisms degraded sodium acetate and produce electrical current, releasing protons into solution (reaction (1)). The electrons ($e^-$) derived from the bio-anode transferred to the photocathode continuously through the external circuit without external bias due to the higher potential of cathode than that of bio-anode. The protons and other cations were transferred to the cathode through the proton exchange membrane. In the cathode, when this MPEC was operated in the dark, $\text{Co}_3\text{O}_4$ functioned as an electrocatalyst and there was only a little formic acid detected in the cathode chamber (Fig. 7A). However, under visible light irradiation, photogenerated electrons ($e_{cb}^-$) and holes ($h_{vb}^+$) were generated on the conduction band and valence band of $\text{Co}_3\text{O}_4$ (reaction (2)), which improved the cathode potential and reduced the charge transfer resistance, as indicated in Table S1 and Fig. 7C. Large amounts of photogenerated electron-hole pairs will recombine and only a fraction of electrons and holes could reach the surface of $\text{Co}_3\text{O}_4$ to take part in the chemical reactions. Thus, the separation of photogenerated electrons and holes is a key issue to influence the photocatalytic activity of $\text{Co}_3\text{O}_4$.

In this MPEC, the assistance of the electrons derived from bio-anode greatly enhanced the charge separation of $\text{Co}_3\text{O}_4$. Electrons produced by the bio-anode were driven to the photocathode through the external circuit because of the improved cathode potential and reduced cathode...
charge transfer resistance caused by the photocatalysis of Co3O4. It is
generally accepted that the energy potentials of electrons from the bio-
anode were gradually lowered during the electron transfer process from
the anode to cathode through the external circuit in an MPEC due to the
electrolyte resistance, the resistance of electron transfer through the
cellular respiratory chain, and electron transfer from microorganisms to
anode. However, the energy potentials of the photogenerated electrons
in cathode were higher than that of the electrons derived from bio-
anode because of the absorption of light energy. Therefore, photog-
genenerated holes on the valence band of Co3O4 preferentially combined
with the electrons transferred from the anode, with the energy being
released in the form of heat or photons (reaction (3)). As a result, the
separation of photogenerated electrons and holes of Co3O4 was greatly
improved, leading to an enhanced reaction kinetics of electrons and
CO2 reduction, and improved catalytic activity for CO2 conversion to
formic acid (reaction (4)), compared with the conditions of the single
Co3O4 nanorod-arrayed photocathode for CO2 reduction under visible
light and the MPEC system in dark. Moreover, the enhanced reaction
rate of CO2 reduction could further enhance the power density of the
MPEC. Thus, the photocathode and the bio-anode in this light sensitive
MPEC system functioned synergistically coupled light energy and
bioenergy for electricity generation and CO2 conversion.

4. Conclusions

A microbial photoelectrochemical cell (MPEC) system using a bio-
anode coupled with a Co3O4 nanorod-arrayed photocathode enabled
efficient power generation and CO2 conversion to formic acid. This
MPEC system produced a maximal power density of 331 ± 4 mW m−2
under light irradiation, which was about 1.9 times of that produced in
dark (175 ± 25 mW m−2). With an external resistance of 300 Ω,
239 ± 10 μmol formic acid was obtained in the catholyte of this MPEC
over a period of 10 h, which was 1.8 times of the formic acid produced
by a bare Co3O4 nanorod-arrayed photocathode under visible light
irradiation, and 4.9 times that produced by the MPEC operated in dark.
The open circuit voltage of the MPEC system was improved to
608 ± 8 mV under light irradiation, which was 1.1 times of that in
dark (571 ± 1 mV).

The enhanced CO2 conversion performance and power density
under light irradiation was due to the photocatalysis by the Co3O4
nanorod-arrayed photocathode, which improved the cathode potential
and reduced the cathode charge transfer resistance. The activity of the
photocathode allowed more electrons produced by the bio-anode to
flow to the photocathode through the external circuit, enhancing the
separation of photogenerated electrons and holes of Co3O4 and
improving the reaction kinetics of electrons and CO2 reduction. The MPEC
therefore provides an efficient approach for simultaneous organic
pollutant degradation and clean energy production due to the sy-
nergic effect of combining bioenergy and light energy.

CRediT authorship contribution statement

Jing Wu: Investigation, Writing - original draft. Xiaoyu Han: Methodology. Da Li: Formal analysis. B.E. Logan: Writing - review &

Declaration of Competing Interest

The authors declare that they have no known competing financial
interests or personal relationships that could have appeared to
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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

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