Spontaneously producing syngas from MFC-MEC coupling system based on biocompatible bifunctional metal-free electrocatalyst

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ABSTRACT The preparation of high-value fuels and chemicals through the electrochemical carbon dioxide reduction reaction (CDRR) is of great significance to the virtuous cycle of carbon dioxide. However, due to the high overpotential involved in this reaction, high power consumption and high-cost noble-metal-based catalysts are required for driving this process. Herein, the electrochemical CDRR was achieved on biocompatible metal-free nitrogen, phosphorus co-doped carbon-based materials (NP-C) in the microbial fuel cell-microbial electrolysis cell (MFC-MEC) coupling system. As the bioelectrochemistry in MFC supplied power to drive the electrocatalysis in MEC, syngas was spontaneously produced from this coupling system without external energy input. With the NP-C materials as the excellent bifunctional electrocatalyst for the CDRR and oxygen reduction reaction (ORR), the current density of the MEC reached -0.52 mA cm^{-2} , and the Faradaic efficiencies (FEs) of CO and H₂ were 60% and 40%, respectively, at a load resistance of 10 Ω . Moreover, the CO/H₂ product ratio can be changed by adjusting the load resistance, which will widely meet various demand of syngas usage in further reactions. This study provides a spontaneous and tunable production of syngas in biogas digesters via an electrochemical strategy.

Keywords: spontaneous production, syngas, MFC-MEC coupling system, N/P-co-doped carbon electrocatalyst

INTRODUCTION

Excessive emissions of carbon dioxide (CO₂) have caused some serious environmental problems due to the massive

burning of fossil fuels, which seriously endangers human sustainable development [1,2]. The preparation of high-value fuels and chemicals by electrochemical reduction reactions of CO₂ may be one of the promising ways to solve this problem [3]. Among them, the electrochemical reduction of CO₂ to produce syngas has attracted widespread attention. Because the syngas currently used in industry mainly comes from coal vaporization and natural gas steam conversion, its energy consumption and cost are relatively high [4–7]. Electrocatalytic reduction of CO₂ may become another promising syngas preparation technology. However, due to the high overpotential in this reaction, high power consumption and high-cost noble-metal-based catalysts are required for driving this process. In order to avoid the loss of energy caused by power generation, other clean energy sources (such as solar and wind) are considered to be the most feasible method for power generation. For example, Ghausi *et al.* [8] used a solar cell coupled with a CO₂ electrolysis cell to catalyze CO₂ reduction. As a self-powered device, the microbial fuel cell-microbial electrolysis cell (MFC-MEC) coupling system can react spontaneously without an external power source. This method provides the possibility to solve the problem of the source of electrical energy in electrocatalytic CO₂ reduction. The system has been used for hydrogen production in the hydrogen production reaction (HER), as well as for wastewater treatment in the absence of an external power source [9–12]. In addition, Zhao *et al.* [13] reported for the first time the storage and conversion of CO₂ using the MFC-MEC coupling system.

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The composite material of multiwall carbon nanotube (MWCNT) and CoTAPc was used as the MEC cathode to catalyze the reduction of CO_2 to formic acid. However, formic acid was a liquid product that was easy to produce but difficult to separate from the system. On this basis, we further studied the use of biocompatible metal-free carbon-based catalysts to spontaneously produce syngas in the MFC-MEC coupling system.

Recently, carbon-based materials have been widely used as an electrode due to their good electrical conductivity, high specific surface area, relatively low cost, and environmental friendliness [14,15]. When heteroatoms were incorporated into carbon materials, their physical and chemical properties can be significantly adjusted, which may promote their catalytic function [16]. In recent years, nitrogen-doped carbon-based materials, such as N-doped graphene [17], mesoporous carbon [18], nanodiamond [19], carbon nanofibers [20] and CNTs [21] have shown good electrocatalytic properties for the carbon dioxide reduction reaction (CDRR), even comparable to precious metal catalysts. In addition, other heteroatom-doped (P, F, and Si) carbon-based materials have also been developed recently [8,22,23]. Meanwhile, for MFCs, the cathode was one of the important compositions that determine the ultimate generated electrical energy. Oxygen (O_2) is considered as the ideal electron acceptor toward the cathodic reaction in MFC because of its high content in the air. However, due to the sluggish rate of oxygen reduction reaction (ORR), a catalyst is necessary [24,25]. Generally, in ORR, the Pt-based catalyst has been extensively used in the MFC system [26,27], but high cost and relatively poor stability hinder its practical application. In order to solve this problem, the heteroatom-doped carbon as a potential candidate for replacing Pt-based catalyst has been greatly developed in the ORR [28–39]. Therefore, suitable metal-free carbon materials with catalytic activity for both ORR and CDRR in the MFC-MEC coupling system can efficiently electrochemically produce syngas.

In this study, a biocompatible metal-free N/P-co-doped carbon material (NP-C) was synthesized *via* a facile pyrolysis of cellulose mixed with urea and phytic acid as nitrogen and phosphorus source, respectively, as an effective bifunctional electrocatalyst for CDRR and ORR in the MFC-MEC coupling system. The combination of the bioelectrochemical process and a catalytic electrode has boosted the spontaneous production of syngas without external energy input.

EXPERIMENTAL SECTION

Chemicals and reagents

Carbon paper (HCP 020N, HeSen), Nafion membrane (Nafion 211, DuPont), Nafion membrane solution (20%, DuPont), KHCO_3 (99.7%, Sigma-Aldrich), phytic acid solution (50% in H_2O , Aladdin), α -cellulose (50 μm , Aladdin), and deionized (DI) water were used as received. All other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. without further purification.

Synthesis of NP-C

The nitrogen-phosphorus co-doped carbon materials were synthesized by the pyrolysis of microcrystalline cellulose (50 μm), urea, and phytic acid. Typically, the mixture of cellulose (4 mmol), urea (40 mmol) and phytic acid (0.8 mmol) was transferred to the tube furnace, followed by annealing at 900°C (5°C min^{-1}) for 1 h under Ar atmosphere. After cooling down to 25°C , NP-C was obtained. As comparison, the P-C and N-C were also obtained in the same way without urea and phytic acid, respectively. Additionally, undoped carbon (C) was also obtained by pyrolyzing microcrystalline cellulose under the same conditions.

Electrochemical measurements

The electrochemical testing was performed with a three-electrode system by an electrochemical workstation (CHI 660E). Pt mesh (1 cm^2) and Ag/AgCl (saturated with KCl) were used as counter and reference electrodes, respectively. For catalyst ink preparation, 10 mg of the sample was dispersed in the mixture of 0.95 mL of isopropyl alcohol and 0.05 mL of 20% Nafion membrane solution with sonication. The suspension was dropped on the carbon paper (0.1 mL cm^{-2} , catalyst loading mass: 1.0 mg cm^{-2}) and dried at room temperature. The electrochemical CDRR was performed in an H-type reactor filled with 0.1 mol L^{-1} KHCO_3 solution separated by a Nafion membrane. Prior to experiments, the catholyte was pumped with CO_2 (purity of 99.999%) for 30 min, and CO_2 was controlled at a rate of 20 mL min^{-1} during experiments. Electrochemical ORR test was conducted in 0.1 mol L^{-1} phosphate buffer solution (PBS: 10.9 g L^{-1} $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 3.04 g L^{-1} $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 0.31 g L^{-1} NH_4Cl , and 0.13 g L^{-1} KCl) with the catalyst loaded on the rotating disk electrode (RDE) with the diameter of 5 mm. Prior to experiments, the electrolyte was pumped with O_2 (purity of 99.999%) for 30 min. During the experiment, O_2 was continuously fed into the electrolyte at a constant flow rate. The potential measured with reference

electrode was converted to RHE scale with the equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + (0.0591 \times \text{pH}) \text{ V}$.

Reactor construction

The coupling system consisted of an H-type MEC for implementing electrochemical CDRR and a single-chamber MFC (4 cm in length and 3 cm in diameter) for producing electric power. The anodes of MFC and MEC were graphite fiber brushes (3 cm long, 3 cm outer diameter), which were soaked in acetone overnight, and then heated at 450°C for 30 min. The catalyst-coated carbon paper (1 mg cm⁻²) was used as the cathodes of MEC and MFC, the surface area of which were 2 cm² and 7 cm², respectively. Each MFC was operated at 30 ± 1 °C and fed with a medium containing acetate (1.5 g L⁻¹) in 50 mmol L⁻¹ PBS.

Gas detection and the Faradaic efficiencies (FEs) of gas products

The gas products produced during the CDRR were detected using a gas chromatograph (GC, 9700II, FULI). Calculation of the FEs for CO and H₂ at a given potential or current was based on the following equations:

$$\text{FE}_{\text{CO}} = \frac{i_{\text{CO}}}{i_{\text{total}}} = \frac{X_{\text{CO}} \times v_{\text{CO}_2} \times n \times 96485}{i_{\text{total}}}, \quad (1)$$

$$\text{FE}_{\text{H}_2} = \frac{i_{\text{H}_2}}{i_{\text{total}}} = \frac{X_{\text{H}_2} \times v_{\text{CO}_2} \times n \times 96485}{i_{\text{total}}}, \quad (2)$$

where i_{CO} (and i_{H_2}) is the partial current for CO (and H₂) production, i_{total} is the total current, X_{CO} (X_{H_2}) is the production rate of CO (and H₂) (measured by GC), v_{CO_2} is the flow rate of CO₂, and n is the number of electrons transferred for each product molecule formation (it is 2 for both CO and H₂).

Characterization

Powder X-ray diffraction (XRD) profiles were collected on a MiniFlex 600 X-ray diffractometer at the scan rate of 3° min⁻¹ (Cu Kα source). High-resolution scanning electron microscopy (SEM) image was obtained using a JEOL-6700F and low-resolution SEM images by using Phenon G2 Scan Electron Microscopy. Transmission electron microscope (TEM, JEOL JEM-2010) equipped with an energy dispersive X-ray detector (EDX) was applied for the morphologies and elemental contents of the as-prepared catalysts. Nitrogen adsorption-desorption isotherms were determined using automatic volumetric adsorption equipment (Autosorb-iQ, Quantachrome). The specific surface areas for the samples were figured by

the Brunner-Emmet-Teller (BET) method, and the pore size distributions for the samples were figured from an adsorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) model. The surface valence state of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) with a VG ESCALAB 250. Raman spectra were obtained from a Raman spectrometer (LabRAM HR) using a 532 nm laser.

RESULTS AND DISCUSSION

Synthesis and characterization of NP-C

The NP-C materials were synthesized by pyrolyzing cellulose in the presence of urea and phytic acid. For comparison, nitrogen-doped carbon (N-C) and phosphorus-doped carbon (P-C) with corresponding single doping and undoped carbon (C) were also synthesized. SEM (Fig. 1a) and TEM (Fig. 1b) images show the crumpled and sheet-like morphology for the prepared NP-C sample. In contrast, N-C (Fig. S1d) and pure C (Fig. S1b) reveal a rod-like structure consistent with the structure of the raw material cellulose (Fig. S1a), while P-C displays a broken block morphology (Fig. S1c). Moreover, the corresponding elemental mapping (Fig. 1c), verifies the uniform dispersion of carbon, nitrogen, and phosphorus in NP-C. The EDX analysis further confirms the existence of carbon, phosphorus, nitrogen, and oxygen in NP-C (Fig. S2). The N₂ adsorption-desorption isotherm (Fig. S3) displays a high specific surface area of 1124 m² g⁻¹ for NP-C. P-C (Fig. S4), N-C (Fig. S5) and pure C (Fig. S6) also show high specific surface areas (1638, 667, and 1021 m² g⁻¹, respectively). The surface area expansion resulting from the P doping (Figs S3–S6) has positive effects on the CDRR activity on NP-C. The XRD patterns (Fig. S7) of NP-C, P-C, N-C and pure C all show a typical peak at 2θ = 24° that can be readily assigned to graphitic carbon (002), consistent with the appearance of the G band (ca. 1600 cm⁻¹) in the Raman spectra (Fig. S8). The D band at about 1360 cm⁻¹ and the higher intensity of G band imply the enriched defects and graphite carbon in NP-C. The XPS spectrum in Fig. 1d shows that NP-C, N-C, P-C and pure C all contain the main elements of C and O, but only NP-C contains both N (5.4%) and P (2.16%) atoms, evidencing the formation of N and P co-doping in NP-C. Moreover, the high-resolution XPS spectra for C 1s (Fig. S9), N 1s (Fig. 1e), and P 2p (Fig. 1f) in NP-C suggest the existence of C–N and C–P bonds. Therefore, the prepared NP-C has a co-doping of N and P, and a high specific surface area, which may play an active role in electrolysis.

Figure 1 (a) SEM image, (b) typical TEM image, and (c) elemental mapping images of NP-C. (d) Survey XPS spectra of cellulose doped carbon NP-C, P-C, N-C and pure C. (e, f) High-resolution XPS spectra of NP-C: (e) N 1s, and (f) P 2p.

CDRR and ORR performance of NP-C

The electrocatalytic performance of NP-C in CDRR and ORR were first tested by linear sweep voltammetry (LSV). Fig. 2a displays the LSV curves of CDRR with a scan rate of 10 mV s^{-1} , in which NP-C has a current density of 1.73 and 1.08 mA cm^{-2} at -0.59 V in CO_2 and Ar, respectively. The large current density gap between CO_2 and Ar suggests the high electrocatalytic activity for CDRR on NP-C. When further compared with N-C, P-C and pure C, NP-C has a larger gap, indicating that NP-C has a better inhibition of competitive HER. In the further potentiostatic electrolysis of CO_2 , NP-C displays a much higher partial current density for CO_2 -to-CO conversion (j_{CO}) than P-C, N-C, pure C and even their sum at potentials ranging from -0.4 to -0.9 V (Fig. 2b), demonstrating the best electrocatalytic CDRR performance of the co-doped NP-C. The maximum FE_{CO} of NP-C is 81% at -0.59 V vs. RHE with j_{CO} reaching 1.3 mA cm^{-2} , matching the reported advanced metal-free carbon-based catalysts (Table S1), which allows further application of NP-C in our designed device. When competitive HER was also accounted, a selectivity map could be obtained by plotting FEs for CO and H_2 , as shown in Fig. 2c and Fig. S10. Compared with P-C, N-C, and pure C, the FE of the competitive HER was well suppressed on NP-C. In order

to further study the intrinsic reasons for the enhancement of CDRR performance by nitrogen and phosphorus co-doping, Tafel plots of CO generation were first conducted. NP-C presented the lowest Tafel slope ($122.6 \text{ mV dec}^{-1}$, Fig. 2d), which was much lower than that of C ($224.2 \text{ mV dec}^{-1}$), N-C ($273.8 \text{ mV dec}^{-1}$) and P-C ($163.2 \text{ mV dec}^{-1}$), suggesting the fastest kinetics of NP-C. Additionally, the electrochemical active surface area (ECSA) was evaluated by measuring the double-layer capacitance (C_{dl}), which was derived from the cyclic voltammogram (CV) at a series of scan rates. Although NP-C shows a lower ECSA than P-C (Fig. S11), it still display the highest ECSA-normalized current density (Table S2), suggesting the active sites on NP-C have a higher intrinsic activity to CDRR than that on the single-doped N-C and P-C, which could partially explain the superior CDRR on NP-C than that on the single-doped P-C and N-C as well as undoped C. The higher intrinsic activity of active sites on NP-C might be derived from the co-doping of N and P hetero-atoms, which was in agreement with the previous reports [40–42]. Because the active site and mechanism were very similar to previous studies [42], the focus of this study was the feasibility of the device, and there was no further in-depth study of the mechanism. Moreover, the low ECSA of N-C can par-

Figure 2 Electrochemical tests of CDRR and ORR n on NP-C, P-C, N-C and pure C catalysts in neutral solution. (a) LSV curves in 0.1 mol L⁻¹ KHCO₃ saturated with CO₂ and Ar. Scan rate: 10 mV s⁻¹. (b) The partial current density of CO (j_{CO}) and (c) FE_{CO} by potentiostatic electrolysis at several applied potentials. (d) Tafel slope of the CDRR. (e) ORR LSV curves of NP-C, Pt/C, P-C, N-C and pure C in 0.1 mol L⁻¹ PBS saturated with O₂. Scan rate: 50 mV s⁻¹. (f) LSV curves of NP-C at different speeds (inset: K-L diagram of NP-C at 0.2, 0.3 and 0.4 V).

tially explain its poor performance compared with the reported nitrogen-doped carbon-based materials [40,43]. After 10-h continuous electrolysis, the CDRR retained half of the initial current density while the FE_{CO} decayed by 20% (Fig. S12), possibly due to the loss of active sites on NP-C. Therefore, NP-C has higher activity and stability of CDRR, and can be an advanced metal-free carbon-based electrocatalyst.

The LSV of the ORR was measured at 1600 rpm on a RDE in the O₂-saturated 0.1 mol L⁻¹ PBS solution to study the ORR performance. As shown in Fig. 2e, the initial potential of NP-C was 0.84 V, which was comparable to commercial Pt/C (0.85 V), and significantly higher than that of P-C (0.76 V), N-C (0.61 V) and pure C (0.64 V). The Koutecky-Levich (K-L) plots of NP-C (Fig. 2f) exhibited good linearity with a mean electron

transfer number (n) of 4.0, indicating that the ORR on NP-C was close to the four-electron transfer process. As a comparison, the K-L plots of Pt/C (Fig. S13), P-C (Fig. S14), N-C (Fig. S15) and pure C (Fig. S16) were also measured and displayed lower or comparable n of 3.9, 3.8, 3.6 and 3.7, respectively. The above results suggest that the NP-C catalyst exhibits higher electrocatalytic ORR performance than the P-C, N-C and pure C catalysts and it is comparable to the commercial Pt/C catalyst. The higher ORR electrocatalytic activity of the co-doped NP-C catalyst than that of the single-doped P-C and N-C could be ascribed to the synergic effect of the N and P doping, which is consistent with the reported literatures [44–46]. Therefore, NP-C is an excellent dual-functional electrocatalyst for the CDRR/ORR, which can well meet the catalyst requirements of the MFC-MEC coupling system.

MFC testing

The single-chamber MFC was tested under optimal conditions using NP-C as the air-cathode catalyst (Fig. S17). After one week of incubation and adaptation, a stable and repeatable peak voltage of 0.650 V for MFC (cathode potential of 0.195 V and anode potential of -0.455 V) was produced on a $1000\ \Omega$ resistor, which lasted for 20 h in each cycle (Fig. S17). As shown in Fig. 3a, the anode potential in the MFC was kept at almost the same value under different resistances, and the cathode potential gradually became negative as the resistance decreased. Fig. 3b shows that the NP-C has an open circuit voltage of 790 mV and a maximum power density of $2021\ \text{mW m}^{-2}$. The polarization and power density curves indicate that MFC with NP-C as the cathode shows a high activity, comparable to those with the reported advanced metal-free carbon-based catalyst

cathodes (Table S3).

MFC-MEC coupling system testing

Based on the successful operation of MFC with NP-C catalyst cathode, the MFC-MEC coupling system could be built by linking MEC and MFC with wire (Fig. S18). The syngas formation from the MFC-MEC coupling system was tested by adjusting the resistance. As shown in Fig. 4a, the circuit current density decreased as the load resistance increased. When the resistance increased from $10\ \Omega$ to $2\ \text{k}\Omega$, the current density decreased from -0.21 to $-0.04\ \text{mA cm}^{-2}$ and the cathode potential decreased from -0.366 to -0.285 V. Meanwhile, syngas production at different cathode potential was analyzed (Fig. 4b). When the load resistance was $10\ \Omega$, the FEs of CO and H_2 were 43% and 57%, respectively. Moreover, as the load resistance increased, the FE_{CO} decreased, while the FE_{H_2} accounted for a higher proportion. Furthermore, another electrically assisted MFC unit was introduced in series in the coupling system to investigate the performance variation of the coupling system performance at increased electric power [9,12]. As shown in Fig. S19, at the loading resistance of $10\ \Omega$, the current density at the cathode of the MEC reached $-0.52\ \text{mA cm}^{-2}$, and the FEs of CO and H_2 were 60% and 40%, respectively. Similarly, as the loading resistance increased, the FE_{CO} decreased and the FE_{H_2} increased. Therefore, with NP-C as the biocompatible bifunctional electrocatalyst, we successfully built a novel MFC-MEC coupling system (Fig. S18) with tunable syngas product by adjusting the load resistance, and the CO/ H_2 ratio in the syngas was suitable for the typical range of syngas ratios (CO/ H_2 , 0.23–2.26) in a thermal catalytic reaction. This study provides a potential electrochemical strategy for the spontaneous production of syngas through microbial systems in biogas digesters, as

Figure 3 (a) Anode and cathode potentials of the MFC. (b) The polarization and power density curves of MFC using NP-C as the air cathode catalyst.

Figure 4 (a) Cathode potential and circuit current density of the MFC-MEC coupled system under different load resistances. (b) Faradaic efficiency of CO and H₂ in the MFC-MEC coupling system at different cathode potentials.

Figure 5 Conceptual diagram toward spontaneous production of syngas by electrochemical strategy in biogas digesters.

shown in Fig. 5.

CONCLUSIONS

In summary, we designed and prepared a biocompatible metal-free N/P-co-doped carbon catalyst *via* facile one-pot pyrolysis of cellulose mixed with urea and phytic acid. The NP-C is an excellent bifunctional electrocatalyst for the CDRR/ORR. For the CDRR, the NP-C catalyst achieved 81% FE_{CO} at -0.59 V vs. RHE, while in the ORR, its performance (initial potential of 0.84 V) was comparable to commercial 20% Pt/C (initial potential of

0.85 V) under the neutral condition. Meanwhile, when NP-C was used as the air cathode, the MFC can generate an open circuit voltage of 790 mV and a maximum power density of 2021 mW m⁻². Based on the MFC-MEC coupling system, the NP-C exhibits excellent performance in the production of syngas without external power supply. When the load resistance was 10 Ω, the current density at the cathode of the MEC reached -0.52 mA cm⁻², and the FEs of CO and H₂ were 60% and 40%, respectively. By adjusting the load resistance, the CO/H₂ ratio was suitable for the typical range of syngas ratios (CO/H₂, 0.23–2.26) in a typical thermal catalytic reaction.

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Supplementary information Supporting data are available in the online version of the paper.

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基于生物相容性双功能无金属电催化剂的MFC-MEC耦合系统自发产生合成气

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摘要 通过二氧化碳的电化学还原来制备高价值的燃料和化学品对二氧化碳的良性循环具有重要意义。然而,由于二氧化碳电化学反应过程中的高过电势,导致驱动该还原反应需要高功耗和高成本贵金属催化剂。在本文中,电化学二氧化碳还原反应是在微生物燃料电池-微生物电解池(MFC-MEC)耦合系统中具有生物相容性的无金属氮磷共掺杂碳基材料上实现的。基于MFC中的生物电化学提供能量以驱动MEC中的电催化作用,无需任何外部能量输入,就可以从该耦合体系中自发产生合成气。在MFC-MEC耦合体系中,对于二氧化碳还原反应和氧还原反应,NP-C材料是一种优良的双功能电催化剂。当负载电阻为10 Ω 时,MEC阴极的电流密度可达 -0.52 mA cm^{-2} ,CO和H₂的法拉第效率分别为60%和40%。此外,可以通过调节负载电阻来改变CO/H₂产物比,可满足进一步反应中对于合成气使用的各种需求。这项工作为通过沼气池中的微生物系统自发产生合成气提供了一种新的电化学策略。