Bimetal-organic framework-derived carbon nanocubes with 3D hierarchical pores as highly efficient oxygen reduction reaction electrocatalysts for microbial fuel cells

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ABSTRACT Noble metal-free and highly efficient electrocatalytic materials with hierarchically porous structures continue to be studied for the oxygen reduction reaction (ORR) in microbial fuel cells (MFCs). We report bimetal-organic framework (bi-MOF)-derived nanocubic Swiss cheese-like carbons with a novel three-dimensional hierarchically porous structure (3D Co-N-C) prepared by utilizing cetyltrimethylammonium bromide (CTAB) as a structure-directing agent to control the formation of a nanocubic skeleton, and silica spheres as a template to form a mesoporous structure. The elemental composition and chemical morphology of this material can be tuned through the Zn/Co ratio to optimize its ORR catalytic activity. The optimized 3D Co-N-C displays excellent ORR catalytic performance (half-wave potential as high as 0.754 V vs. reversible hydrogen electrode and diffusion-limiting current density of 5.576 mA cm⁻²) in 0.01 mol L⁻¹ phosphate-buffered saline (PBS electrolyte), showing it can compete with the commercial 20 wt% Pt/C catalysts. The catalytic capability and long-term durability of 3D Co-N-C as an air-filled cathode electrocatalyst in an MFC device are tested, showing that the 3D CoNC-MFC can reach a high power density of 1257 mW m⁻² and provide a competitive voltage during a periodic feeding operation for 192 h; these values are much higher than those of the Pt/C-MFC.

Keywords: Co-N-doped carbon, structure-oriented approach, 3D hierarchically porous nanocubes, oxygen reduction reaction, microbial fuel cells

INTRODUCTION

Microbial fuel cells (MFCs), as a new type of electrochemical energy conversion system, are widely praised as an up-and-coming candidate for replacing traditional fossil energy and have promising application prospects in energy recovery from factory wastewater, biomass energy, and marine sediment [1–4]. In particular, MFCs use active bacteria that decompose carbohydrates as the anode electrode to release electrons, while the oxygen on the cathode is reduced by electrons to generate electricity [5–7]. At present, the oxygen reduction reaction (ORR) performance on the MFC cathode has become the main limiting factor in the further improvement of this technology due to its high overpotential and slow reaction kinetics. Platinum (Pt)-based electrocatalysts have long been counted as the most suitable catalysts for the ORR. Nonetheless, the poor durability, high cost, and scarce reserves of Pt resources have become obstacles to the amplification and commercialization of MFCs [8,9], thereby promoting a surge of research on inexpensive nonnoble metal catalysts with comparable activity and long-term durability.

Transition metal- and nitrogen-doped carbon (Me-N-C) materials, as a promising electrocatalyst for the ORR, have been widely investigated as prospective substitutes for Pt-free electrocatalysts on account of their relatively low price, superior electrocatalytic performance, environmental friendliness, and distinguished durability [10,11]. Moreover, this research field has undergone considerable foundational work, which has been widely

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recognized [12–18]. Metal-organic frameworks (MOFs), as a novel type of porous crystal material assembled by the coordination bond self-assembly of inorganic metal ions/clusters and organic ligands, are universally taken as precursors of Me-N-C electrocatalysts [19,20]. These derivatives show excellent catalytic performance with regard to ORR catalytic activity because they have various structures with a high specific surface area, a stable microcellular structure, and the unique properties of functional groups on the ligands to expose more active area. However, current research on the Me-N-C of MOF derivatives is hindered, and the reasons are summarized [21–24] as follows. (i) The lack of precise control of the composition and structure of the catalyst leads to uneven numbers of active sites, insufficient exposure, and microstructural agglomeration, which often limits the effective mass and electron transfer [25]. (ii) Most of the Me-N-C materials derived from MOFs possess a lower density than Pt-based precious metal materials, increasing the occupied volume and the thickness of the electrode film; this structure affects the enrichment and diffusion of specific gas molecules and effectively hinders mass transfer. (iii) It is necessary to simultaneously explore and optimize these materials in different harsh environments, such as in acidic, neutral, and alkaline electrolytes. Therefore, there is an urgent need to explore a new type of porous carbon, in which the elemental composition and structure can be precisely adjusted, while also being able to be widely used under various harsh conditions [26–30].

The inspiration of science often comes from life. Based on attention to food in daily life, some cheeses possess a loose and porous shape, which inspired us to consider making MOF-derived materials with porous structures that look like Swiss cheese. Herein, we report an MOF-derived Swiss cheese-like carbon with a novel three-dimensional hierarchically porous nanocubic framework (3D Co-N-C) by the self-adjusted thermal decomposition of Co/Zn bi-MOFs, in which cetyltrimethylammonium bromide (CTAB) acts as a structure-orienting surfactant to control the formation of a cubic skeleton, and silica spheres act as a template to form a hierarchically porous structure. 3D Co-N-C possesses unique structural advantages of an interconnected network of hierarchical pores, a high specific surface area, excellent electronic conduction, and evenly dispersed Co/N/C species [31–35]. Hierarchically porous materials can not only provide multidimensional electron transport pathways, shorter diffusion paths, and transport channels, but also provide an abundance of active sites for catalyzing the

ORR. The above structure and characteristics exhibit superb ORR catalytic performance, long-term durability, and methanol resistance, making 3D Co-N-C competitive with commercial 20 wt% Pt/C catalysts in alkaline, neutral, and acidic electrolytes. Moreover, these novel catalysts are assembled into an air-filled cathode of an MFC apparatus (CoNC-MFC) as a diffusion electrode, and the high performance of the MFC device is verified with a maximum output power density up to 1257 mW m^{-2} . Furthermore, the CoNC-MFC has excellent durability and can stably run for more than 192 h.

EXPERIMENTAL SECTION

Synthesis of the $\text{Zn}(100-x)\text{Co}_x(\text{MeIM})@\text{SiO}_2$ nanocubes

Nitrogen-doped carbons with 3D hierarchically porous nanocubes were prepared by hard template casting and structure-oriented self-assembly. In general, 30 mg of CTAB was dispersed in 60 mL of aqueous solution containing 6 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or a mixture of both with stirring to obtain a homogeneous colloidal solution. This solution was subsequently mixed with 210 mL of aqueous solution containing 27.24 g of 2-methylimidazole (MeIM) and 0.5 g of silicon dioxide (SiO_2) nanospheres (particle size of approximately 15 nm) by vigorous stirring for 30 min. This homogeneous colloidal mixture was separated by centrifugation, washed thoroughly at least six times and fully dried for 12 h at 80°C to obtain $\text{Zn}(100-x)\text{Co}_x(\text{MeIM})@\text{SiO}_2$, wherein x ($x = 0, 5, 10, 20, 50, 100$) represents the molar fraction of Co ions. For comparison purposes, a powder sample was prepared with a similar synthesis process and composition, except that SiO_2 nanospheres were not included; this sample was denoted as $\text{Zn90Co10}(\text{MeIM})$.

Synthesis of the Mes-C-N- $\text{Zn}(100-x)\text{Co}_x$ and Mic-C-N- Zn90Co10 Swiss cheese-like nanocubes

The powders of the prepared structures dominated by mesoporous nanocubes (Mes-C-N- $\text{Zn}(100-x)\text{Co}_x(\text{MeIM})$) and micropore nanocubes (Mic- $\text{Zn90Co10}(\text{MeIM})$) were annealed at 850°C for 2 h at a heating speed of 5°C min^{-1} in a N_2 -filled atmosphere, and the product was further etched with a 10 wt% solution of hydrofluoric acid (HF) for 3 h to eliminate the nanosilica template and yield 3D Mes-Co-N-C porous electrocatalysts. All of the above-obtained products were denoted as Mes-C-N- $\text{Zn}(100-x)\text{Co}_x$, while the sample without the SiO_2 template was labeled Mic-C-N- Zn90Co10 as a reference substance.

Characterization of materials

X-ray diffraction (XRD, BRUKER AXS GMBH, D8 Advance) measurements were recorded on a D/MAX-RB X-ray diffractometer by using a Cu K α radiation source. The microstructure of the prepared materials was characterized by scanning electron microscopy (SEM, Zeiss Ultra Plus), transmission electron microscopy (TEM, JEOL JEM-2100F), and energy dispersive spectroscopy (EDS, JEM 2100F). The valence state and content of each element were characterized by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000X-spectrometer PHI 5000 Versa Probe ULVAC). The N₂ adsorption-desorption isotherms were subjected to a vacuum at 150°C for 10 h in a nitrogen atmosphere using a Micromeritics Tristar II 3020 analyzer to calculate the specific surface area and pore size distribution.

Electrochemical ORR measurements

The electrochemical tests were accomplished by a CHI 660E electrochemical workstation with a standard three-electrode system consisting of an ORR catalyst-loaded rotating disc electrode (RDE), platinum substrate, and reversible hydrogen electrode. Before adequately manufacturing the working electrode, the ink containing the electrocatalyst, composed of the catalyst sample (5.0 mg), deionized water (100 μ L), a 5 wt% Nafion[®] solution (20 μ L), and isopropanol (900 μ L), was ultrasonically treated for at least 30 min, dropwise added on a glassy carbon electrode (loading of 0.5 mg cm⁻²) and dried naturally. Linear sweep voltammetry (LSV) experiments were accomplished in the potential range of 0.2–1.2 V at a sweep speed of 10 mV s⁻¹; additionally, different speeds were used in 0.01 mol L⁻¹ N₂/O₂-saturated phosphate-buffered saline (PBS) electrolyte (pH 7.0), 0.1 mol L⁻¹ HClO₄, and 0.1 mol L⁻¹ KOH. The long-term durability was obtained by appraising the amperage current vs. time (*i*-*t* method) curve at a voltage of 0.6 V. The durability of the sample toward methanol was also tested by the *i*-*t* method, except that 3 mol of methanol was added at the appropriate time point (400 s).

The electron transfer number (*n*) can be calculated by the Koutecky-Levich (K-L) equation:

$$1/j = 1/j_L + 1/j_k = 1/(B\omega^{1/2}) + 1/j_k,$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6},$$

where *j*, *j_k*, and *j_L* represent the measured current density and the kinetic- and diffusion-limiting current densities, respectively; ω and *n* represent the rotational speed and electron transfer number, respectively; *F* represents the

Faraday constant (96,485 C mol⁻¹); *C₀* is the bulk concentration of oxygen (1.2 $\times 10^{-6}$ mol cm⁻³); *D₀* is the diffusion coefficient of oxygen in 0.01 mol L⁻¹ PBS electrolyte (1.9 $\times 10^{-5}$ cm² s⁻¹); and ν stands for the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹).

MFC test

The application of the 3D Co-N-C nanocubes in MFCs is an indicator of their potential industrialization. Taking a Pt/C-MFC as a contrast, the electrocatalytic performance of 3D hierarchically porous Co-N-C in an MFC (3D CoNC-MFC) was examined with an air-filled cathode. In this case, the carbon cloth purchased from Fuel Cell Earth (AvCarb 1071 HCB) was used as the anode, while the air cathode was carbon paper (area of 16 cm²) loaded with the catalyst (0.5 mg cm⁻²). The 3D Co-N-C nanocube catalyst or Pt/C catalyst was added to 100 μ L of isopropanol and 7 μ L mg⁻¹ 15% Nafion[®] from DuPont to make a catalyst slurry that was subsequently dropwise added onto the air cathode. After the synthesized air cathode was dried for 24 h, a membrane electrode was formed by hot pressing on the surface of the proton exchange membrane. Regarding the MFC test experiments, 1 mL of mature *Escherichia coli* K-12 strain was injected into 10 mL of anolyte (0.01 mol L⁻¹ PBS, 5 $\times 10^{-3}$ mol L⁻¹ 2-hydroxy-1,4-naphthoquinone (HNQ), 5 g L⁻¹ glucose, and 5 g L⁻¹ yeast extract). HNQ was chosen as the mediator mainly because it has a high Coulomb output and can boost the electron shuttle transport [36,37]. The battery voltage vs. time (*V*-*t*) curve of the MFCs was recorded by a voltage collector (Agilent, 34901A), in which the external load resistance was 1000 Ω . After the membrane electrode was immersed for at least 6 h to stabilize it, the polarization curve and power output of the MFC were tested. The MFC durability tests were performed separately for 192 h.

RESULTS AND DISCUSSION

Nanocubic Co-Zn-N-C electrocatalysts with 3D hierarchically porous structures were synthesized by hard template casting and structure-oriented self-assembly combined with annealing in a nitrogen atmosphere, as shown in Fig. 1a. First, Zn_xCo(100-*x*)(MeIM)@SiO₂ was generated by a coordination reaction with cobalt and zinc nitrate as the coordination metal source, MeIM as the carbon source, CTAB as the surfactant and SiO₂ microspheres as templates under water system conditions. Next, the Co-Zn-N-C@SiO₂ carbon material was formed by annealing Zn_xCo(100-*x*)(MeIM)@SiO₂ at 850°C for 2 h in a N₂-filled atmosphere.

Figure 1 (a) Diagram showing the synthesis of the 3D hierarchically porous Co-N-C skeleton; (b) XRD patterns of Zn(100- x)Co(x)MeIM@SiO₂ (x = 0, 5, 10, 20, 50, 100), Zn90Co10(MeIM), simulated ZIF-8 and ZIF-67; (c) XRD patterns of Mes-C-N-Zn(100- x)Co(x) (x = 0, 5, 10, 20, 50, 100) and Mic-C-N-Zn90Co10.

Finally, hierarchically porous Co-Zn-N-C nanocubic Swiss cheese-like carbon was fabricated through etching with 10 wt% HF solution. The macrophysical picture of the bi-MOF with a content of 100% zinc is milky white, while the color of the powder turns light blue with the addition of Co (Fig. S1). With an increasing Co content, the blue color becomes obvious, which preliminarily indicates the successful synthesis of bi-MOF. This synthesis method has the following advantages: (1) the synthesis of the cubic MOF of this material is carried out at room temperature instead of under high-temperature and high-pressure hydrothermal synthesis conditions. In addition, the reaction time is short, and the operation is very simple, which is suitable for large-scale mass production. (2) Compared with the toxic, flammable and explosive methanol used in the traditional preparation of ZIF-8, we use environmentally friendly, safe, and inexpensive deionized water as the solvent. The crystal structure of carbonized Zn(100- x)Co(x)MeIM (bi-MOF) was confirmed by XRD, revealing that the typical crystal structure matches well with that of ZIF-8 and ZIF-67 (Fig. 1b). It is worth noting that the peak of the crystal structure becomes increasingly sharper as the Zn content increases. The crystal peak of Zn90Co10(MeIM)@SiO₂ is the sharpest, which illustrates its higher crystallinity and provides favorable conditions for the catalytic reaction. After high-temperature carbonization, these seven samples show diffraction peaks at 26°, corresponding to the carbon (002) diffraction peak in the catalyst material. When 5% cobalt nitrate and 95% zinc nitrate are used, the XRD

pattern only shows the diffraction peak of the above carbon, indicating that when the proportion of cobalt nitrate used in the preparation process is small, no metal particles are present or the content is too low to detect. As the proportion of cobalt nitrate is increased to 10%, Search Match software shows that the diffraction peak of Co (PDF No. 15-0806) appears in the XRD pattern, indicating that Co exists in the form of metallic Co in Mes-C-N-Zn90Co10. As the proportion of cobalt nitrate continues to increase, the prepared samples also have diffraction peaks of metallic Co. In addition, Mic-C-N-Zn90Co10, which uses the same proportion of metal salt without the introduction of SiO₂, is similar to Mes-C-N-Zn90Co10, and the detected Co-containing phase is only metallic Co (Fig. 1c).

The as-obtained Mic-Zn90Co10(MeIM) and Mic-C-N-Zn90Co10 were visualized by using SEM and TEM. The SEM images recorded at high magnification clearly show that Mic-Zn90Co10(MeIM) and Mic-C-N-Zn90Co10 consist of well-defined nanocubic shapes with sizes of approximately 100 nm and are characterized by uniform shapes and flat surfaces, as illustrated in Fig. 2a-d. The above results are completely different from the structure of the ZIF-8/ZIF-67 dodecahedron in previous studies [38,39]. In this reaction system, CTAB not only acts as a surfactant but also an encapsulant. The surface energy and adhesion energy of the long hydrophobic hydrocarbon chain of CTAB interacts differently with the various crystal planes of ZIF-8 crystals. For instance, comparing the (110) and (111) crystal faces, CTAB mo-

Figure 2 Physical characterizations. SEM images: (a, b) Mic-Zn90Co10(MeIM) nanocubes, (c, d) Mic-C-N-Zn90Co10 nanocubes and (e, f) Mes-C-N-Zn90Co10 nanocubes. TEM images: (g) HRTEM and (h) TEM images of the Mes-C-N-Zn90Co10 nanocubes. (i) Elemental mapping of the Mes-C-N-Zn90Co10 nanocubes.

lecules are more inclined to adsorb on the (100) crystal face, thereby suppressing the growth rate of the (100) crystal face; thus, the morphology and particle size of the ZIF crystal change from a rhombic dodecahedron to a cube [40,41]. This theory was also verified by the Material Studio© morphology software package simulation calculation. Furthermore, the cube-structured material created by CTAB has also been widely confirmed and applied [42,43]. The Mes-C-N-Zn90Co10 prepared by the nanocasting method using silica nanospheres as hard templates has a nanocubic structure with a highly porous structure and a pore size of 15 nm, as shown in Fig. 2e, f. The high-resolution picture indicates that the lattice fringes of the Co nanoparticles embedded in the face-centered cubic lattice (111) are 0.20 nm (Fig. 2g). As presented in Fig. 2h, Mes-C-N-Zn90Co10 displays a porous nanocubic structure. The highly dispersed state of C, N, and Co on the nanocube was confirmed by the corresponding elemental mapping in Fig. 2i [44].

To further explore and verify the microscopic hierarchical porosity of the prepared materials formed by SiO₂ as a hard template, the properties of the ZIF-derived carbon were evaluated by nitrogen adsorption/desorption isotherms. The porous Mes-C-N-Zn(100-x)Cox nanocubic catalysts show the type-IV isothermal characteristics of mesoporous materials (Fig. 3a). Mes-C-N-Zn(100-x)Cox exhibits a greater adsorption in the region of $P/P_0 > 0.4$ with a visible hysteresis curve, demonstrating the presence of mesopores [45]. The surface area of the Mes-C-N-Zn(100-x)Cox nanocubes decreases significantly

from 1123.92 to 493.56 m² g⁻¹ with increasing Co content because of the fusion of cobalt species to severe clusters of graphene during carbonization; additionally, as the proportion of zinc decreases, the number of micropores produced by volatilization decreases (Table S1). The evaporation of Zn atoms in the MOF produces a large number of micropores during annealing pyrolysis, so an increase in the content of Zn contributes to expanding the specific surface area and providing more catalytically active sites, which are beneficial for the catalytic reaction. The pore diameter distribution of all samples, which is calculated by the Barrett-Joyner-Halenda (BJH) method, indicates that Mes-C-N-Zn(100-x)Cox has hierarchical micropores-mesopores, while Mic-C-N-Zn90Co10 has an abundance of only micropores in Fig. 3b, which is consistent with the TEM images.

The elemental composition of the near-surface region and the bond energy state in Mes-C-N-Co100, Mes-C-N-Zn90Co10, and Mes-C-N-Zn100 were measured by XPS (Fig. 4). Fig. 4a shows the XPS survey spectra of Mes-C-N-Zn100, Mes-C-N-Co100, and Mes-C-N-Co100, which contain obvious C 1s, N 1s, and O 1s peaks. Fig. 4b shows that Mes-C-N-Zn100 exhibits obvious Zn 2p characteristic peaks, while Mes-C-N-Zn90Co10 has no obvious Zn 2p characteristic peaks. The elemental analysis in Table S2 shows that the Zn content of Mes-C-N-Zn90Co10 is only 0.28%, indicating that the addition of Co lowers the boiling point of Zn and promotes its volatilization. The N 1s XPS spectrum of the three samples show three obvious characteristic peaks with the chemical

Figure 3 (a) N₂ adsorption/desorption isotherms and (b) corresponding pore size distributions of Mes-C-N-Zn(100-*x*)Co_{*x*} and Mic-C-N-Zn90Co10.

Figure 4 XPS survey spectra of the (a) full spectrum; (b) Zn 2p; (c) N 1s; and (d) Co 2p of the Mes-C-N-Zn100, Mes-C-N-Zn90Co10, and Mes-C-N-Co100 catalysts.

binding energies of graphitic-N (401.1 ± 0.3 eV), pyrrolic-N (400.5 ± 0.3 eV), and pyridinic-N (398.5 ± 0.2 eV) [46] (Fig. 4c and Table S3); these peaks demonstrate that there are more active sites that are conducive to charge transfer [47]. As the Co/Zn ratio increases, the N content of the material decreases, and thus the intensity of the N 1s peak

decreases. In addition, we find the presence of Co-N in Mes-C-N-Zn90Co10 and Mes-C-N-Co100, and the coordination sites of the Co and N in the materials act as the electrocatalytic active sites for the ORR. Fig. 4d shows the Co 2p peaks of Mes-C-N-Zn90Co10 and Mes-C-N-Co100, confirming that Mes-C-N-Co100 has a large

proportion of zero-valent Co (778.5 eV), which is consistent with the Co metal present in the XRD results, while Mes-C-N-Zn10Co90 has a low Co peak because excess Co particles do not chemically coordinate with C, N or O, thereby existing independently in Mes-C-N-Co100. In addition, based on the analysis of the Co 2p spectrum of Mes-C-N-Zn90Co10 and the elemental mapping by TEM, the oxidation states of Co and N inside the Mes-C-N-Zn90Co10 material form a ligand and are evenly distributed throughout the carbon material. Coupled with the well-developed hierarchically porous structure, the catalytic active sites can be fully used in the catalytic reaction, which is beneficial to improving the catalytic activity and stability of the material [48].

In this work, the working electrodes, formed by coating Mes-C-N-Zn(100-*x*)Co_x and Mic-C-N-Zn90Co10 on an RDE, were immersed in oxygen-saturated 0.01 mol L⁻¹ PBS electrolyte (pH 7.0), 0.1 mol L⁻¹ HClO₄, and 0.1 mol L⁻¹ KOH, respectively, to appraise the electrocatalytic activity based on the half-wave potentials (labeled $E_{1/2}$) and limiting current densities (labeled J) at 0.2 V vs. RHE of the RDE polarization curves. In particular, the LSV tests of Mes-C-N-Zn_xCo100-*x*, Mic-C-N-Zn90Co10 and Pt/C were correspondingly scanned from high to low voltages.

It is quite clear that Mes-C-N-Zn90Co10, which presents superior ORR catalytic activity ($E_{1/2}$ of 0.754 V, and J of 5.576 mA cm⁻² at 1600 r min⁻¹), is more remarkable than Mic-C-N-Zn90Co10 ($E_{1/2}$ of 0.745 V, and J of 4.705 mA cm⁻²) and Pt/C ($E_{1/2}$ of 0.746 V, J of 5.336 mA cm⁻²) in 0.01 mol L⁻¹ PBS electrolyte (pH 7.0) (Fig. 5a). This result is mainly because compared with Mic-C-N-Zn90Co10, Mes-C-N-Zn90Co10 not only contains a large number of exposed micropores but also possesses a large number of mesopores that promote the mass transfer of oxygen, which is conducive to an increase in the limiting current and promotes the catalysis process. Additionally, Mes-C-N-Zn90Co10 exhibits the best catalytic activity among other carbon-based electrocatalysts with different Co/Zn ratios (Fig. 5d). Furthermore, LSV was performed at speeds of 400, 800, 1200, 1600, and 2000 r min⁻¹ to explore the catalytic performance of the different electrocatalysts (Fig. S2). A highly porous structure is conducive to oxygen transfer, which promotes the performance of the catalyst with regard to the limiting current and potential.

The K-L graph and number of electrons transferred per O₂ molecule (n) were determined and fitted from the LSV curves to more deeply explore the catalytic mechanism of the ORR. The K-L plots of Mes-C-N-Zn(100-*x*)Co_x show

good linearity with analogous parallel fitting lines and first-order reaction kinetics from 0.2 to 0.5 V. The electron transfer number of Mes-C-N-Zn90Co10 ($n = 3.95$) is larger than that of Mic-C-N-Zn90Co10 ($n = 3.89$), showing that the ORR process by Mes-C-N-Zn90Co10 approaches a 4-electron pathway. The calculated Tafel slope of Mes-C-N-Zn90Co10 (65.01 mV dec⁻¹) is smaller than that of Pt/C (65.69 mV dec⁻¹), and the prepared Mic-C-N-Zn90Co10 MOF-derived catalyst (65.09 mV dec⁻¹), indicating that Mes-C-N-Zn90Co10 has better kinetics during the ORR (Fig. S3). Electrochemical impedance spectroscopy was also obtained at 0.75 V. It can be seen from the Nyquist diagram that the charge transfer resistance (R_{ct}) of Mes-C-N-Zn90Co10 is lower than that of other prepared catalysts, confirming that Mes-C-N-Zn90Co10 shows excellent neutral ORR electron transfer performance, as shown in Fig. S4.

To further investigate the application of the porous material in different solution environments, the catalytic performance under alkaline and acidic conditions was tested separately. The ORR performance of the porous material Mes-C-N-Zn90Co10 exhibits an $E_{1/2}$ of 0.774 V and J of 5.554 mA cm⁻² in 0.1 mol L⁻¹ HClO₄ solution, showing relatively high values compared with those of Mic-C-N-Zn90Co10 ($E_{1/2}$ of 0.737 V, and J of 4.971 mA cm⁻²) and Pt/C ($E_{1/2}$ of 0.824 V, and J of 5.256 mA cm⁻²) (Fig. 5b). Similarly, the ORR test was also performed in a 0.1 mol L⁻¹ KOH solution filled with oxygen. The catalytic performance of Mes-C-N-Zn90Co10 ($E_{1/2}$ of 0.882 V, and J of 5.743 mA cm⁻²) is superior to that of Mic-C-N-Zn90Co10 ($E_{1/2}$ of 0.847 V, and J of 5.009 mA cm⁻²) and Pt/C ($E_{1/2}$ of 0.869 V, and J of 5.489 mA cm⁻²) (Fig. 5c). Actually, the ORR electrocatalytic activity of the Mes-C-N-Zn90Co10 in different pH solutions also shows advantages over the other carbon materials reported recently (Tables S4–S6). In addition, methanol resistance tests were carried out. Mes-C-N-Zn90Co10 shows almost no attenuation after methanol injection in a 0.1 mol L⁻¹ HClO₄ solution (Fig. 5e) and 0.1 mol L⁻¹ KOH solution (Fig. 5f), while the electrocatalytic performance of the commercial Pt/C catalyst decreases rapidly after mixing with methanol. Apparently, Mes-C-N-Zn90Co10 shows better methanol resistance performance than Pt/C, demonstrating outstanding catalytic selectivity, which is an important indicator for their application in fuel cells.

The long-term durability of Mes-C-N-Zn90Co10 and Pt/C was evaluated and compared in oxygen-saturated 0.01 mol L⁻¹ PBS electrolyte (pH 7.0) (Fig. 5g), 0.1 mol L⁻¹ HClO₄ (Fig. 5h), and 0.1 mol L⁻¹ KOH

Figure 5 LSV curves of Mes-C-N-Co100, Mic-C-N-Zn90Co10, and commercial Pt/C at 1600 r min⁻¹ in O₂-saturated (a) 0.01 mol L⁻¹ PBS, (b) 0.1 mol L⁻¹ HClO₄, and (c) 0.1 mol L⁻¹ KOH. (d) LSV curves of Mes-C-N-Zn(100-x)Cox at 1600 r min⁻¹ in 0.01 mol L⁻¹ PBS. Methanol resistance curves of Pt/C and Mes-C-N-Zn90Co10 in (e) 0.1 mol L⁻¹ HClO₄ and (f) 0.1 mol L⁻¹ KOH. Durability curves of Pt/C and Mes-C-N-Zn90Co10 in (g) 0.01 mol L⁻¹ PBS, (h) 0.1 mol L⁻¹ HClO₄, and (i) 0.1 mol L⁻¹ KOH.

(Fig. 5i). Mes-C-N-Zn90Co10 possesses excellent long-term stability over a broad pH range. Such high stability may be ascribed to its hierarchical porosity, in which mesopores stabilize the porous carbon structure and expose more pore volume to boost the transport of reactants, intermediates, and products, thereby maintaining a continuous electronic transport pathway for the ORR [49].

Based on the above analysis and discussion, the reason for the excellent catalytic activity of the proposed material is attributed to the following characteristics: (1) Co species can provide more catalytically active sites, while a microporous structure with a large specific surface area can be created by the Zn species. Through the optimization of the Co/Zn ratio, the synergistic effect of these

two elements can fully and evenly disperse the Co and N species on the surface of the catalyst, exposing more active sites and promoting the catalytic reaction. (2) The structural characteristics of microporous-mesoporous hierarchical pores create a short path for oxygen diffusion and ion mass transfer, which can accelerate the diffusion reaction at the gas-liquid-solid interface. (3) Highly graphitized pyridinic-N, graphitic-N, and pyrrolic-N with excellent electrical conductivity can promote electron transfer and accelerate the conversion of chemical energy into electrical energy.

Since the prepared Mes-C-N-Zn90Co10 shows excellent ORR electrocatalytic performance, it was applied as the catalyst in an MFC to further explore the feasibility of its industrial application. Therefore, carbon paper

Figure 6 (a) Diagram showing the working principle of MFCs. (b) Polarization curves and discharge power densities of the 3D CoNC-MFC and Pt/C-MFC devices. (c) Voltage trend recorded for 192 h for the MFCs equipped with Mes-C-N-Zn90Co10 and Pt/C. The voltage was recorded across a 1000- Ω resistor.

supported by Mes-C-N-Zn90Co10 (denoted as 3D CoNC-MFC) or Pt/C (denoted as 3D CoNC-MFC) was used as the cathode in a single-chamber MFC device and studied to ascertain the probability of using Mes-C-N-Zn90Co10 as a substitute for Pt/C as the cathode catalyst (Fig. 6). The anode chamber contained a certain amount of *E. coli* to generate electrons by decomposing a glucose solution, while the cathode chamber was filled with air and the catalyst promoting the ORR (Fig. 6a). The maximum discharge watt density of the 3D CoNC-MFC is 1257 mW m^{-2} , which is 17% higher than that of the Pt/C-MFC (1078 mW m^{-2}) (Fig. 6b). This result is consistent with the previous LSV electrochemical performance results, indicating the power generation potential of 3D Mes-C-N-Zn90Co10 as an electrocatalyst. More importantly, the 3D CoNC-MFC shows outstanding durability with the regular feeding of nutrients. Fig. 6c shows that the voltage gradually decreases with the con-

sumption of nutrients in the MFC. After adding fresh anodic nutrient solution, the voltage can quickly recover to the initial value. During periodic feeding operation for 192 h, the voltage of the 3D CoNC-MFC device has no obvious attenuation. The experimental data indicate that compared with Pt/C, Mes-C-N-Zn90Co10 as a cathode catalyst can generate a competitive voltage, showing it has potential application prospects in MFCs that stably operate for a long time. This potential is mainly because micropores contribute to exposing the active areas, and mesopores help O_2 adequately diffuse to the active sites [50–53]. The hierarchically porous framework formed by the combination of micropores and mesopores contributes to enhancing the ORR catalytic activity and MFC-cathode power output performance.

CONCLUSIONS

In summary, a bi-MOF-derived carbon with a novel 3D

hierarchically porous nanocubic Swiss cheese-like structure was successfully synthesized through a simple, novel, and green strategy in a water system. The combination of micropores formed by the high-temperature evaporation of Zn and mesopores formed by the nanocasting of a SiO₂ template promoted the generation of hierarchical pores in the catalyst. Due to its good 3D layered porosity, large specific surface area, and good distribution of the 3D Co-N-C active components, the prepared 3D hierarchically porous catalyst exhibited excellent ORR catalysis in neutral environments and had excellent resistance to methanol, showing significant durability. In addition, we reported Mes-C-N-Zn₉₀Co₁₀ as an air cathode catalyst for MFC devices. Compared with the Pt/C-MFC device (power density of 1078 mW m⁻²), the 3D CoNC-MFC device showed a higher power density (1257 mW m⁻²) and had excellent durability. In short, the 3D porous Co-N-C material with a unique hierarchical pore structure provided a large number of O₂ transport channels and exposed abundant catalytically active sites. The results of this study are not only essential for the industrial production of non-Pt-based ORR catalysts for use in MFC cathodes but also expand an original perspective to invent novel nanomaterials for alternative new energy materials, such as batteries, supercapacitors, and catalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

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

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双金属有机骨架衍生的3D多级孔结构纳米立方碳在微生物燃料电池中的应用

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摘要 多级孔结构的非贵金属高性能催化剂在微生物燃料电池(MFC)氧化还原反应(ORR)中的应用, 是近年来备受关注的话题. 在此, 我们报道了一种在双金属MOFs中衍生出的奶酪状三维多级孔结构立方碳材料. 该材料通过十六烷基三甲基溴化铵(CTAB)作为结构导向剂来控制形成纳米立方骨架, 同时采用二氧化硅微球作模板形成介孔结构, 并通过调节双金属MOFs的Co/Zn比例来优化材料的物理化学性质, 从而提升催化剂的ORR电化学性能. 经过优化的3D Co-N-C在中性 0.01 mol L^{-1} 磷酸盐缓冲液电解质中具有优异的ORR催化性能(相对于可逆氢电极的半波电势高达 0.754 V , 扩散极限电流密度为 5.576 mA cm^{-2}), 可与商用 $20 \text{ wt\% Pt/C}$ 的催化性能相匹敌. 同时, 这种催化剂与Pt/C相比具有更长的寿命. 将三维多级孔材料(3D CoNC-MFC)作为MFC装置中阴极的催化剂, 测试了其功率密度和长期耐用性, 结果表明3D CoNC-MFC能达到 1257 mW m^{-2} 的高功率密度, 并且在 192 h 的常规加料操作下仍然保持较高的电压, 性能远高于Pt/C-MFC.