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Article

3D-ordered macroporous N-doped carbon encapsulating Fe-N alloy derived from a single-source metal-organic framework for superior oxygen reduction reaction

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ABSTRACT

Fe-N compounds with excellent electrocatalytic oxygen reduction activity are considered to be one of the most promising non-precious metal materials for fuel cells. Fe-N compounds with excellent electrocatalytic oxygen reduction activity are considered to be one of the most promising non-precious metal materials for fuel cells, which focuses on the Fe-N₄ single-atom catalysts and the iron nitride materials (such as Fe₂N and Fe₃N). A hybridized catalyst having a hierarchical porous structure with regular macropores could enable the desired mass transfer efficiency in the catalytic process. In this study, we have constructed a new type of hybrid catalyst having iron and iron-nitrogen alloy nanoparticles (Fe-N austenite, termed as Fe-NA) embedded in the three-dimensional ordered macroporous N-doped carbon (3DOM Fe/Fe-NA@NC) by direct pyrolysis of single-source dicyandiamide-based iron metal-organic frameworks. The as-synthesized composites preserve the hierarchical porous carbon framework with ordered macropores and high specific surface area, incorporating the uniformly dispersed iron/iron-nitrogen austenite nanoparticles. Thereby, the striking architectural configuration embedded with highly active catalytic species delivers a superior oxygen reduction activity with a half-wave potential of 0.88 V and a subsequent superior Zn-air battery performance with high open-circuit voltage and continuous stability as compared to those using a commercial 20% Pt/C catalyst.

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1. Introduction

The oxygen reduction reaction (ORR), that occurs at cathode, plays a major role in controlling the performance of advanced renewable energy conversion systems, such as fuel cells and metal-air batteries [1,2]. Until now, platinum-based materials have been recognized as the most efficient and commercially available cathode catalysts. Nevertheless, inadequate

stability and limited resources along with prohibitive cost greatly restrict their further commercialization [3]. To overcome these bottlenecks, remarkable efforts have been undertaken to developing several high-performing and durable non-noble-metal based catalysts [4–7]. The porous carbon matrix-supported Fe-species hybrid catalysts (Fe@C) are of particular concern [8]; especially the state-of-the-art Fe-N@NC hybrid system (NC: nitrogen-doped carbon matrix that inte-

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grate the merits of a conducting matrix and catalytically active heteroatom doping site), such as the Fe-N₄ single-atom species and iron nitride nanoparticles embedded in nitrogen-doped porous carbon materials [9–11], demonstrate excellent ORR catalytic performance due to a synergistic effect between the active Fe-species and N-doped carbon [12]. Nitrogen austenite, which is a type of interstitial Fe-N alloy prepared using a gas nitriding process, exhibits significantly improved hardness and corrosion resistance as compared to the elemental iron [13]. However, studies on the ORR catalytic performance of this iron-nitrogen material have rarely been reported [14]. Additionally, the nitrogen austenite is generally obtained using the alloy of iron at an elevated temperature under ammonia atmosphere; the harsh synthetic condition may be one of the important factors that limit its extensive research [13,14].

To prepare catalysts with a controllable composition and uniform distribution of active sites by pyrolysis of hybrid precursors is a difficult process. Nevertheless, it is gratifying that metal-organic frameworks (MOFs), which are composed of uniformly separated metal nodes and periodic organic linkers, have recently gained extensive interest as the most attractive precursors in the fabrication of the desired carbon-based hybrid materials [15–21]. Moreover, auxiliary cyanamide ligands such as dicyandiamide and melamine are usually used as the N-dopant, which are introduced in the MOF-precursor, due to their N-rich content [22,23]. The formation of Fe-N species is inevitable due to the abundant nitrogen environment surrounding the metal centers at high temperatures, and ammonia is the key for the nitriding reaction of metal [24]. The iron-based MOF, which is a promising single-source precursor that not only promotes the formation of iron nitride but also allows in situ doping of N in the carbon matrix, constructed using the cyanamide-ligand should receive more attention to address the aforementioned issue. The porous materials, with the sole of micropores, demonstrate a high Brunauer-Emmett-Teller (BET) surface area. However, a restricted diffusion process frequently hinders the occurrence of a more powerful activity such as the electrocatalytic ORR, involving three-phase interfaces (solid, liquid, and gas). The porous catalyst having multiscale porosity can improve the mass transfer and accessibility of the active sites in the entire hybrid system. Moreover, a well-ordered internetwork can promote a continuous electronic transmission [25–27]. Therefore, the construction of a hierarchically porous carbon-matrix with evenly permeable macropores is an effective strategy to minimize the impact on the mass transfer process, which can significantly promote the electrocatalytic ORR.

In this study, we constructed a new type of hybrid catalyst having hierarchically three-dimensional ordered macroporous N-doped carbon framework encapsulating iron and iron-nitrogen alloy hybrid nanoparticles (3DOM Fe/Fe-NA@NC), which was easily obtained by the direct pyrolysis of the single-source Fe-MOF precursor (Table S1) under nitrogen atmosphere, avoiding the need for synthesis of the mechanical mixture. Polystyrene spheres (PS) were used as hard templates to manufacture the ordered macroporous Fe-MOF precursor, which was the key to obtain the final inter-

connected macroporous carbon matrix. The distinctive hierarchically ordered macroporous structure not only exposes the active nanoparticles completely but also strengthens the transport channel for successive electronic transmission and mass transfer through the entire reaction system. In the Fe-MOF (Fe(dca)₂pyz, dca is dicyandiamide, pyz is pyrazine) [28], each iron center coordinates with two pyrazine ligands and four N(CN)₂⁻ anions, forming an Fe-N₆ moiety (Fig. 1). The periodically linked N-ligands (dicyandiamide and pyrazine) within the Fe-MOF precursor ensured an even in situ doping of heteroatom (nitrogen) into the resulting carbon matrix during the process of calcination. Owing to the aforesaid advantages, the prepared 3DOM Fe/Fe-NA@NC catalyst exhibited remarkable ORR activity with a half-wave potential of 0.88 V (vs. RHE) and excellent catalytic stability, which were superior to those exhibited by platinum carbon. Furthermore, the Zn-air battery composed of the 3DOM Fe/Fe-NA@NC, which was used as an air cathode catalyst, exhibited a high open-circuit voltage of 1.59 V as well as considerable power density.

2. Experimental

2.1. Materials

In this work, all the chemicals including ferrous sulfate (FeSO₄·7H₂O, 99%), sodium dicyandiamide (Na(dca), 99%), pyrazine (C₄H₄N₂, 99%), styrene (C₈H₈, 99.5%), potassium persulfate (K₂S₂O₈, 99%), polyvinyl pyrrolidone (C₆H₉NO)_n, and commercial Pt/C (Pt 20 wt%) were obtained commercially. They were used directly as received without further purification. All the solvents used were analytical grade.

2.2. Synthesis of polystyrene microspheres

The polystyrene microspheres were synthesized according to a previous study [29]. 50 mL of styrene was separately washed using 30 mL of 10% sodium hydroxide and demonized water to completely remove the polymerization inhibitor. 6 mL of the above treated styrene was then added into a three-necked flask, followed by 50 mL of an aqueous solution containing 0.06 g of PVP. After passing the mixture through nitrogen for 15 min, it was continuously stirred and refluxed at

Fig. 1. Schematic diagram of the process for synthesizing 3DOM Fe/Fe-NA@NC catalyst.

75 °C for 30 min. 5 mL of an aqueous solution containing 0.02 g of $\text{K}_2\text{S}_2\text{O}_8$ was then quickly added into the above mixture and stirred for 24 h. Monodisperse polystyrene microspheres were obtained after centrifugation and dispersion in water and ethanol several times to remove the residues.

2.3. Synthesis of 3DOM PS@Fe(dca)₂pyz

The precursor of 3DOM Fe(dca)₂pyz was synthesized using polystyrene microspheres according to a previous literature report [28]. The prepared polystyrene was added into 100 mL of water and treated with ultrasound for 30 min. 0.96 g of pyrazine and 2.0 g of sodium dicyandiamide were then added and stirred at room temperature for 12 h to form slurry A. Subsequently, 3.5 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 100 mL of hot water (90 °C) to form solution B. The solution B was then slowly added into slurry A, during the stirring. After further stirring at room temperature for 10 h, the precipitate was suction filtered, and washed thoroughly with water and ethanol. It was then vacuum dried at 60 °C to obtain PS@Fe(dca)₂pyz. The PS@Fe(dca)₂pyz obtained was soaked in toluene for 2 days to completely remove the polystyrene and obtain the 3DOM Fe(dca)₂pyz.

2.4. Synthesis of 3DOM Fe/Fe-NA@NC catalysts

The synthesized 3DOM Fe(dca)₂pyz sample was placed in a quartz tube and purged with nitrogen for 30 min. It was then heated from room temperature to 700, 800, and 900 °C at a heating rate of 10 °C min⁻¹ and maintained for 3 h. In order to remove the unstable iron species from the surface of the catalyst, the carbonized samples were treated with 1 M hydrochloric acid, and the samples were then washed several times using deionized water and ethanol until the pH was nearly neutral. The resulting compounds were dried in vacuum at 80 °C for 12 h. The series of samples obtained at different temperatures were termed as 3DOM Fe/Fe-NA@NC-700 (700 °C), 3DOM Fe/Fe-NA@NC-800 (800 °C), and 3DOM Fe/Fe-NA@NC-900 (900 °C).

2.5. Synthesis of Fe/Fe-NA@NC catalyst

The experimental method used was similar to that used for 3DOM Fe/Fe-NA@NC, except that the polystyrene template was not added.

2.6. Synthesis of NC catalyst

The Zn(dca)₂pyz was prepared according to a previous study [28]. The obtained Zn(dca)₂pyz was used as a precursor to manufacture the NC material. The Zn was removed after calcination at 900 °C under N_2 atmosphere, and the resulting black power was termed as NC.

2.7. Characterization

Powder X-ray diffraction (PXRD) patterns of the compounds

were recorded using a D/MAX-3D diffractometer with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). The elements analysis results were obtained using a Thermo Flash EA 1112. X-ray photoelectron spectroscopy (XPS) measurements were obtained using ESCALAB 250 system (Thermo Electron) with an Al K_α (300 W) X-ray resource. FT-IR spectra were measured on the Nexus 870 FT-IR spectrometer using KBr pellets as the sample matrix. Field-emission scanning electron microscopy (FESEM) measurement was carried out using Zeiss Sigma 500. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using the FEI TalosF200S equipment. Raman spectrum was recorded on a LabRam HR Evolution using the 532 nm line of an Ar-ion laser as an excitation source. Nitrogen sorption isotherm was measured at 77 K using an automatic volumetric adsorption equipment (Belsorp Max) after degassing at 80 °C for 12 h. Specific surface areas were obtained using the Brunauer-Emmet-Teller model. The pore size distributions were simulated using the nonlocal density functional theory (NLDFT) model, and the pore volumes were calculated from the amount adsorbed at $P/P_0 = 0.99$.

2.8. Electrochemical measurements

The working electrode was prepared as follows: 2 mg of the catalyst was dispersed in a solution containing 100 μL of DMF and 20 μL of 5 wt% Nafion solution. It was then treated by ultrasound for 30 min to obtain a uniform solution. 8 μL of the above slurry was applied onto a platinum-carbon electrode (5 mm diameter, $S = 0.1962 \text{ cm}^2$) and dried naturally at room temperature. Electrochemical testing was carried out using a typical three-electrode system; Ag/AgCl (saturated) electrode was used as the reference electrode, Pt electrode as the counter electrode, and the working electrode was a glassy carbon electrode (GCE) coated with the above prepared catalyst ink. The cyclic voltammetry (CV) test was performed in a N_2 or O_2 -saturated 0.1 M KOH solution at a scan rate of 50 mV s^{-1} . The linear sweep voltammetry (LSV) test was performed using a rotating disk electrode (RDE) at a scan rate of 5 mV s^{-1} at different rotational speeds (from 400 to 2500 rpm). All potentials were converted to a reversible hydrogen electrode (RHE) using: $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 + 0.059 \times \text{pH}$. The Tafel slopes were calculated based on the corresponding LSV curves (1600 rpm) at low over-potentials, which were obtained by plotting the current density on a logarithmic scale vs the working potential.

The Koutecky-Levich (K-L) plots could be analyzed to determine the electron transfer number (n) at various electrode potentials.

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

$$B = 0.2nF(D_{\text{O}_2})^{2/3}\nu^{-1/6}C_{\text{O}_2} \quad (2)$$

where j is the measured current density; j_k is the kinetic current; ω is the angular velocity of rotating electrode ($\omega = 2\pi N$, N is the linear rotation speed); F is the Faraday constant (96485 C mol^{-1}); D_{O_2} is the diffusion coefficient of O_2 ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$) in

0.1 M KOH electrolyte and the C_{O_2} is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$).

$$n = \frac{4 \times i_d}{i_d + \frac{i_r}{N}} \quad (3),$$

$$HO_2^-(\%) = \frac{200 \times \frac{i_r}{N}}{i_d + \frac{i_r}{N}} \quad (4),$$

where n is the electron transfer number, i_d is the disk current, i_r is the ring current, and N is the current collection efficiency (0.37) of the Pt ring of rotating ring-disk electrode (RRDE).

2.9. Zn-air battery tests

Figure 5(a) displays a schematic diagram of a self-made Zn-air battery. As shown in the figure, the polished Zn plate acts as the anode, the catalysts loaded on the nickel foam are used as the air cathode, and the 6 M KOH with 0.2 M zinc acetate solution acts as the electrolyte. As described in the electrochemical measurement section, the catalyst ink prepared above was evenly coated onto the nickel foam, and the catalyst load was 2.5 mg cm^{-2} .

3. Results and discussion

Figure 1 depicts a schematic diagram of the process for synthesizing the 3DOM Fe/Fe-NA@NC catalyst. In this method, the structure of the dicyanamide-based Fe-MOF is crucial for the successful formation of the desired hybrid carbon-based materials. The mixed ligands (pyrazine and sodium dicyandiamide) could simultaneously coordinate with iron and rapidly nucleate to form crystal particles in the solution. Each iron center is approximately octahedrally coordinated with six nitrogen atoms from four dca ligands and two pyz ligands, leading to the Fe-N₆ moiety [28]. After calcination under different

temperatures, the Fe atoms were reduced to iron nanoparticles. Meanwhile, the ammonia molecules released due to the decomposition of dca ligands were partially alloyed with iron to form the nitrogen-permeable solid solution structure (Fe-N austenite) in which the N atoms occupied the center of the face-centered cubic unit cell. The surrounding nitrogen-rich environment can effectively promote the nitriding reaction during the calcination process. The colloidal PS (Fig. S1) were used as equalized porogen to incorporate the above system, which resulted in the formation of PS@Fe-MOF composites in which the PS were periodically aligned. The PS template was then removed by soaking in toluene to obtain the three-dimensional ordered porous Fe(dca)₂pyz skeleton. The ordered macroporous structure etched by PS was well maintained after calcination at high temperatures. Finally, we obtained the new type of hybrid catalysts having iron-nitrogen alloy nanoparticles embedded in the three-dimensional ordered macroporous N-doped carbon (3DOM Fe/Fe-NA@NC). For comparison, Fe/Fe-NA@NC and NC were also prepared.

The crystallinity of 3DOM Fe(dca)₂pyz was observed using the PXRD technique. As shown in Fig. S2, the PXRD pattern of the as-synthesized 3DOM Fe(dca)₂pyz is well-matched with the pattern simulated from the single-crystal data. The FTIR spectroscopy indicated distinct peaks at 2186 and 920 cm^{-1} , which could be attributed to C≡N and C–N stretching, respectively. As shown in Fig. S3, it can be observed that the initial Fe(dca)₂pyz shows a rod-shaped particle, and after etching with the PS templates, the 3DOM Fe(dca)₂pyz retains the entire morphology along with abundant macropores that are neatly arranged. It is well known that the calcination temperatures significantly influence the final physical/chemical properties of calcined materials, which in turn influence the catalytic performance [30]. Therefore, the 3DOM Fe-MOF precursor was pyrolyzed at various temperatures under an inert atmosphere to fabricate the macroporous hybrid catalysts. The obtained materials were

Fig. 2. (a) Powder XRD patterns of 3DOM Fe/Fe-NA@NC-800 and Fe/Fe-NA@NC-800; (b, c) SEM images of 3DOM Fe/Fe-NA@NC-800; (d) TEM image of 3DOM Fe/Fe-NA@NC-800; (e) HRTEM image of 3DOM Fe/Fe-NA@NC-800; (f) Elemental mapping images of 3DOM Fe/Fe-NA@NC-800 showing the uniform presence of C, N, and Fe.

characterized systematically using diverse techniques. As shown in Fig. 2(a) and Fig. S4, the distinct characteristic broad peak at approximately 26° corresponded to the (002) plane of graphitic carbon [22]. The strong diffractive peaks appearing at 44.8° and 65.2° could be assigned to the (110) and (220) planes of Fe (JCPDS, 87-0722), respectively. Also, the distinct peaks at 43.6° , 50.8° , and 74.6° could be indexed to the (110), (200), and (220) planes of $\text{FeN}_{0.0324}$ austenite (JCPDS, 75-2127), respectively, which indicates the occurrence of in situ nitridation during the carbonization process under N_2 atmosphere.

The morphology of the constructed materials was characterized using SEM and TEM. As shown in Fig. 2(b), Fig. 2(c), and Fig. S5, the carbonized materials show a three-dimensional ordered macroporous framework with a pore size of approximately 240 nm, which is equal to the diameter of the PS template. This indicated the complete replication of the PS template onto the ordered macroporous arrays. Meanwhile, as the adjacent pore walls between the spherical pores are very thin, the penetration of electrolyte into the entire system was facilitated; these are further verified in the TEM images. As shown in Fig. 2(d), a cross-linked macroporous structure is formed in the entire framework, and the iron species are well encapsulated in the graphene-like layers (Fig. S6). The geometric constraints of the graphite layers on the metal nanoparticles could enhance the interface contact between the metal nanoparticles and conductive carbon matrix. More importantly, it could significantly weaken the dissolution and aggregation of the metal nanoparticles during the catalytic process and is expected to improve the catalytic activity and stability [31]. The HRTEM results showed the (110) plane for Fe with an evident lattice spacing of 0.20 nm (Fig. 2(e)), and the (002) facet graphitic carbon was distinct in the calcined material (Fig. S6) [9]. The N-dopant and Fe species of the 3DOM Fe/Fe-NA@NC were

uniformly distributed over the entire architecture owing to the periodic arrangement of the Fe-MOF single precursor (Fig. 2(f) and Fig. S5). The above characterization results indicated that after the pyrolysis of the 3DOM Fe-MOF precursor, the ordered macroporous structure along with the evenly dispersed active sites, including Fe species and N-doping in the carbon matrix, was well preserved.

The Brunauer-Emmett-Teller surface area and porosities of the as-prepared materials were investigated using N_2 adsorption isotherms at 77 K. As shown in Fig. 3(a) and Fig. S7(a), all the 3DOM Fe/Fe-NA@NC samples demonstrate the characteristics of type I and IV isotherms with an evident uptake in the low partial-pressure region and hysteresis loops at the relatively high-pressure region [32]. Furthermore, the pore size distribution analyzed using the NLDFT method showed the hierarchical porous structure with the coexistence of micro-, meso-, and macropores. The macropores having a size of 100 nm in the 3DOM Fe/Fe-NA@NC could be attributed to the interspersing between two adjacent macropores (Fig. 3(b) and Fig. S7(b)) [29]. Except for the macropores, the similar micro- and mesoporous feature exhibits in the Fe/Fe-NA@NC material obtained by the pyrolysis of bulk Fe-MOF precursor at the same condition, which indicated that the three-dimensional ordered macroporous structure did not affect the formation of the inherent porous structure. Furthermore, the regular macroporous structure exposed the internal space completely, which was conducive to the heat penetration and mass transfer during the high-temperature calcination process. Moreover, it could promote the production of more mesopores as compared to the nonporous Fe-MOF precursor (Fig. 3(b)). This was also confirmed by the value of total pore volume. 3DOM Fe/Fe-NA@NC-800 exhibited a total pore volume of $1.64 \text{ cm}^3 \text{ g}^{-1}$, which was much higher than that of Fe/Fe-NA@NC-800

Fig. 3. (a) N_2 adsorption-desorption curves of Fe/Fe-NA@NC-800 and 3DOM Fe/Fe-NA@NC-800; (b) Corresponding pore size distribution curves; (c) Raman spectra of Fe/Fe-NA@NC-800 and 3DOM Fe/Fe-NA@NC-800; (d) High-resolution XPS profile of N 1s for 3DOM Fe/Fe-NA@NC-800; (e) N content for different materials; (f) High-resolution XPS profile of Fe 2p for 3DOM Fe/Fe-NA@NC-800.

($0.80 \text{ cm}^3 \text{ g}^{-1}$). The porous characteristic of the final hybrid carbon-based materials was significantly affected by the different pyrolysis temperatures. A relatively low carbonization temperature gave a smaller specific surface area value ($246.23 \text{ m}^2 \text{ g}^{-1}$) for 3DOM Fe/Fe-NA@NC-700. A high carbonization temperature was favorable for the formation of a porous structures (Table S2). Figure 3(c) shows the Raman spectra of Fe/Fe-NA@NC-800 and 3DOM Fe/Fe-NA@NC-800. The small peak that appears at approximately 2700 cm^{-1} belongs to a 2D-band. The evident signals at 1587 cm^{-1} (G-band) and 1352 cm^{-1} (D-band) are attributed to the E_{2g} vibrational mode of the C–C stretching and A_{1g} vibrational mode, respectively [33,34]. The former represents the graphitized degree and the latter reflects the existence of structural defects. Hence, the ratio of I_D/I_G can intuitively reflect the degree of defects in the porous carbon-based materials. As shown in Fig. 3(c) and Fig. S8, higher calcined temperatures will induce higher number of defects in the final material. 3DOM Fe/Fe-NA@NC-800 exhibits a higher I_D/I_G ratio of 1.10 as compared to Fe/Fe-NA@NC-800 ($I_D/I_G = 0.99$). This resulted in more defects in the porous carbon matrix, which may be due to the regular macroporous structure that can promote complete pyrolysis under high temperatures. Consequently, the 3DOM Fe/Fe-NA@NC-800 catalyst having a hierarchical porous structure and high specific surface area could effectively promote the mass transfer of molecular species such as O_2 , OH^- , and H_2O , which is extremely beneficial for the ORR [35].

The surface composition and chemical composition of the prepared 3DOM Fe/Fe-NA@NC hybrids were analyzed using XPS. The results indicated the existence of N, C, O, and Fe elements, with no other impurities (Fig. S9(a)). The O mainly stemmed from the partial surface oxidation of the catalyst due to air exposure. The high-resolution XPS profile of C 1s was fitted into three peaks. The main peak at 284.6 eV corresponded to C=C, while the C=N occurring at 285.4 eV verified the N-doping in the carbon matrix, and the peak at 288.8 eV can be assigned to C=O (Fig. S9(b) and Fig. S10) [36,37]. The high-resolution N 1s spectrum indicated the coexistence of three types of N species, which correspond to pyridinic-N (398.3 eV), pyrrolic-N (400.4 eV), and graphitic-N (401.5 eV) (Fig. 3(d) and Fig. S10) [38]. Different kinds of nitrogen species have different effects on the electrocatalytic ORR performance of the nitrogen-doped carbon materials. The pyridinic-N and pyrrolic-N have lone pair electrons in the aromatic plane, which might coordinate with the metal ions to form Fe-N species [26,39]. The presence of Graphitic-N atoms in the carbon lattice can accelerate the transfer of electrons from the carbon electronic bands to the antibonding orbitals of O_2 , which is beneficial for a four-electron ORR reaction [40]. Generally, graphitic-N and pyridinic-N are identified as valid active sites for oxygen reduction [41]. The calcination temperature critically affected the total nitrogen content and the relative content of different nitrogen components in the final materials. Evidently, as the pyrolysis temperature increased, the content of nitrogen decreased (Table S3). Meanwhile, the relative percentage of graphitic-N gradually became higher, and the pyrrolic-N and pyridinic-N exhibited the opposite trend (Fig. 3(e)), which may

be due to the formation of highly graphitized carbon matrix at high temperatures (Fig. 3(c) and Fig. S8). Intriguingly, the N-content tested using the XPS far exceeded the results based on the elemental analysis for each 3DOM Fe/Fe-NA@NC material (Table S3). This may be caused due to the hierarchical porous structure that exposed more nitrogen onto the surface. The high-resolution spectrum of Fe 2p for the 3DOM Fe/Fe-NA@NC and Fe/Fe-NA@NC-800 are analyzed in Fig. 3(f) and Fig. S10, showing the valence of Fe. The main peaks at 720.5 and 707.2 eV are assigned to $\text{Fe}^0 2p_{1/2}$ and $\text{Fe}^0 2p_{3/2}$ (metallic iron), respectively, corresponding to the results of PXRD (Fig. 2(a)). The peaks at 724.0 and 710.6 eV are ascribed to $\text{Fe}^{2+} 2p_{1/2}$ and $\text{Fe}^{2+} 2p_{3/2}$, respectively [42,43]. The interaction between nitrogen and Fe enhances the electronic properties of carbon and promotes the ORR [44].

The hierarchical porous N-doped carbon framework with ordered macropores, incorporating the uniformly dispersed iron-nitrogen specie, was expected to significantly promote the electrocatalytic oxygen reduction reaction. The ORR performance of prepared materials was measured using cyclic voltammetry and linear sweep voltammetry tests on a rotating disk electrode in an O_2 -saturated 0.1 M aqueous KOH. As shown in Fig. 4(a), the electrochemical response does not notably fluctuate in N_2 -saturated 0.1 M aqueous KOH. In contrast, a significant oxygen reduction peak at 0.75 V (vs. RHE) is observed in the O_2 -saturated 0.1 M aqueous KOH for 3DOM Fe/Fe-NA@NC-800, which indicates its efficient oxygen reduction activity. The LSV polarization curves presented in Fig. 4(b) and Fig. S11 indicate that the 3DOM Fe/Fe-NA@NC and Fe/Fe-NA@NC-800 materials demonstrate excellent electrocatalytic ORR performance. The onset potentials (defined as the potential required for reaching an ORR current density of 0.1 mA cm^{-2}) are 0.98 , 1.00 , 0.99 , and 0.98 V ; the limiting current densities are 5.37 , 5.36 , 5.53 , and 4.79 mA cm^{-2} for 3DOM Fe/Fe-NA@NC-700, 800, 900, and Fe/Fe-NA@NC-800, respectively (Table S4). The distinct peak that appears at 0.8 V for the 3DOM Fe/Fe-NA@NC is probably due to the faster ORR rate than the O_2 diffusion rate. The 3DOM Fe/Fe-NA@NC-800 displays excellent ORR activity, which significantly exceeds that of the Fe/Fe-NA@NC-800 material (Fig. 4(b) and Fig. S15(d)). This demonstrates that the 3D ordered macroporous structure of 3DOM Fe/Fe-NA@NC-800 can maximize the exposure of active Fe/Fe-N sites for enhancing the catalytic activity and promote the efficient mass transfer of O_2 molecules and reduction products. Furthermore, 3DOM Fe/Fe-NA@NC-800 exhibits a superior ORR performance than that of the commercial 20% Pt/C catalyst (positive $E_{1/2}$ potential of 0.03 V and diffusion-limiting current of 0.19 mA cm^{-2}). This also exceeds most of the previously reported iron nitrides and iron-based hybrid catalysts (Table S5). The 3DOM Fe/Fe-NA@NC-800 material exhibits the smallest Tafel slope of 80 mV dec^{-1} , which indicates its excellent kinetics for the ORR due to the hierarchical porous structure with ordered macropores [45].

The RRDE measurement at various rotating speeds was further carried out to reveal the ORR kinetics of 3DOM Fe/Fe-NA@NC, Fe/Fe-NA@NC-800, and 20% Pt/C (Fig. 4(d) and Fig. S12). The LSV curves of all the samples exhibited a

Fig. 4. (a) CV curves of 3DOM Fe/Fe-NA@NC-800 in O_2 and N_2 -saturated 0.1 M KOH; (b) LSV curves of 3DOM Fe/Fe-NA@NC, Fe/Fe-NA@NC and 20% Pt/C in O_2 -saturated 0.1 M KOH at 1600 rpm; (c) Corresponding Tafel slopes; (d) ORR polarization curves at different rotating speeds; inset shows the corresponding K-L plots and electron transfer numbers (n) at different potentials of 3DOM Fe/Fe-NA@NC-800; (e) Electron transfer number n and HO_2^- yield based on RRDE; (f) CV curves measured over 3DOM Fe/Fe-NA@NC-800 modified electrode 10–50 $mV s^{-1}$; inset shows the corresponding scan rate dependence of the current density; (g) Chronoamperometric response; (h) Methanol tolerance for 3DOM Fe/Fe-NA@NC-800 and 20% Pt/C; (i) PXRD patterns of 3DOM Fe/Fe-NA@NC-800 after stability tests.

distinct diffusion-limited current density platform varying from 400 to 2500 rpm, and the corresponding Koutecky-Levich plots exhibited a good linear relationship between J^{-1} versus $\omega^{-1/2}$, suggesting the first-order reaction kinetics for the electrocatalytic ORR. The electron transfer number (n) calculated from the K-L plots is approximately 3.78–3.83 for Fe/Fe-NA@NC and 3.86–4.04 for 3DOM Fe/Fe-NA@NC, indicating a dominant $4e^-$ transfer process. To further verify the excellent ORR performance, all the materials were detected using the RRDE technique. As shown in Fig. 4(e), the electron transfer number of 3DOM Fe/Fe-NA@NC-800 remains above 3.9 within the potential range of 0.2 to 0.8 V, which is slightly higher than that of Fe/Fe-NA@NC-800. Meanwhile, the HO_2^- yield is below 5% for 3DOM Fe/Fe-NA@NC-800 in the same potential range, and the value was lower than that of Fe/Fe-NA@NC-800. The results indicate that 3DOM Fe/Fe-NA@NC-800 demonstrates a higher selectivity of ORR towards the $4e^-$ transfer pathway, which is comparable to that of the 20% Pt/C. The 3DOM Fe/Fe-NA@NC-700 and 3DOM Fe/Fe-NA@NC-900 demonstrate similar catalytic selectivity (Fig. S13). The high ORR performance of 3DOM Fe/Fe-NA@NC could be associated to their

high electrochemical surface area (ECSA) that originated from the three-dimensional order macroporous architecture. As shown in Fig. 4(f) and Fig. S14, the double-layer capacitance (C_{dl}) that is proportional to the ECSA was tested to evaluate the efficient exposure of active sites. The measured C_{dl} values are 4.20, 8.39, and 9.73 $mF cm^{-2}$ for 3DOM Fe/Fe-NA@NC-700, 3DOM Fe/Fe-NA@NC-900, and 3DOM Fe/Fe-NA@NC-800, respectively, which are much larger than that of the bulk Fe/Fe-NA@NC material (1.94 $mF cm^{-2}$). This is one of the factors that could significantly enhance the electrocatalytic ORR activity for 3DOM Fe/Fe-NA@NC hybrid catalyst. Previous studies have indicated that there are two different speculations that describe the active sites in metal/nitrogen-doped carbon hybrid catalysts; one is the energetic sites caused by N-doping in the carbon matrix, and the other is the embedded metal nanoparticles [12,46]. In order to confirm whether the iron species are explicitly involved in the electrocatalytic reaction, the NC (nitrogen-doped carbon that does not contain Fe element) was prepared by a similar method and was tested under the same conditions (Fig. S15). The two PXRD peaks located at 26° and 43° could be assigned to the (002) and (100) crystal plane

of the graphitic carbon, respectively (Fig. S15(a)). It could be seen from the SEM image that NC exhibited a loose porous carbon structure (Fig. S15(b)). The loose NC material demonstrated a higher surface area ($1322.2 \text{ m}^2 \text{ g}^{-1}$) and an abundant microporous structure (Fig. S15(c)), which can expose more catalytic sites during the ORR process, as compared to the case of the Fe/Fe-NA@NC-800. However, the NC material showed a negative shift of half-wave potential (nearly 30 mV) as compared to the Fe/Fe-NA@NC-800 material under the same conditions (Fig. S15(d)), which unambiguously revealed the importance of Fe species (Fe/Fe-N) in the electrocatalytic ORR [26,46].

In addition, stability and durability are also essential for the electrocatalyst to be applied in practical applications. As shown in Fig. 4(g), the relative current of 3DOM Fe/Fe-NA@NC-800 is still maintained at 94% after 20,000 s chronoamperometric measurements in the O_2 -saturated 0.1 M KOH electrolyte, while it drops to 78% for 20% Pt/C catalyst. Meanwhile, methanol tolerance was further investigated under the same condition by injecting 3 mL methanol. As shown in Fig. 4(h), when the methanol is quickly introduced into the system, the current density of 3DOM Fe/Fe-NA@NC-800 exhibits only a slight fluctuation. However, the 20% Pt/C displays a significant current drop, indicating that the 3DOM Fe/Fe-NA@NC-800 hybrid catalyst is extremely resistant to methanol. Furthermore, we characterized the 3DOM Fe/Fe-NA@NC-800 after the stability tests. As shown in Fig. 4(i), the PXRD patterns of Fe species (Fe and Fe-N austenite) match well with those of the original 3DOM Fe/Fe-NA@NC-800, revealing the stability of metal components protected by the carbon shell. The ordered porous architecture of the carbon matrix and the uniform elemental dispersion are well-maintained even after long-duration tests (Fig. S16), demonstrating the superior ORR durability of 3DOM

Fe/Fe-NA@NC-800.

We assembled the 3DOM Fe/Fe-NA@NC-800 catalyst into the Zn-air battery to further evaluate its practical application owing to its exceptional ORR activity (Fig. 5(a)). As shown in Fig. 5(b), the open-circuit voltage (OCV) of the 3DOM Fe/Fe-NA@NC-800-based Zn-air battery is 1.59 V, which is higher than that of 20% Pt/C-based Zn-air battery (1.56 V). Two Zn-air batteries connected in series has the capacity to illuminate red light-emitting diodes (LEDs), demonstrating that 3DOM Fe/Fe-NA@NC-800 has good catalytic performance in practical conditions. Fig. 5(c) depicts the discharging polarization curves and corresponding power density plots. The maximum power density of the 3DOM Fe/Fe-NA@NC-800-based Zn-air battery reaches up to 96.48 mW cm^{-2} with a corresponding current density of $157.75 \text{ mA cm}^{-2}$, which exceeds that of 20% Pt/C catalysts (88.12 mW cm^{-2} at $133.24 \text{ mA cm}^{-2}$). As shown in Fig. S17, the 3DOM Fe/Fe-NA@NC-800 exhibits a lower voltage gap between charging and discharging as compared to the 20% Pt/C catalysts. Especially, the voltage gap is more significant at higher current densities, demonstrating that 3DOM Fe/Fe-NA@NC-800 have better charge-discharge ability. This may be due to the hierarchical porous carbon matrix with permeable macropores that enables rapid mass transfer. Moreover, the charge/discharge cycle stability of Zn-air batteries constructed with 3DOM Fe/Fe-NA@NC-800 and 20% Pt/C at a current density of 5 mA cm^{-2} was further evaluated (Fig. 5(d)). The 3DOM Fe/Fe-NA@NC-800-based Zn-air battery exhibits a lower voltage gap of 0.9 V as compared to the 20% Pt/C catalysts (1.25 V); the original charging and discharging potentials were 2.02 and 1.12 V, respectively. After 40 h of continuous operations, the voltage gap of 20% Pt/C catalyst becomes larger, while the battery performance of the 3DOM Fe/Fe-NA@NC-800 remains fairly excellent throughout the

Fig. 5. (a) Schematic diagram of homemade Zn-air battery; (b) Open-circuit plots of a single battery of the homemade Zn-air battery using 3DOM Fe/Fe-NA@NC-800 and 20% Pt/C as the air cathode, respectively (Left: photograph of the assembled battery using the 3DOM Fe/Fe-NA@NC-800 as the air-cathode with an open-circuit voltage of 1.59 V; Right: red LED powered by two-series batteries); (c) Polarization curves and the corresponding power density curves of the homemade Zn-air batteries constructed with 3DOM Fe/Fe-NA@NC-800 and 20% Pt/C as the air-cathode catalysts, respectively; (d) Long-term cycling tests of the Zn-air battery using 3DOM Fe-N-C-800 and 20% Pt/C as the air cathode at the charging and discharging current density of 5 mA cm^{-2} (10 min for each cycle).

cycles, which is attributed to its superior catalytic activity and stability. The results demonstrate that the 3DOM Fe/Fe-NA@NC-800 catalyst is an efficient and durable catalyst for Zn-air batteries, similar to the recently developed state-of-the-art electrode materials (Table S6).

4. Conclusions

In summary, we constructed a new type of hybrid catalyst having iron-nitrogen alloy nanoparticles embedded in a three-dimensional ordered macroporous N-doped carbon by direct pyrolysis of the single-source dicyandiamide-based Fe-MOFs. The dicyandiamide linker having high nitrogen content enabled the capability for nitridding of iron nanoparticles and simultaneous doping of nitrogen into the carbon matrix of the calcined products. The 3DOM Fe/Fe-NA@NC materials with regular micron-sized macropores, which were obtained by etching the pre-embedded PS template, not only offered sufficient catalytic sites for the ORR but also promoted mass-penetration into the interiors of the entire carbon framework. Owing to the distinctive hierarchical porous carbon framework, the high specific surface area, and the uniformly dispersed iron/iron-nitrogen alloy active sites, the obtained 3DOM Fe/Fe-NA@NC-800 material delivered a superior oxygen reduction activity with a half-wave potential of 0.88 V (vs. RHE) along with catalytic stability and methanol tolerance as compared to the commercial 20% Pt/C catalyst. Especially, the Zn-air batteries based on the 3DOM Fe/Fe-NA-800 catalyst exhibited a high open-circuit voltage of 1.59 V, considerable power density, and excellent durability. This promising discovery pioneered the high catalytic activity of hybrid Fe-N alloy moieties for the electrocatalytic ORR, broadening the scope of

research on efficient Fe-based catalysts. This facile strategy could provide guidance for preparing other electrocatalysts with metal-encapsulated in carbon for energy conversion applications.

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Graphical Abstract

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3D-ordered macroporous N-doped carbon encapsulating Fe-N alloy derived from a single-source metal-organic framework for superior oxygen reduction reaction

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A 3D ordered macroporous N-doped carbon framework encapsulating Fe-N alloy nanoparticles was prepared by direct pyrolysis of dicyandiamide-MOF pre-embedded with polystyrene spheres template. It delivers a remarkable ORR activity and Zn-air battery performance with long-term durability.

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单源MOF衍生具有三维有序大孔结构的氮掺杂碳包覆铁-氮合金复合材料用于高效氧还原

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摘要: 氧还原反应在一些能源转换系统如金属-空气电池中起着至关重要的作用。目前贵金属基材料(Pt/C)被认为是最有效的氧还原电催化剂, 然而价格昂贵和储量有限等因素限制了它的商业化应用, 因此探索高效的非贵金属氧还原电催化剂具有重要的意义。近年来, 负载过渡金属铁的多孔碳催化剂由于独特的结构和优异的氧还原催化活性成为替代铂基催化剂最有潜力的候选者。该类材料的合成通常采用直接煅烧含有氮源、碳源和铁盐的混合前驱体的制备方法, 但是热解时材料的多孔结构以及活性位点的均匀分布很难得到有效的控制。近年来, 金属有机框架(MOFs)由于其多孔结构和组成可控等优点而经常被用作自牺牲模板来制备负载铁基纳米材料的多孔碳催化剂, 并表现出优异的电催化活性。目前以MOF为前驱体制备高活性的载铁氮掺杂碳复合材料通常需要引入额外的氮源或铁源, 因此选择氮含量丰富的铁基MOF材料作为单源前驱体制备载铁氮掺杂多孔碳复合材料具有重要的意义。除此之外, 具有多级孔隙率的催化剂可以改善反应时的传质过程, 同时有序交联的网络结构能够提供连续的电子传输。

本文报道了一种简单可控的制备具有三维有序大孔结构的载铁氮掺杂多孔碳复合催化剂的合成方法, 该材料表现出优异的电催化氧还原性能和优异的催化稳定性。首先, 以氮含量丰富的双氰胺和吡嗪配体所构筑的Fe-MOF作为前驱体, 利用具有均一尺寸的聚苯乙烯微球作为造孔剂, 合成得到了具有三维有序大孔结构的Fe-MOF前驱体, 然后通过高温煅烧该单源前驱体制备得到具有三维有序大孔结构的氮掺杂多孔碳包覆铁-氮合金的复合型催化剂(3DOM Fe/Fe-NA@NC)。

扫描电镜和透射电镜结果表明, 材料内形成了有序交联的大孔结构; 氮气吸附测试表明, 刻蚀之后材料的比表面积明显增加, 结合分级多孔特性可以共同促进催化反应的传质过程。粉末X射线衍射结果证实了多孔碳材料中铁和铁-氮合金物种的成功合成。电化学测试结果表明, 在0.1 M KOH电解液中, 3DOM Fe/Fe-NA@NC-800催化剂表现出优于Pt/C的氧还原活性, 其半波电位($E_{1/2}$)为0.88 V, 大于商业Pt/C的半波电位($E_{1/2} = 0.85$ V)。同时, 3DOM Fe/Fe-NA@NC-800表现出更加优

异的稳定性, 经过20000 s测试后, 其电流保持率为94%, 而Pt/C只保持了78%. 关于活性位点探究的对比实验证明在所制备的复合材料中, 铁物种作为高效的活性位点参与了电催化氧化还原反应, 与氮掺杂多孔碳之间的协同作用共同主导了3DOM Fe/Fe-NA@NC优异的氧还原活性. 得益于其优异的氧还原活性, 将其作为阴极活性材料组装为锌-空气电池进一步探究了其在实际应用中的可行性. 本结果拓宽了高效的铁基催化剂的类型, 同时也为制备封装非贵金属的多孔碳基催化剂提供了实验指导和理论依据.

关键词: 金属有机框架; 单源前驱体; 氧化还原反应; 铁-氮合金

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