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# Fe-N-Doped Hierarchical Mesoporous Carbon Nanomaterials as Efficient Catalysts for Oxygen Reduction in Both Acidic and Alkaline Media

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Fe-based electrocatalysts are known as the one of best options to replace the platinum in the polymer electrolyte membrane fuel cells (PEMFCs) for the future application in small portable or automotive power sources. One key obstacle for the application of Fe-based catalysts is their dissatisfactory activity toward the oxygen reduction reaction (ORR). Here, it is demonstrated that the agglomerate Fe<sub>2</sub>O<sub>3</sub> nanoparticles are capable of improving the performance of Fe-based catalysts. The impacts of the shape, size, and microstructure of Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the ORR activity of Fe-based catalysts are well discussed. All results point out that the Fe<sub>2</sub>O<sub>3</sub> nanoparticles bound by high-index (110) facets might involve in the formation of more active sites for ORR. The best Fe-based catalysts in this study exhibits a superior ORR catalytical activity with the half-wave potential ( $E_{1/2}$ ) only 32 mV negative shifts than that of commercial Pt/C in 0.1 M HClO<sub>4</sub> solution. Based on this catalyst, the peak power density of air-breathing PEMFCs reaches approximately 63% to that of the Pt/C (91 mW cm<sup>-2</sup>) in an air-conditioned room with temperature of 20 °C.

# Introduction

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The emergence of polymer electrolyte membrane fuel cells (PEMFCs) is essential to solve the global energy shortage and environmental pollution problems due to their high energy conversion efficiency and environmentally friendly features.<sup>1,2</sup> However, in practice, the oxygen reduction reaction (ORR) of the cathodic is relatively sluggish, which is a bottleneck for the commercialization of PEMFCs.<sup>3-5</sup> Although Pt or Pt-based catalysts have been recognized as the most efficient catalysts toward ORR, the high cost, low abundance, poor stability, as well as the intolerance to fuel crossover (e.g., methanol, CO, etc.) of Pt/C significantly limit their widespread application, which leads to enormous efforts devoted to investigating alternative cost-effective materials.<sup>6-8</sup> Therefore, rational design of extremely stable non-precious metal (NPM) catalysts with closing or even higher ORR activity than Pt is the core of fuel-cell research.<sup>9-13</sup> During the past decades, transition metalnitrogen-carbon (M-N<sub>x</sub>-C) materials, especially for Fe-N<sub>x</sub>-C, which were generally prepared by heat-treating the Fe source, N source with as-prepared carbon materials, have attracted great interests because of the high reaction activity toward ORR in both alkaline and acidic electrolytes.<sup>14,15</sup> Whereas, due to the poor intrinsic catalytic activity of a single active site, most of the

reported Fe-N<sub>x</sub>-C catalysts (turnover frequency, TOF = 0.4 s<sup>-1</sup>) are generally difficult to achieve better catalytic activity than that of Pt/C (TOF = 25 s<sup>-1</sup>) for ORR in acidic media.<sup>16</sup> Therefore, many efforts should be focused on fabricating the efficient M-N<sub>x</sub>-C catalysts with plenty of active sites and the high surface area.

In this regard, porous carbon materials are of significance for the design and synthesis of high-performance M-N<sub>x</sub>-C catalysts, in which the microporous can create the catalytic active sites and the mesoporous can offer better channels for mass transportation.<sup>17</sup> There are various methods to tune nanostructure of M-N<sub>x</sub>-C catalysts, such as the hard-templating methods, soft-templating methods and liquid phase methods. Although the M-N<sub>x</sub>-C catalysts with silica colloid, ordered mesoporous silica SBA-15 or montmorillonite as template have the well-controlled mesoporous structures and high catalytic performance in acidic media, it is not economic and environment friendly because of the additional methods and the utilization of dangerous hydrofluoric acid or hot alkaline liquor in removing the templates.<sup>18,19</sup> Therefore, searching a facile and effective strategy to synthesize high performance mesoporous M-Nx-C nanomaterials toward ORR is highly desirable.

Covalent triazine frameworks (CTFs) are microporous 1,3,5triazine units conjugated polymers with abundant nitrogen atoms for transition metal coordination, which make them potentially suitable as novel platforms for the synthesis of electrocatalysts.<sup>20-22</sup> In our group, iron-modified CTFs catalysts (Fe-CTFs) with comparable ORR activity to that of commercial Pt/C were successfully prepared by simply one-pot ionothermal polymerization of aromatic nitrile monomers in molten ZnCl<sub>2</sub> containing FeBr<sub>2</sub>.<sup>23</sup> However, the repeatability of our method

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still needs further improvement. One possible explain is that the one-pot ionothermal preparation method cannot ensure the formation of large proportion of highly active sites in Fe-CTFs materials. Therefore, more witty designs require further development of more effective Fe-CTFs catalysts. Recently, the iron-based nanoparticles were proven to play a synergetic role in activating the catalytic activity of ORR.<sup>24,25</sup> One explanation is that Fe/Fe<sub>3</sub>C nanoparticles can potentially promote the activity of the neighboring  $\ensuremath{\mathsf{Fe}}-N_X$  for catalyzing ORR. The roles that ironderived nanoparticles play on the formation of high ORR active sites are not explored, though the theory on the indispensability of iron in the formation of active structures of Fe-based catalysts is well admitted.<sup>26,27</sup> Therefore, it is highly desirable to explore the impacts of iron-derived nanoparticles on the development of Fe-based catalysts, simply utilizing one-pot ionothermal polymerization Fe-CTFs method.



Scheme 1 Illustration of synthetic process.

In this study, we demonstrate a one-pot ionothermal polymerization method to synthesize carbon-encapsulated Fedoped mesoporous carbon nanomaterials, in which the Fe<sub>2</sub>O<sub>3</sub> hollow microspheres (h-Fe<sub>2</sub>O<sub>3</sub>) acted as multifunctional soft template are encapsulated by a CTFs carbon shell (Scheme 1). In order to verify the impacts of parameters of Fe<sub>2</sub>O<sub>3</sub> nanoparticles, Fe<sub>2</sub>O<sub>3</sub> hollow microspheres (h-Fe<sub>2</sub>O<sub>3</sub>), Fe<sub>2</sub>O<sub>3</sub> polyhedrons (p-Fe<sub>2</sub>O<sub>3</sub>) and Fe<sub>2</sub>O<sub>3</sub> nanorods (r-Fe<sub>2</sub>O<sub>3</sub>) with different shape, size, and microstructure were deliberately designed and prepared in this study. The physical and electrochemical properties of these Fe-CTFs catalysts were systematically characterized and discussed.

## Experimental

#### **Materials synthesis**

All reagents are of analytical grade and used without further purification. The anhydrous  $ZnCl_2$ , aromatic nitrile and 20 wt% Pt/C were purchased from Alfa Aesar (China) Chemical Co., Ltd. (Shanghai, China); the *h*-Fe<sub>2</sub>O<sub>3</sub>, *p*-Fe<sub>2</sub>O<sub>3</sub> and *r*-Fe<sub>2</sub>O<sub>3</sub> were prepared according to the reported literature.<sup>28-31</sup> Typically, glycerol (5 mL) is first mixed with deionized water (35 mL) to form a uniform quasi-emulsion, followed by the addition of 120 mg FeSO<sub>4</sub>·7H<sub>2</sub>O with continued vigorously stirring to get a

transparent solution. Then the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave for hydrolysis to get the Fe<sub>2</sub>O<sub>3</sub> hollow microspheres. Fe<sub>2</sub>O<sub>3</sub> hollow microspheres (50 mg), m-Phthalodinitrile (200 mg) and anhydrous ZnCl<sub>2</sub> (1000 mg) were transferred into quartz tubes in a glovebox, then the quartz tubes were evacuated, sealed and heated at 700 °C for 20 h. After cooling to room temperature, this carbon material was washed with 1 M HCl solution to remove ZnCl<sub>2</sub> and possible iron compounds, and then washed with the deionized water and the tetrahydrofuran, dried in a vacuum overnight to get the catalyst. The other catalysts were also prepared via the similar process used p-Fe<sub>2</sub>O<sub>3</sub>, r-Fe<sub>2</sub>O<sub>3</sub> and commercial Fe<sub>2</sub>O<sub>3</sub> nanoparticles to replace the Fe<sub>2</sub>O<sub>3</sub> hollow microspheres respectively.

#### **Materials Characterizations**

The morphologies of these catalysts were characterized by transmission electron microscopy (TEM) and scanning electron microscope (SEM). The TEM images were obtained on a FEI Tecnai F20 electron microscope diffractometer with a copper target ( $\lambda$  = 0.154 nm) and the SEM images were obtained on a Hitachi SU8010 under high vacuum with an acceleration voltage of 5 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB to test the element composition of these samples. The Brunauer-Emmett-Teller (BET) method was performed by the adsorption/desorption of N<sub>2</sub> using the ASAP2020 volumetric adsorption analyzer (Micromeritics, U.S.A.) to determine the specific surface area and the pore size distribution. The structures of all samples were examined by powder X-ray diffraction (XRD) with a MiniFlex-II diffractometer (Rigaku, Japan) using a Cu Ka radiation source. Raman spectra was collected on a Renishaw 2000 with a 532 nm laser excitation.

#### Electrochemical measurements

To evaluate the ORR activity, rotating disk electrode (RDE, disk area: 0.196 cm<sup>2</sup>) and rotating ring-disk electrode (RRDE, disk area: 0.247cm<sup>2</sup>, ring area: 0.1866 cm<sup>2</sup>) were utilized to do the electrochemical tests. In the three-electrode electrochemical cell, a glassy carbon RDE was used as the working electrode, a Pt wire electrode was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. All the potentials mentioned in this text were calibrated to the reversible hydrogen electrode (RHE) potentials according to the Nernst equation ( $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197$ , at 25°C).

In the test, 4 mg as-prepared catalysts were ultrasonically mixed with 785  $\mu$ L ethanol, 200  $\mu$ L deionized water and 38  $\mu$ L Nafion (5 wt.%) to get the electrocatalyst inks. Then, the RDE and RRDE were polished with alumina powder and sonicated with ethanol and deionized water for two minutes respectively, dried at room temperature. The prepared catalyst ink was transferred onto the surface of the working electrode (RDE: 20  $\mu$ L: RRDE: 25  $\mu$ L) with a loading of 0.4 mg cm<sup>-2</sup> and dried at room temperature for 30 min. Meanwhile, the commercial 20 wt%

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Pt/C was also coated onto the RDE and RRDE in the same way with a loading of 20  $\mu g$  Pt  $cm^{\text{-}2}$  for comparison.

All the ORR measurements of prepared catalysts were determined by using a VHI Electrochemical Station (Model 760e) in 0.1 M HClO<sub>4</sub> and 0.1 M KOH solution as the acidic and alkaline electrolyte at room temperature. In the RDE tests, the cyclic voltammetry (CV) measurements were carried out in  $N_2/O_2$ -saturated electrolyte with a scan rate of 10 mV s<sup>-1</sup>. The linear sweep voltammetry (LSV) measurements were performed in electrolyte with a scan rate of 10 mV s<sup>-1</sup> at various rotating speed from 400 to 2500 rpm, and the curve recorded in  $N_2$ -saturated electrolyte was subtracted from the curve recorded in  $O_2$ -saturated electrolyte. The electron transfer number (n) and kinetic current density (J<sub>K</sub>) were calculated from the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$
$$B = 0.62nFC_0 D_0^{2/3} V^{-1/6} \quad (2)$$

Where J is the measured current density;  $J_L$  and  $J_K$  are the limiting and kinetic current density, respectively;  $\omega$  is the rotation rate of electrode; n is the electron transfer number; F is the Faraday constant (96485 C mol<sup>-1</sup>), C<sub>0</sub> is the concentration of oxygen ( $1.2 \times 10^{-6}$  mol cm<sup>-3</sup>); D<sub>0</sub> is the diffusion coefficient of oxygen ( $1.90 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>), and V is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>).

The hydrogen peroxide yield  $(H_2O_2\%)$  and the electron transfer number (n) were implemented by the RRDE, which values were calculated via the following equations:

$$H_2 O_2 = \frac{2I_R}{N|I_D| + I_R} \times 100 \quad (3)$$
$$n = 4 - \left(2\frac{H_2 O_2(\%)}{100}\right) \quad (4)$$

Where N = 0.37 is the current collection efficiency of Pt ring,  $I_D$  represents the disk current, and  $I_R$  represents the ring current.

#### **Cell measurements**

**Air-breathing PEMFCs:** To evaluate the performance of the proton exchange membrane fuel cell, a homemade battery was built. The battery was carried in an air-condition room with temperature of 20 °C, the flow of H<sub>2</sub> was not humidified and the cathode obtained O<sub>2</sub> directly from atmosphere. The *h*-FeNC ink was coated onto carbon paper with a loading mass of 1 mg cm<sup>-2</sup> as the cathode and the 70% Pt/C ink was coated onto carbon paper with a loading mass of 1 mg cm<sup>-2</sup> as the cathode and the 70% Pt/C ink was coated onto carbon paper with a loading mass of 0.5 mg cm<sup>-2</sup> as anode. The fuel cell performance was measured by LSV technique with CHI 760E electrochemical working station. For comparison, 70% Pt/C with a loading of 0.5 mg cm<sup>-2</sup> was used as cathode.

**Zinc-air battery:** To prepare Zn-air batteries, the *h*-FeNC loading on the carbon paper with a loading mass of  $1 \text{ mg cm}^{-2}$  was used

as cathode, a piece of Zinc plate was used as angle and  $G_{\rm A}$  M KOH was used as electrolyte. The Zn-air Batteries were electrolyte at room temperature, and the polarization curves were calculated by LSV technique from 1.5 V to 0 V at the scan rate of 5 mV s<sup>-1</sup> on the CHI 760E electrochemical workstation. For comparison, 20% Pt/C with a loading of 1 mg cm<sup>-2</sup> was used as cathode.

#### **Results and discussion**

All these Fe<sub>2</sub>O<sub>3</sub> nanoparticles (*h*-Fe<sub>2</sub>O<sub>3</sub>, *p*-Fe<sub>2</sub>O<sub>3</sub> and *r*-Fe<sub>2</sub>O<sub>3</sub>) were synthesized by a simple hydrothermal method. The morphologies of the obtained Fe<sub>2</sub>O<sub>3</sub> nanoparticles were characterized by scanning electron microscope (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). As shown in Fig. 1a-b, the *h*-Fe<sub>2</sub>O<sub>3</sub> retain its microsphere structure with a diameter around 700 nm, and these spherical particles have relatively thin shells (100-200 nm). The shells of *h*-Fe<sub>2</sub>O<sub>3</sub> have the similar size to *p*-Fe<sub>2</sub>O<sub>3</sub> and *r*-Fe<sub>2</sub>O<sub>3</sub> (Fig. 1d-e and Fig. 1g-h). Furthermore, the images shown in Fig. 1c, f and i reveal that *h*-Fe<sub>2</sub>O<sub>3</sub> have the crystal plane spacing of about 2.53 Å and 3.7 Å, indexed to be (110) and (012) planes; *p*-Fe<sub>2</sub>O<sub>3</sub> and *r*-Fe<sub>2</sub>O<sub>3</sub> have the crystal plane spacing of about 3.7 Å, indexed to be (012) plane.



Fig. 1 SEM, TEM and HRTEM of *h*-Fe<sub>2</sub>O<sub>3</sub> (a-c), *p*-Fe<sub>2</sub>O<sub>3</sub> (d-f) and *r*-Fe<sub>2</sub>O<sub>3</sub> (g-i), respectively.

These Fe<sub>2</sub>O<sub>3</sub>-doped Fe-CTF catalysts were prepared by onepot ionothermal polymerization of m-Phthalodinitrile in molten ZnCl<sub>2</sub> at the presence of different Fe<sub>2</sub>O<sub>3</sub> nanoparticles, followed by acid etching to remove ZnCl<sub>2</sub> and iron products. These catalysts doped with h-Fe<sub>2</sub>O<sub>3</sub>, p-Fe<sub>2</sub>O<sub>3</sub>, r-Fe<sub>2</sub>O<sub>3</sub> and commercially available Fe<sub>2</sub>O<sub>3</sub> were labelled as h-FeNC, p-FeNC, r-FeNC, and c-FeNC, respectively. The crystal structure and the natures of these samples were characterized by powder X-ray diffraction (XRD) patterns and Raman spectroscopy. Fig. 2a shows the XRD patterns of these samples. Two broad peaks at

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 $2\theta = 25^{\circ}$  and  $2\theta = 43.5^{\circ}$  can be indexed to the (002) and (101) diffractions of graphitic carbons, respectively.<sup>32,33</sup> The *h*-FeNC has a relatively strong (101) diffraction peak, indicating a higher graphitization degree than the other three catalysts. Also, no impurity phase peak can be found in those XRD patterns, suggesting that iron atoms were incorporated well into carbon framework, while the ZnCl<sub>2</sub> and possible iron-derived nanoparticles were removed completely through the acid leaching. To further confirm this assumption, we performed the XRD test of the *h*-FeNC with and without acid leaching, respectively. The catalyst before acid leaching shows the obvious peaks for ZnCl<sub>2</sub> (16.61°, 25.5°) and the iron oxide hydrate (14.01°, 21.29°), while these peaks were removed after acid leaching (Fig. S1). In the Raman spectrum, all these catalysts display two typical D band (about 1360 cm<sup>-1</sup>) and G band (about 1585 cm<sup>-1</sup>), wherein the ratio of the D and G band intensities  $(I_D/I_G)$  is used to evaluate the amounts of defects and disorder. As shown in Fig. 2b, the corresponding  $I_D/I_G$  ratios in Raman spectra decrease from 2.68 to 2.48 for h-FeNC, p-FeNC, r-FeNC, and c-FeNC. The obtained results demonstrate that the h-FeNC could provide more structure defects to serve as active sites, and then promote the activity for electrocatalysis.<sup>34-36</sup>



Fig. 2 (a) XRD patterns, (b) Raman spectrums, (c) Nitrogen adsorption-desorption isotherms and (d) Pore size distributions of h-FeNC, p-FeNC, r-FeNC and c-FeNC.

The porous structures of these samples were determined by the N<sub>2</sub> adsorption/desorption method. As shown in Fig. 2c, all the samples display a fast uptake at the low relative pressure  $(P/P_0 < 0.1)$  and a distinct hysteresis loop between the adsorption and desorption branches, indicating the coexistence of both micropores and mesoporous. The BET surface areas of *h*-FeNC (2454 m<sup>2</sup> g<sup>-1</sup>), *p*-FeNC (2248 m<sup>2</sup> g<sup>-1</sup>) and *r*-FeNC (1934 m<sup>2</sup>  $g^{-1}$ ) are significantly larger than that of *c*-FeNC (1864 m<sup>2</sup> g<sup>-1</sup>). Also, the average pore diameter of these catalysts was calculated by the Barrett-Joyner-Halenda (BJH) model. As shown in Fig. 2d, the average pore diameter of h-FeNC, p-FeNC, r-FeNC, and c-FeNC decrease from 3.4 to 3.2 nm, which further demonstrates the existence of mesoporous structure of h-FeNC. Similarly, the total pore volume of h-FeNC (1.9 cm<sup>3</sup> g<sup>-1</sup>) is

The morphologies of the *h*-FeNC are shown in Fig. 3. The SEM images in Fig. 3a indicate that numerous loosely agglomerated particles with a size of around 10 nm are homogeneously distributed on the surface of h-FeNC, and there are abundant pore structures (50-100 nm) inside the *h*-FeNC. The SEM images of p-FeNC, r-FeNC and c-FeNC also reveal that these catalysts consist of loosely agglomerated particles, and there is no obvious difference in the structure of these catalysts (Fig. S2). The TEM and HRTEM images of *h*-FeNC illustrate the existence of graphite structure (Fig. 3b-c), in consistence with the XRD results. The selected-area electron diffraction (SAED) pattern of h-FeNC further confirms the existence of graphitic structure (Fig. 3d). We further investigate the elemental distribution of h-FeNC using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The energy dispersive Xray spectroscopy (EDS) mapping images reveal that the N and Fe atoms can be homogeneously distributed in the architecture of the *h*-FeNC (Fig. 3e). Meanwhile, the Fe atoms are adjacent to N atoms at atomic level, which are believed to contribute to the formation of highly active Fe-N<sub>x</sub> sites.<sup>25,37</sup>



Fig. 3 (a) SEM, (b) TEM, (c) HRTEM, (d) SAED, (e) HAADF-STEM and EDS mapping images of h-FeNC.

X-ray photoelectron spectroscopy (XPS) measurement was used to reveal the elemental compositions of the catalysts. As shown in Fig. S3a, h-FeNC contains more Fe element than p-FeNC, r-FeNC and c-FeNC, mainly composed of C (85.72 at.%), O (8.21 at.%), N (5.86 at.%), Fe (0.21 at.%), which may be attributed to the fact that high surface area of h-FeNC can expose more Fe for the XPS detection. Meanwhile, no Zn ions were found in the XPS spectrum, which was consistent with the XRD results (Fig. S3b and S1). The high-resolution N 1s XPS spectrums (Fig. S4) were used to analyze the nitrogen type of these catalysts, which were deconvoluted into four types of common nitrogen, corresponding to pyridinic N (N1 398.3 eV), pyrrolic N (N2 399.65 eV), graphitic N (N3 400.8 eV) and oxidized

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N (N4 402.2 eV), respectively. As shown in Fig. S3c and Table S2, the total ratio of pyridinic N and pyrrolic N of *h*-FeNC is higher than that of the other three samples. It has been reported that the total content of pyridinic N and pyrrolic N are related with the activity of ORR, because their locating at the edge of graphite are capable of coordinating with Fe to form Fe-N<sub>x</sub> active sites for ORR in acid solution.<sup>38,39</sup> To obtain further insight of these catalysts, the high-resolution Fe 2p XPS spectrums of these catalysts were deconvoluted into five peaks. Fig. S5 shows that the peaks at 710.8 eV and 713.2 eV are assignable to the  $2p_{3/2}$  orbitals of the N-coordinated Fe<sup>2+</sup> and Fe<sup>3+</sup> species, while the peaks at 721.2, 724.6 and 718.1 eV are respectively assigned to Fe<sup>2+</sup>  $2p_{1/2}$ , Fe<sup>3+</sup>  $2p_{1/2}$  and the satellite peaks. The Fe 2p around 711 eV are favorable for the formation of Fe-N<sub>x</sub> species, which further suggests the existence of Fe-N<sub>x</sub> configuration.<sup>38,40</sup>



**Fig. 4** (a) RDE polarization curves of Pt/C, *h*-FeNC, *p*-FeNC, *r*-FeNC and *c*-FeNC in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution at 1600 rpm, with a scan rate of 10 mV s<sup>-1</sup>. (b) Voltammograms of *h*-FeNC at various speeds with a scan rate of 10 mV s<sup>-1</sup>; inset is the corresponding K–L plots at different potentials. (c)  $H_2O_2$  yield (bottom) and electron-transfer number (top) of Pt/C, *h*-FeNC, *p*-FeNC, *r*-FeNC and *c*-FeNC. (d-f) Area and mass-specific ORR kinetic current densities of *h*-FeNC, *p*-FeNC, *r*-FeNC and *c*-FeNC in 0.1 M HClO<sub>4</sub> solution at a scan rate of 10 mV s<sup>-1</sup> (Fe mass for (e) and N mass for (f)). (g) Tafel plots of Pt/C, *h*-FeNC, *p*-FeNC, *r*-FeNC and *c*-FeNC in 0.1 M HClO<sub>4</sub>. (h) Methanol tolerance test of *h*-FeNC and Pt/C in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution and (i) RDE results of *h*-FeNC and Pt/C before and after 10000 potential cycles in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution.

The ORR activity of the series of samples as well as the commercial Pt/C were systematically studied by using RDE in  $O_2$ -saturated 0.1 M HClO<sub>4</sub>. Cycle voltammetry measurements (CVs) were firstly carried out to investigate the catalysts activities in  $N_2$ - and  $O_2$ -saturated 0.1 M HClO<sub>4</sub> solution (Fig. S6). The typical catholic ORR peaks of these catalysts were found in  $O_2$ -saturated electrolyte while no peaks were observed under  $N_2$ -saturated electrolyte. The *h*-FeNC exhibits a cathodic peak at around 785 mV, which suggests the efficient catalyst ORR activity of *h*-FeNC in acidic electrolyte.<sup>41</sup> RDE measurements were carried out to further evaluate the catalytic performance of these samples. As shown in Fig. 4a, *h*-FeNC exhibits much higher ORR activity compared with the other three catalysts in 0.1M HClO<sub>4</sub>, whose half-wave potential ( $E_{1/2}$ ) is only 32 mV more negative than that of Pt/C, exceeding most of the

reported non-noble catalysts (Table S3). Meanwhile, we compared the ORR activity of this catalysts1With9diffErenew1  $Fe_2O_3$  contents (40mg, 50 mg, 60 mg), the content of h- $Fe_2O_3$ (50 mg) we used in this work has the best ORR activity of the catalyst (Fig. S7). The half-wave potential ( $E_{1/2}$ ) of h-FeNC is 25 and 33 mV more positive shift than that of *p*-FeNC and *r*-FeNC, respectively. The *p*-FeNC shows only 8 mV slightly more positive half wave shifts comparing to that of r-FeNC. It is well known that the activity of Fe-based catalysts is closely related to BET surface area, the content and form of iron atoms and nitrogen atoms. To verify their impacts, the ORR activities of our Febased catalysts were normalized according to the surface area, Fe and N content. As shown in Fig. 4d-f, the area-specified kinetic current densities (Jarea), Fe and N mass-specified kinetic current densities (J<sub>mass</sub>) at 0.85 V were calculated by using the Koutecky-Levich equation. The *h*-FeNC has the highest J<sub>area</sub> and J<sub>mass</sub> among these catalysts, which suggests that *h*-FeNC has the most optimal composition for catalyzing the ORR.42 Therefore, it is of significance to explore the factors affecting the highest intrinsic activity of h-FeNC. As described in previous sections, all of our catalysts were obtained by the same procedure except for the use of different Fe<sub>2</sub>O<sub>3</sub> nanoparticles. This means that Fe<sub>2</sub>O<sub>3</sub> nanoparticles play an important role on the formation of high activity Fe-based catalysts. The iron species were speculated to serve as catalysts (catalyzing the formation of a special type of ORR active carbon), active sites center (generating the M–N species), auxiliary (promoting a reaction between chelate and subjacent carbon).<sup>43</sup> The shapes and sizes of Fe<sub>2</sub>O<sub>3</sub> nanoparticles are very important when they are considered as catalysts to catalyze the formation of highly intrinsic ORR active carbon during high temperature treatment.

To identify the impacts of Fe<sub>2</sub>O<sub>3</sub> nanoparticles' size, the p-Fe<sub>2</sub>O<sub>3</sub> with different sizes ranges from 50 nm, 150 nm, and 250 nm were synthesized respectively. However, the ORR activity test clearly demonstrated that the activity of *p*-FeNC type catalysts were not sensitive to the sized of p-Fe<sub>2</sub>O<sub>3</sub> (Fig. S8 and S9). We further explored the microstructure of Fe<sub>2</sub>O<sub>3</sub> nanoparticles by HRTEM after excluded the impacts of the size and shape of Fe<sub>2</sub>O<sub>3</sub> nanoparticles (Fig. 1c, f and i). The h-Fe<sub>2</sub>O<sub>3</sub> have not only the crystal plane spacing of about 3.70 Å assignable to (012) planes but also the crystal plane spacing of about 2.53 Å assignable to the high-index (110) planes, while the p-Fe<sub>2</sub>O<sub>3</sub> and r-Fe<sub>2</sub>O<sub>3</sub> have only the (012) plane. It's well documented that high-index facets can endow nanocrystals with high surface energy, which can endow nanocrystals with high activity.<sup>29,44,45</sup> Therefore, h-Fe<sub>2</sub>O<sub>3</sub> with high-index facets would be more conducive to catalyze the formation of highly intrinsic ORR active sites during high temperature treatment.

In addition, the ORR kinetics of these samples were carried out by RDE measurements at different rotating speeds from 400 to 2500 rpm with a scan rate of 10 mV s<sup>-1</sup>. We can see that the current density enhances with the increase of rotating speed (Fig. 4b and Fig. S10). Koutecky–Levich (K–L) equations were used to analyze the kinetic parameters. The K–L plots show excellent linearity and are parallel for all these catalysts at various potentials, suggesting the first-order reaction kinetics towards the ORR and the similar electron transfer number for

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the ORR at different potentials. The electron transfer number (n) of h-FeNC was thus calculated to be an average value of 3.91 at potentials ranging from 0.2–0.7 V, indicating a four-electron transfer pathway for the ORR. Besides, the RRDE tests of these catalysts (the potential of Pt ring electrode was set to 1.2 V vs. RHE) were conducted in 0.1 M HClO<sub>4</sub> solution to calculate the H<sub>2</sub>O<sub>2</sub> yields and the corresponding electron transfer numbers (Fig. 4c). Similar to the catalytic behavior of Pt/C, the peroxide species yield of *h*-FeNC is less than 3.41% over the potential range from 0.2 to 0.8 V, and the electron transfer number is higher than 3.93. This result confirms that the h-FeNC is beneficial to reduce the intermediate yield of two-electrontransfer pathway to promote the reduction of oxygen to water through four-electron-transfer process.46,47 To further understand the inherent electrochemical catalytic processes for ORR, Tafel slope was calculated. Fig. 4g illustrates that the h-FeNC has a smallest Tafel slope of 52 mV per decade at low over-potentials, which is close to 59 mV per decade for the Pt/C catalyst. Similar to the Pt/C catalyst, the transfer of the first electron is probably the rate-determining step of the ORR for the *h*-FeNC catalyst in acidic media.<sup>48-50</sup>

Compared with p-FeNC, r-FeNC, c-FeNC and Pt/C catalysts, the *h*-FeNC catalyst has a lower charge-transfer resistance as evidenced by the smaller semicircle, further demonstrating the relatively high catalytic activity of *h*-FeNC in acidic electrolyte (Fig. S11).<sup>51,52</sup> Apart from the high catalytic activity, *h*-FeNC also exhibits better methanol tolerance and stability than commercial Pt/C catalyst in the acidic electrolyte. The tolerance to methanol crossover was performed by the method of current-time (I-T) at 0.677 V vs RHE with an RDE rotation of 1600 rpm upon the addition of 1 M methanol into the O<sub>2</sub>-saturated electrolyte after 300 s. It can be seen that the ORR current density of h-FeNC only slightly decrease while the Pt/C suffers a sharp decrease (Fig. 4h). Meanwhile, the stability test was carried out by RDE in the potential window of 0.6 to 1.0 V vs RHE at the scan rate of 50 mV s<sup>-1</sup> in  $O_2$ -saturated 0.1 M HClO<sub>4</sub>. After 10000 continuous cycles, the  $E_{1/2}$  of the *h*-FeNC exhibits only a 30 mV negative shifts, which is lower than that of the commercial Pt/C (77 mV negative shifts) (Fig. 4i). XPS survey spectra and SEM showed that the composition and structure of h-FeNC did not change significantly before and after the stability test (Fig. S12, S13 and Table S4). All these results indicate that the *h*-FeNC has high stability.



**Fig. 5** (a) RDE polarization curves of Pt/C, *h*-FeNC, *p*-FeNC, *r*-FeNC and *c*-FeNC in O2-saturated 0.1 M KOH solution at 1600 rpm, with a scan rate of 10 mV s<sup>-1</sup>. (b) Voltammograms of h-FeNC at various speeds with a scan rate of 10 mV s<sup>-1</sup>; inset is the corresponding K–L plots at different potentials. (c)  $H_2O_2$  yield (bottom) and electron-transfer number (top) of Pt/C, *h*-FeNC, *p*-FeNC, *r*-FeNC and *c*-FeNC in 0.1 M KOH. (d) Methanol tolerance test of *h*-FeNC and Pt/C in  $O_2$ -saturated 0.1 M KOH solution.

Besides the efficient catalytic activity in acidic electrolyte, h-FeNC also put up a competitive electrocatalytic performance for ORR in 0.1 M KOH solution. Fig. S14 displays the CV curves of these samples in  $N_{2}\text{-}$  and  $O_{2}\text{-}saturated 0.1$  M KOH solution. A well-defined cathodic peak of h-FeNC appears at around 900 mV in O2-saturated electrolyte. The RDE measurements show that *h*-FeNC displays a comparable onset potential ( $E_{onset} = 996$ mV) and half-wave potential ( $E_{1/2}$  = 883 mV) to that of Pt/C  $(E_{onset}$ = 954 mV,  $E_{1/2}$  = 843 mV) in 0.1 M KOH solution with a rotating speed of 1600 rpm (Fig. 5a). It indicates that the ORR activity of h-FeNC exceeds most of the other nonprecious catalysts (Table S5). Furthermore, the H<sub>2</sub>O<sub>2</sub> yield of h-FeNC ranges from 0.42% to 6.40% at all potentials and the electron transfer number ranges from 4 to 3.88 respectively, revealing a four-electron-pathway dominated ORR process, which is almost in keeping with the results from the K-L plots (Fig. 5b, c and S15). And then we carried out the methanol-tolerance test of Pt/C and h-FeNC by adding 1M methanol to 0.1 M KOH, h-FeNC exhibits a much better methanol-tolerance ability than Pt/C (Fig. 5d).

To further understand the nature of the active sites, the electrochemical poisoning tests of *h*-FeNC were conducted by adding 5 mM SCN<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> ions into the 0.1 M HClO<sub>4</sub> electrode, respectively. As shows in Fig. S16a, after adding 5 mM SCN<sup>-</sup> into the electrode, the diffusion current density of *h*-FeNC significantly decreased at 0.75 V. Fig. S16b-d show that the  $E_{1/2}$  of *h*-FeNC negatively shifted by 103 mV after adding 5 mM SCN<sup>-</sup> into the electrolyte, which is bigger than the effect of Cl<sup>-</sup> and Br<sup>-</sup> ions on ORR activity (the potential are negatively shift by only 23 and 16 mV, respectively). It is well known that SCN<sup>-</sup> coordinate strongly to iron and poison the iron-centered catalytic sites for ORR. The result strongly illustrated that the Fe ions combined with nitrogen to form Fe-N<sub>x</sub> species active sites

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in h-FeNC, which can greatly improve the ORR catalytic



**Fig. 6** (a) Air-breathing proton exchange membrane fuel cells polarization plots. (b) Zn-air fuel cells polarization plots. (c, d) Photographic images of two series of *h*-FeNC-based Zn-air fuel cell lighting green (c) and blue LED (d).

To corroborate the excellent catalytic activities under real fuel cell operation conditions, air-breathing proton exchange membrane fuel cell (AB-FEMFC) and zinc-air battery were assembled using either *h*-FeNC or Pt/C as cathodic catalyst. Fig. 6a shows the polarization and power density of air-breathing proton exchange membrane fuel cell (AB-FEMFC) on h-FeNC and Pt/C (0.5 mg Pt cm<sup>-2</sup>), which was carried in an airconditioned room with temperature of 20 °C. The open-circuit voltage of h-FeNC is 0.96 V, higher than that of Pt/C (0.92 V), and the peak power density is 57 mW cm<sup>-2</sup>, which reachs approximately 63% of commercial Pt/C (91 mW cm<sup>-2</sup>) under identical test conditions. To our knowledge, this performance is better than most of the reported Fe-N<sub>x</sub>-C catalysts. In the zincair battery, the open-circuit voltage of h-FeNC is 1.6 V with a peak power density of 215 mW cm<sup>-2</sup>, which is higher than that of 1.5 V and 135 mW cm<sup>-2</sup> for the Pt/C (Fig. 6b). As exemplified in Fig. 6c and 6d, two series of h-FeNC-based Zn-air batteries were applied to power various light-emitting diode (LED) to demonstrate the potential application for the device. All these results demonstrate that the h-FeNC exhibits excellent electrocatalytic activity in both alkaline and acidic conditions, and the *h*-FeNC can be successfully employed as a promising cathode catalyst in fuel cells.

## Conclusions

In conclusion, we have demonstrated a reliable strategy for the synthesis of high-performance Fe-CTF ORR catalysts by direct heating the dry mixture of  $ZnCl_2$ , dinitrile monomer and  $Fe_2O_3$  nanomaterials. The  $Fe_2O_3$  nanomaterials were proven not only to be an eco-friend multifunctional template but also play an important part in improving the ORR activity of Fe-CTF catalysts. It is noteworthy that the catalyst we got exhibits higher stability and superior methanol tolerance to commercial 20 wt% Pt/C for ORR in both acidic and alkaline conditions. Furthermore, the *h*-FeNC can be a promising cathode catalyst in both PEMFCs and

Zn-air batteries, and the performance outperformed most of the reported nonprecious metal catalysts. This Work opens a new way to prepare highly efficient and cost-effective ORR catalysts for advanced energy conversion and storage.

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The hierarchical mesoporous carbon nanomaterials synthesized by using  $Fe_2O_3$  hollow microspheres as multifunctional template exhibits efficient catalytic performance for oxygen reduction in both acidic and alkaline media.

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