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Hierarchical carbon-based material was synthesized through grinding by employing metal salt as both template and metal source for catalyzing ORR.
Green Synthesis of Hierarchical Carbon Coupled with Fe$_3$O$_4$/Fe$_2$C as Efficient Catalyst for Oxygen Reduction Reaction

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A green synthesis strategy is reported here for fabrication of hierarchical Fe-based carbon electrocatalyst for catalyzing oxygen reduction reaction. This strategy involves grinding of organic ligand (1,4-benzenedicarboxylic acid) and metal salt (iron chloride hexahydrate) with minute solvent at room temperature and thermal annealing in N$_2$ atmosphere. The metal salt introduced plays dual roles. One is as hard template for creating hierarchical porous structure, which is important in controlling the overall mechanism and kinetics of the catalysis process by affecting the mass transport and exposure of active sites. The other one is as metal source for building of MOF structure that can drive Fe$_3$O$_4$ and Fe$_2$C active sites for catalyzing oxygen reduction reaction. Combining the merits of porosity and MOFs, the catalyst synthesized by 120 min grinding (BM-Fe@NC-120) possesses good ORR performance in 0.1 M KOH with half-wave potential of 0.80 V, limiting current density of $-5.08$ mA cm$^{-2}$, excellent long-term durability and resistance to methanol, indicating the validity of this eco-friendly route for scalable synthesis of catalysts for future practical fuel–cell applications.

Introduction

Increasing demand for solving the worldwide energy crisis and environmental issues has triggered extensive research interests on sustainable energy conversion and storage systems, such as fuel cells and metal–air batteries, the commercialization of which, nevertheless, depends significantly on the development of electrocatalysts for the oxygen reduction reaction (ORR).$^{1-4}$ Platinum (Pt) and Pt-based materials exhibit superior ORR activity and have been recognized as the bench mark for ORR catalysts so far. However, the prohibitive cost, low reserve, and limited durability of these materials hinder their large scale applications.$^{5,6}$ Thus, it is of vital importance to explore alternative low-cost electrocatalysts with competitive performance and improved durability.

To date, great efforts have been devoted and a wide range of catalysts have been developed, including the metal-free heteroatom (nitrogen (N), boron (B), sulfur (S), phosphorus (P), etc.)-doped carbon materials,$^{7-10}$ and their composites with transition-metal (iron (Fe), cobalt (Co), nickel (Ni), copper (Cu)) or transition-metal oxide, carbide, chalcogenide and phosphide.$^{11-20}$ Among these materials, Fe-based carbon composites are expected to exhibit good activity towards ORR due to the synergy between the ORR-effective Fe (Fe$_3$O$_4$, Fe$_2$C, etc.) and N (pyridinic N, graphitic N) species, as well as the carbon substrates with good conductivity and moderate defects, which has been confirmed by recently reported researches.$^{21-25}$

To fabricate such catalysts, the precursor-carbonization method has been considered as one of the best ways.$^{26-30}$ Although several methods have been utilized to prepare the precursors, the physical blending of the metal, carbon and nitrogen sources and using the metal-organic frameworks (MOFs) as self-sacrificing template are the most favorable and effective ways.$^{31-35}$ The physical blending is simple and efficient for acquiring the precursor, but there is no effective way to control the final distribution of active sites and the structure. In respect of inheriting structural features of the precursor, MOFs that built from periodically linked organic ligands and metal centers are attractive candidates owing to their structural diversity and metal centers uniformity.$^{36-43}$ Although many MOFs have been explored as precursors for deriving non-precious metal/carbon-based materials,$^{44-49}$ it is still challenging to introduce meso- and/or macro-porosity into the final carbon structure since the architecture plays an important role in controlling the overall mechanism and kinetics of the catalysis process by affecting the reactive sites exposure, reactant accessibility and conductivity of the materials. Furthermore, conventional synthesis of MOFs is heat and organic-solvent consuming, which is not beneficial for large scale synthesis. Therefore, it would be favorable and challenging to combine the advantages of physical blending to develop more environmental-friendly synthetic methods of MOFs and introduce porosity into the final carbon structure as well.

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Herein, a green synthesis strategy is reported for fabrication of hierarchical Fe-based carbon electrocatalysts for catalysing ORR. This strategy involves simple grinding of organic ligand (1,4-benzenedicarboxylic acid) and metal salt (iron chloride hexahydrate) with minute quantity of solvent at room temperature and thermal annealing in N\textsubscript{2} atmosphere. The metal salt used in this strategy performs two major roles: First, excess metal salt was added as hard template to introduce meso- and/or macro-porosity into the final carbon structure, which is favorable for improving mass transport and providing sufficient exposure of active site; Second, it provides the metal source needed for construction MOF structure, which serves self-sacrificing template for deriving Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}C active sites to catalyzing the ORR process. By optimizing the grinding time to 120 min, the best catalytic performance was obtained in 0.1 M KOH with half-wave potentials of 0.80 V, limiting current density of ~5.08 mA cm\textsuperscript{-2}, excellent long-term durability and resistance to methanol. It indicates the effectiveness of this eco-friendly route, which will provide new insight into the synthesis of hierarchical carbon catalysts for future practical fuel-cell applications.

**Experimental**

**Materials**

All chemical were used directly without further refinement. Iron chloride hexahydrate (FeCl\textsubscript{3} \cdot 6H\textsubscript{2}O), hydrochloric acid (HCl, 12 mol L\textsuperscript{-1}) and potassium hydroxide (KOH) were supplied by Sinopharm Chemical Reagent Co., Ltd. 1,4-benzenedicarboxylic acid (H\textsubscript{2}BDC) was purchased from Energy Chemical Co., Ltd. N,N-dimethylformamide (DMF), methanol, ethanol and isopropanol were received from Tianjin Fuyu Fine Chemical Co. Ltd. The commercial 20 wt % Pt/C and 5 wt % Nafion solution were obtained from Sigma-Aldrich.

**Preparation of the MOF precursor**

Typically, a certain amount of FeCl\textsubscript{3} \cdot 6H\textsubscript{2}O (1.1474 g, 4.2 mmol) and H\textsubscript{2}BDC (0.3526 g, 2.1 mmol) were added into the agate grinding jar. Then, 1 ml DMF were injected into the jar, and the mixture were grinded at a rotating speed of 700 rpm for different times (30, 60, 90, 120 and 150 min). Finally, the products were preserved at room temperature for 5 h.

**Preparation of BM-IM-T**

The as-prepared precursor was washed with ethanol to remove the unreacted metal salt and the collected samples were denoted as BM-IM-T (T represents the grinding time from 30 to 150 min).

**Preparation of BM-Fe@NC-T catalyst**

The as-prepared precursor were transferred to a crucible, which were placed in a tubular furnace and heated at 800 °C under N\textsubscript{2} atmosphere for 3 h with a heating rate of 5 °C min\textsuperscript{-1}. After cooling to room temperature, the obtained sample was immersed in HCl (12 mol L\textsuperscript{-1}) for 30 min, collected by centrifugation, washed with deionized water to neutral and dried at 80 °C overnight, respectively. The samples were denoted as BM-Fe@NC-T (T represents the grinding time from 30 to 150 min).

**Characterization**

The phase purity and crystallinity were tested on a Bruker D8 Advance X-ray diffractometer with Cu K\alpha radiation (λ = 0.15418 nm). The scanning electron microscopy (SEM, JEOL-7900) and transmission electron microscopy (TEM, JEM-2100F) were employed to investigate the detailed structure and morphology of synthesized samples. Structure information of the carbon matrix was acquired from a LABRAM HR EVO Raman spectrometer with a 532 nm excitation wavelength. X-ray photoelectron spectra were recorded on an ESCA250Xi Spectrometer and the binding energies were calibrated based on the graphite C 1s peak. The content of Fe was determined by an Agilent 710 inductively coupled plasma optical emission spectrometer (ICP-OES). The BET surface areas and pore size distributions were characterized on a JW-BK200 surface area analyzer.

**Electrochemical measurements**

All electrochemical measurements were collected from Gamry electrochemical work station (INTERFACE 1000 T) under a three-electrode cell configuration, using glassy carbon rotating disk electrode (RDE, 5 mm in diameter) as working electrode, platinum plate as counter electrode and Ag/AgCl (KCl saturated solution) electrode as reference electrode. The measured potentials were referenced to reversible hydrogen electrode (RHE) on the basis of the formula $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059pH + E^{\theta}_{\text{Ag/AgCl}}$. For preparation of the catalyst ink, 4 mg samples was added to a solution of 970 μL isopropanol and 30 μL Nafion (5 wt %). After ultrasonic dispersion for 1 h, the homogeneous catalyst ink was obtained. The working electrode was prepared by pipetting 15 μL catalyst ink onto the GC electrode with a loading equivalent to 0.300 mg cm\textsuperscript{-2}. The linear sweep voltammograms (LSVs) and Cyclic voltammetry (CV) were tested at N\textsubscript{2}/O\textsubscript{2} saturated 0.1 M KOH solution in the potential range from 0.2 to 1.2 V with a scan rate of 10 mV cm\textsuperscript{-1}. The long time stability experimented by CV cycling and current vs. time (i-t) chronoamperometry respond were compared with 20 % Pt/C.

The electron transfer number was evaluated by two methods. One is using the Koutecky–Levich (K–L) equation:

$$ \frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_l} = \frac{1}{J_k} + \frac{1}{B_0 \nu^{-1/2}} $$

where $J$ is the measured current density, $J_k$ and $J_l$ are the kinetically limited and diffusion-limited current densities, $\nu$ is the angular velocity of the disk, $n$ is the electron transfer number, $F$ is the Faraday constant (96485 C mol\textsuperscript{-1}), $C_0$ is the bulk concentration of O\textsubscript{2} ($C_0 = 1.2 \times 10^{-6}$ mol cm\textsuperscript{-3} in 0.1 M KOH), $D_0$ is the diffusion coefficient of O\textsubscript{2} ($D_0 = 1.9 \times 10^{-5}$ cm\textsuperscript{2} s\textsuperscript{-1} in 0.1 M KOH), and $V$ is the kinematic viscosity of the electrolyte ($V = 0.01$ cm\textsuperscript{2} s\textsuperscript{-1} in 0.1 M KOH).
According to the rotating ring-disk electrode (RRDE) test, the yield of hydrogen peroxide \((\text{H}_2\text{O}_2 \% )\) and electron transfer number \((n)\) in the ORR process can be calculated using the following equations:

\[
\text{H}_2\text{O}_2(\%) = \frac{200 I_d/N}{I_d + I_r/N}
\]

\[
n = \frac{4 I_d}{I_d + I_r/N}
\]

Where \(I_d\) and \(I_r\) are the disk and ring current densities, respectively. \(N\) is the ring collection efficiency (0.37).

**Results and discussion**

A typical synthesis route of the BM-Fe@NC-T composites is illustrated in Fig. 1. Metal salts and organic ligand were added into the grinding jar with 1 mL DMF as solvent, which was grinded for a certain time and further heated at 800 °C under an inert atmosphere to construct the hierarchical porous N doped carbon flakes with enchased Fe\(_3\)O\(_4\)/Fe\(_2\)C active sites (see the Experimental section for more details) for catalyzing ORR.

Fig. 2a, the peaks in the 2θ range of 8 °–10 ° gradually appears with the increase of grinding time. The highest peak intensity can be acquired when the grinding time reaches 120 min, which are well consistent with the simulated pattern of MOF MIL-101, proving the successful synthesis of MIL-101 structure in BM-IM-T. However, longer grinding time of 150 min would result in the destruction of formed MOF structure, which can be attributed to the following three reasons: 1) the oxygen energy delivered from the mechanical force. All the other diffraction peaks of BM-IM-T observed in the range of 17 °–70 ° are in accordance with the characteristic peaks of H\(_2\)BDC, indicating that a large part of the ligand was not involved in the construction of MOF structure. Detailed morphology of BM-IM-T was analyzed by scanning electron microscopy (SEM). As shown in Fig. 2b-d and Fig. S2, the unreacted ligands present a similar stacking structure under the mechanical force, and spaces are observed between the bricks. These spaces were filled with metal salt and produced when the metal salt was removed, which would be preserved after thermal annealing, facilitating the fabrication of hierarchical porosity. That is where the metal salt plays the template role. Furthermore, a growing number of a new honey-comb-shaped phase that associated with the MOF structure can also be recognized with the increase of grinding time from 30 to 120 min. Unlike its counterparts, this honeycomb structure no longer exists in the sample of BM-IM-150, and only amorphous phase can be found on the surface of ligand blocks, which is consistent with the PXRD results. Control experiment was carried out by using BM-IM-120 as the precursor. After the same heating procedure, there was little carbon left due to the decomposition of H\(_2\)BDC. This suggests the protective role of metal salt on carbon source by reacting with H\(_2\)BDC to form metal terephthalate, which possesses much higher decomposition temperature and can be retained after the annealing process. \(^{51}\)

After thermal annealing in an inert atmosphere, the ground mixtures were successfully transformed into BM-Fe@NC-T composites, the detailed morphology of which were characterized by SEM and shown in Fig. 3a-b and Fig. S3. As revealed by the SEM images (Fig. 3a and b), the built MOF structure and unreacted organic ligand in BM-Fe@NC-120 had been converted to the carbon matrix in the form of carbon flakes with hierarchical porosity. Such hierarchical porosity is desirable for ORR since it is beneficial for mass transport during catalytic process. The formation of this hierarchical structure can be attributed to the following three reasons: 1) the oxygen atoms in the organic ligand carried away part of the carbon element during the thermal annealing process, turning the stacking structure of unreacted organic ligand into thinner carbon flakes; 2) the unreacted metal salt embedded in the stacking ligand by grinding force had acted as a template for generating pores; 3) part of the solvent DMF preserved in the precursor escaped in high temperature, leaving pores in the final structure. Similar carbon flakes were also synthesized for BM-Fe@NC-30, 60 and 90 (Fig. S3a-f). For the sample of BM-Fe@NC-150, the carbon flakes becomes much thicker due to
the longer grinding time (Fig. S3g-h). Additionally, it can be noted that the BM-Fe@NC-120 shows more compact hierarchical porosity than its counterparts. The distance between carbon flakes is narrowed because that the honeycomb-shaped MOF fabricated by grinding has played the “binder” role in the thermal annealing process since MOF itself can also derive carbon species in high temperature and inert atmosphere. To reveal the detailed structure of BM-Fe@NC-120, transmission electron microscopy (TEM) was used and the results are presented in Fig. 3c-e. It indicates that the BM-Fe@NC-120 is composed of Fe$_3$O$_4$, Fe$_2$C and carbon matrix. The high-resolution TEM (HRTEM) images (Fig. 3d and e) present the lattice fringes with interplanar distances of 0.252 and 0.297 nm, which are in accordance with the (311) and (220) crystal planes of Fe$_3$O$_4$, respectively. The lattice spacing of 0.201 nm can be ascribed to the lattice distance of the (111) plane of Fe$_2$C. As shown in Fig. 3e, the derived Fe$_2$C phase is covered by Fe$_3$O$_4$ phase, which is probably due to the contact with the ligand-O of its outer surface. This might protect the Fe$_2$C from the chemical etching in the ORR environment and extending its service life in the BM-Fe@NC-120. EDS elemental mapping was further performed to confirm the distribution of different species in BM-Fe@NC-120. As revealed in Fig. 3f-j, the participating elements (C, O, N, Fe) are dispersed homogeneously throughout the carbon matrix. As no other N source was added to the synthesis system, it can be concluded that the small amount of doped N comes from the solvent DMF wrapped in the precursor. That is one of the three reasons that the as prepared precursor was not dried thoroughly. The other two reasons to keep the solvent DMF in the precursor are to provide a better growth environment for MOF and probably generates pores afterwards during thermal annealing as mentioned above.

The structure and composition of as-synthesized BM-Fe@NC-T samples were further confirmed by PXRD characterization. As recorded in Fig. 4a, the formation of carbon matrix can be illustrated by the broad diffraction peak centered around 26°, which is assigned to the (002) plane of hexagonal graphite structure. Other diffraction peaks observed at 35.4°, 43.2°, 57.3° and 68.1° are corresponding to the (311) plane of Fe$_3$O$_4$ (JCPDS-19-0629), the (101), (102) and (110) planes of Fe$_2$C (JCPDS-36-1249), respectively. These Fe-based diffraction peaks gradually show up with grinding time and the intensities reach the maximum in BM-Fe@NC-120, indicating that they are related with the building of MOF structure and not involved with the unreacted metal salt. Thus, it is not surprise to find attenuation of these peaks for BM-Fe@NC-150. The structural characteristics of the carbon in BM-Fe@NC-T samples were further investigated by Raman spectra (Fig. 4b). In all the examined samples, two sharp peaks centered at 1343 and 1584 cm$^{-1}$ are observed, which correspond to the featured D-band...
(disordered, sp³ hybridized carbon) and G-band (ordered, sp² hybridized carbon) of carbon-based nanostructures. Also, the relative intensity ratio of D-band to G-band (I_D/I_G) was calculated to reflect the defects or graphitization degree of carbon for each sample. The I_D/I_G value for BM-Fe@NC-120 (0.95) is slightly lower than BM-Fe@NC-30 (1.02), BM-Fe@NC-60 (0.99), BM-Fe@NC-90 (0.97) and BM-Fe@NC-150 (0.99). This lower I_D/I_G value indicates that the graphitization degree of BM-Fe@NC-120 is slightly higher than its counterparts, which is favorable for improving the electrical conductivity and ORR catalytic performance. The N₂ adsorption-desorption isotherm were tested to characterize the hierarchical structure of BM-Fe@NC-T. As observed in Fig. 4c, except for BM-Fe@NC-30, all the other samples exhibit the type-IV isotherms and H₂-type hysteresis loops, revealing their mesoporous structure characteristics. From the inset pore size distribution plot, two main pore systems are identified to be centered around 2.5 ± 3.5 nm and 10 ± 11 nm, confirming the formed hierarchical structure of these samples. The total BET surface areas of BM-Fe@NC-30, 60, 90, 120 and 150 were calculated to be 112.1, 365.9, 502.4, 964.8 and 646.9 m² g⁻¹. The built hierarchical structure and higher BET surface area of BM-Fe@NC-120 are beneficial for producing more active sites and rapid mass transfer during ORR process.

The X-ray photoelectron spectroscopy (XPS) was further used to provide insights into the surface elemental chemical states and electronic structures of the BM-Fe@NC-120 sample. Elemental C, Fe, N and O were detected in the survey spectrum (Fig. S4) and the XPS results of surface elemental contents were summarized in Table S1. In the high-resolution C 1s spectrum (Fig. 4d), five peaks at 283.8, 284.3, 285.5, 287.6 and 290.1 eV can be deconvoluted that correspond to the formation of C-Fe bonding in BM-Fe@NC-120. The N₁s spectrum illustrated in Fig. 4f, the deconvoluted three peaks at 398.1, 400.5 and 402.1 eV are assigned to pyridinic N, pyrrolic N and graphitic N respectively. Among these doped N species, the pyridinic N and graphitic N are considered as contributors for boosting the ORR catalytic activity. Since these two kinds of N species accounts for the minority, the catalytic ability of BM-Fe@NC-120 for ORR can be affirmed mainly come from the formed Fe₃O₄ and Fe₃C sites. Three fitted peaks at 715.5, 719.6 and 733.8 eV are attributed to the Fe(II) binding energy of Fe²⁺ and Fe³⁺, while the peaks at 724.8 and 727.2 eV are respectively related to the Fe(III) binding energy of Fe³⁺ and Fe⁴⁺. Three fitted peaks at 715.5, 719.6 and 733.8 eV are satellite peaks. This coexistence of Fe²⁺ and Fe³⁺ matches well with the above discussed TEM and XRD results.

Fig. 5 (a) CV curves of the BM-Fe@NC-T samples and 20 % Pt/C in both O₂-saturated 0.1 M KOH solution; (b) LSV curves and (c) the corresponding Tafel plots of the BM-Fe@NC-T samples in comparison with 20 % Pt/C in O₂-saturated 0.1 M KOH solution; (d) LSV curves of BM-Fe@NC-120 recorded at different rotation rate in O₂-saturated 0.1 M KOH solution (inset: the K–L plots). The accurate content of Fe in BM-Fe@NC-120 was determined from an inductively coupled plasma optical emission spectrometer (ICP) to be 0.96 wt %. By dissolving the ligand in BM-IM-120 with DMF, the amount of formed MOF-related structure was calculated around 4.64 wt %, based on which it can be estimated that the Fe content in BM-Fe@NC-120 would be in the range of 1.17-1.85 wt % with or without the consideration of the O atoms of the unreacted ligand in BM-IM-120. Since the HCl treatment
after thermal annealing may also take away a small amount of Fe metal, it is reasonable to have a low Fe content of 0.96 wt % in BM-Fe@NC-120. These results confirm an important point that the Fe$_3$O$_4$ and Fe$_3$C presented in BM-Fe@NC-120 comes a much more important role in catalyzing the ORR process than the Fe$_3$C phase.

Fig. 5c presents the corresponding Tafel plots of as-prepared BM-Fe@NC-T catalysts, in which, BM-Fe@NC-120 shows a smaller Tafel slope (114 mV dec$^{-1}$) in relative to BM-Fe@NC-30 (133 mV dec$^{-1}$), BM-Fe@NC-60 (132 mV dec$^{-1}$), BM-Fe@NC-90 (126 mV dec$^{-1}$) and BM-Fe@NC-150 (116 mV dec$^{-1}$), and larger Tafel slope than that of Pt/C (89 mV dec$^{-1}$), indicating the better ORR activity of BM-Fe@NC-120 than its counterparts and slower catalytic kinetics than Pt/C. The Nyquist plots of these samples further confirms the smallest charge-transfer resistance of BM-Fe@NC-120, revealing its better electron conductivity towards ORR process (Fig. S6).

To gain detailed insight into the catalytic behaviors and ORR mechanism of BM-Fe@NC-T samples, electrocatalytic kinetics measurements were also carried out and the LSVs at electrode rotating rate of 400, 625, 900, 1225, 1600 and 2025 rpm were recorded (Fig. Sd and Fig. S5). Enhancement in the current density with the increase of rotation speed is observed for all these samples, based on which, the Koutecky–Levich (K–L) plots were recorded (Fig. 5d and Fig. S5). The Nyquist plots of these BM-Fe@NC-120 before (black) and after (dark yellow) 3000 CV cycles in 0.1 M KOH solution for 10 h; (d) the ratio of rate constants $k_2/k_1$ for BM-Fe@NC-90, BM-Fe@NC-120 and BM-Fe@NC-150 in the potential range from 0.20 to 0.80 V.

The electrocatalytic properties of the BM-Fe@NC-T samples toward the ORR were first evaluated by cyclic voltammetry (CV) in N$_2$- or O$_2$-saturated 0.1 M KOH aqueous solution. As presented in Fig. 5a, well-defined cathodic peaks appear for all the samples in O$_2$-saturated 0.1 M KOH aqueous solution, while no obvious peaks can be observed when the electrolyte is saturated with N$_2$. The most positive reduction current peak was occurred at 0.830 V vs the reversible hydrogen electrode (RHE) for BM-Fe@NC-120, indicating its good catalytic activity toward ORR. Further evidence was provided by the linear sweep voltammetry (LSV) curves tested at a rotating rate of 1600 rpm(Fig. 5b). For comparison, the commercial 20 % Pt/C was also examined under the same conditions. Similar to the CV results, the BM-Fe@NC-120 exhibits the best ORR performance among its counterparts with the onset reduction potential, half-wave potential and diffusion-limited current density of 0.89 V, 0.80 V and -5.08 mA cm$^{-2}$, respectively, which is comparable to that of 20 % Pt/C (0.94 V, 0.85 V and 5.33 mA cm$^{-2}$) and other reported carbon-based materials (Table S2). In this work, HCl treatment was applied before obtaining the BM-Fe@NC-T catalysts, during which, the species that can be removed have been washed away. The Fe$_3$C phase retained in BM-Fe@NC-120 was due to the protection of Fe$_3$O$_4$ shell formed on its outer surface (Fig. 3e). Thus, it is believed that the Fe$_3$O$_4$ phase plays a more important role in catalyzing the ORR process than the Fe$_3$C phase.
chronoamperometry measurements were carried out in competition with 20 % Pt/C. Fig. 6b presents the LSVs of BM-Fe@NC-120 before and after long-term CV cycles. As illustrated, only a slight decrease of half-wave potential (12 mV) and diffusion-limited current density (3.1%) were observed after 3000 CV cycles, indicating the good durability of BM-Fe@NC-120 for ORR. Chronoamperometry response was also recorded at 0.80 V vs RHE and the time-dependent current density curve is shown in Fig. 6c. The BM-Fe@NC-120 can reserve 88.7 % of its initial current after continuously working for 10 h in O2-saturated 0.1 M KOH aqueous solution, while the current of the 20 % Pt/C gradually dropped by 46.1 % within the same time frame, revealing the superior catalytic stability of BM-Fe@NC-120. The small reduction of catalytic activity after the CV and chronoamperometry measurement is probably caused by the gradually electrooxidation of Fe2C during the ORR process. To further investigate the influence of crossover effect on BM-Fe@NC-120, about 3 % volume methanol was injected into the 0.1 M KOH solution after 300 s (Fig. 6d). Compared with the dramatic current decline of 20 % Pt/C (50 %) due to the catalytic oxidation of methanol, the BM-Fe@NC-120 only presents a small current reduction of 3.8 %, showing great promise as a methanol-tolerant cathode catalyst to be applied in alkaline direct-methanol fuel cells.

By using the model proposed by Damjanovic et al. and Hsueh et al. (Scheme 1 in the supporting information), the kinetics of electron transfer in ORR can be revealed by RRDE voltammetry tests. On the basis of equations (S1-S9), the rate constants (k1, k2, and k3) were calculated by the slope and intercept of i2/i1 versus ω-1/2 and i0/(i0-i1) versus ω-1/2 within the potential range from 0.20 to 0.80 V vs RHE (Fig. 7a-c). In Fig. 7b, the k1 ≫ k2 ≈ k3 reveals that the reduction of O2 to OH- catalyzed by BM-Fe@NC-120 is predominantly driven through k1 pathway with four-electron kinetics. In the cases of BM-Fe@NC-90 and BM-Fe@NC-150, the rate constant k2 is close to k1 although k3 is larger than k2, indicating that the formation of HO2- a rapid process with a sluggish reduction to OH-. The ratio of k1/k2 of these samples are also calculated and the results are presented in Fig. 7d. It is noteworthy that the BM-Fe@NC-120 presents a much higher value of k1/k2 compared with its counterparts, whose k1/k2 values are only a little larger than 1, further confirming the four-electron k1 pathway kinetics on BM-Fe@NC-120 for catalyzing ORR process. As the difference between BM-Fe@NC-T only lies in the mechanical grinding time, the best ORR performance of BM-Fe@NC-120 is due to the optimized 120 min that is crucial for maximum formation of MOF structure, deriving more catalytic active sites and generating more efficient hierarchical structure for rapid mass transfer.

By combining all the discussions above, the BM-Fe@NC-120 shows a superior ORR performance, which is the result of a combination of factors synergies: 1) adequate Fe3O4/Fe2C active sites derived from the synthesized MOF structure and doped N species for catalyzing ORR process; 2) hierarchical structure with large surface area built using the metal source template for rapid mass transfer; 3) partially graphitized carbon matrix formed for better electron transportation. By utilizing the mechanical grinding method, metal source can be used as template for building hierarchical structure, which is of crucial importance in this work for boosting the kinetic processes for ORR of BM-Fe@NC-120. This work will provide new insight into the synthesis of hierarchical carbon catalyst from this simple and eco-friendly strategy for future practical fuel-cell application.

Conclusions
In summary, ORR catalysts with hierarchical structure was developed by utilizing the simple and scalable mechanical grinding strategy. Metal salt, organic ligand and minute quantity of solvent were used as starting materials and ground at room temperature for different time, followed by a subsequent calcination process. The metal salt played the roles of metal source for MOF and template for hierarchical porosity, while the organic ligand participated in the building of MOF and served as the carbon matrix. As for the minute solvent, it was favorable for MOF growth and N doping, and may generate pores from volatilization as well. The 120 min grinding time is optimized for MOF synthesis and the corresponding catalyst (with Fe3O4/Fe2C active sites) shows the best ORR performance, which can be attributed to the synergy between the active sites, hierarchical structure, large surface area and good electron conductivity. This work provides a guideline for future synthesis of hierarchical catalysts from this simple and scalable mechanical grinding strategy.

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

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