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A General Approach for Hierarchically Porous Metal/N/C Nanospheres Electrocatalysts: Nano-Confined Pyrolysis of In-Situ Formed Amorphous Metal-Ligand Complex

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A nano-confined pyrolysis approach is developed for constructing highly nitrogen-doped metal/N/C hierarchically porous nanospheres (typically Fe/N/C-HP). Hierarchically porous silica nanospheres (NKM-5) is used as hard template and amorphous Fe/Zn-(Melm)₂ complex is employed as carbon and nitrogen source. During the pyrolysis process, firstly, the molten Fe/Zn-(Melm)₂ complex can diffuse into hierarchically porous tunnels of NKM-5. Secondly, the interface confinement effect of the nanopore in NKM-5 can effectively immobilize nitrogen to coordinate with iron atom, prevent the aggregation of the Fe-based species and form single-atom Fe sites. After removing the silica template, the catalyst exhibits hierarchically porous structure and uniform spherical morphology. This hierarchically porous structure of Fe/N/C-HP can enhance mass transport/electron transfer and greatly improve the accessibility of Fe/N/C sites. As a result, the Fe/N/C-HP catalyst exhibits excellent oxygen reduction performance with a half-wave potential ($E_{1/2}$) of 0.90 V in alkaline media and 0.78 V in acidic media. A primary Zn–air battery with Fe/N/C-HP as the cathode catalyst exhibits a large peak power density of 181 mW cm⁻² and discharge stability. This nano-confined pyrolysis of amorphous M/Zn-(Melm)₂ complex is a general method to construct hierarchically porous M/N/C (M=Fe, Co, Cu, Mn and Ni) electrocatalyst with well-defined morphology.

1. Introduction

The ever-increasing energy issues and environmental deterioration have attracted extensive attention to develop clean energy devices.¹ Highly efficient electrochemical oxygen reduction reaction (ORR) plays crucial roles in renewable and sustainable energy systems, such as fuel cells and metal-air batteries.² Platinum group metal (PGM) catalysts are predominantly used as the state ofthe-art ORR catalysts.³ Unfortunately their prohibitive cost, geological scarcity, as well as poor durability greatly impede the large-scale utilization in sustainable energy systems. Therefore, it is extremely imperative to explore efficient and durable non-precious metal catalysts (NPMC) to replace Pt-based catalysts. Tremendous efforts have been devoted in the field of NPMC involving perovskites,⁴ transition metal (TM)-based oxides,⁵ carbides,⁶ phosphides.⁷ sulfides⁸ and heteroatom-doped carbon materials⁹ to fulfill the stringent activity and durability requirements of practical systems. Among them, atomically dispersed M-N-C (M = Fe, Co) electrocatalysts, 10-12 especially Fe-N-C, have been considered to be the most promising candidates due to their earth abundance, high atom utilization, modified electronic structure, as well as their excellent activity in both alkaline and acidic media.13

Significant efforts have been devoted to design the atomically dispersed Fe/N/C catalysts.¹⁴⁻¹⁶ Metal Organic Framework (MOF) materials, which contain organic ligands and metal cations, are being widely employed as precursors and MOF-derived carbon generally hosts functional single-atomic metal active centers for electrocatalysis.¹⁷ However, synthesis of crystalline MOFs requires a large consumption of organic solvents, and generally during pryolysis of MOFs there is a lack of strategy to create hierarchically porous structures in the MOF-derived carbon materials. Most synthetic strategies of carbon-based electrocatalysts also unavoidably involve a high temperature pyrolysis of organic precursors, the introduction of inorganic interface is helpful to retain more Fe/N/C active sites during pyrolysis process.¹⁸⁻²⁰ For example, Joo and his coworkers¹⁸ reported a "silica-protective-layer-assisted" strategy to prepare catalytically active Fe-Nx sites and suppress the formation of large Fe-based particles. The SiO₂-protecting shell coated on carbonaceous nanofibers restricted free migration of iron species and led to formation of highly active Fe–Nx sites catalysts.²⁰ On the other hand, limited exposure of active sites and poor mass transport/electron transfer are still issues affecting the catalytic efficiency of Fe/N/C. It is highly desirable to construct hierarchically porous Fe/N/C catalysts, because high microporosity could act as host for Fe/N/C sites to boost the ORR catalytic properties and abundant meso- or macropores can promote the mass transport/electron transfer of ORR-related species (O₂, H₂O and proton) into the cathode.²¹⁻²³ Xu and coworkers²⁴ developed a silica-mediated MOF templating approach to prepare three-phase boundaries/interfaces with enhanced mass transport of reactants to single-atom iron sites, showing superior ORR performances in both alkaline and acidic electrolytes. Therefore, simultaneous control of atomically dispersed Fe/N/C and hierarchically porous structures of the catalysts is extremely attractive.

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Journal Name

Herein, we report a general approach for hierarchically porous metal/N/C nanospheres by nano-confined pyrolysis of in-situ formed amorphous metal-ligand complex. Instead of pre-synthesis of crystalline MOFs, solid phase organic ligands and metal salts are simply mixed with hierarchically porous silica nanosphere template, and then the mixture is subjected to pyrolysis. During the heating process, molten amorphous metal-ligand complex is formed and driven into the nanopores of the silica template by capillary force. and undergo pyrolysis within the nanopores. Due to the nanoconfinement effect after pyrolysis the derived carbon contains high nitrogen content, which can effectively coordinate with metal atoms, giving rise to single atomic metal active centers for electrocatalysis. After etching of the silica template, hierarchically porous metal/N/C nanospheres can be obtained. Typically hierarchally porous silica nanospheres (NKM-5),²⁵⁻²⁶ which contained ordered mesopores and secondary mesopores, was used as a hard template, providing nanospace for pyrolysis of amorphous Fe/Zn-(MeIm)₂ complex to obtain Fe/N/C hierarchically porous nanospheres (Fe/N/C-HP). The prepared Fe/N/C-HP exhibited a hierarchically porous structure with a high surface area of 1389 m² g⁻¹ and high N-doping content up to 9.4 at%. These unique structural features make Fe/N/C-HP an excellent ORR catalyst both in alkaline media and acidic media. Furthermore, the Fe/N/C-HP catalyst shows high long-term stability and methanol resistance. As an air cathode catalyst, the primary Fe/N/C-HP exhibits excellent electrocatalytic performance with high open-circuit voltage, high power density and discharge durability.

2. Results and discussion

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2.1 The fabrication of Fe/N/C-HP

The synthesis of Fe/N/C-HP catalyst is illustrated in Scheme 1. Briefly, a mixture of $ZnCl_2$, 2-methylimidazole (2-MeIM), ferrous oxalate, 1,10-phenanthroline hydrochloride (Phen) and NKM-5 (Fig. S3) were grinded to mix homogenously, and then was subjected to pyrolysis and template-eching (the details are described in Supporting Information).



Fig. 1. (a) XRD pattern of 2-MeIM and the grinded mixture after ball milling, (b) TGA curves of MIX and MIX–no-Zn²⁺ in N₂ atmosphere and (c) In situ XRD patterns of the formation for amorphous Fe/Zn-(MeIm)₂ complex.

Phen was measured. As a control, another mixed precursor of 2-MeIM, ferrous oxalate and Phen was prepared (denoted as MIX-no-Zn²⁺, i.e. without the addition of ZnCl₂). In the TG curve of MIX-no-Zn²⁺, 2-MeIM volatiles at ~200 °C without coordination assembly with Zn²⁺, leaving very low carbon yield. As for the MIX, the TG curve is quite different with greatly increased thermal stability, which can be attributed to the formation of Fe/Zn-(MeIm)₂ complex. In-situ variable temperature XRD was further performed to investigate the dynamic structure of the mixed precursors during heating process (Fig. 1c). The peaks of 2-MeIM became gradually weaker by increasing the temperature stepwise to ~200 °C, upon which 2-MeIM



Scheme 1. Schematic illustration of the preparation of hierarchically porous nanospheres Fe/N/C-HP.

As shown in the X-ray diffraction (XRD) spectra in Fig. 1a, after grinding the mixture exhibits intense diffraction peaks of 2-MeIM, indicating that Zn^{2+} does not react with 2-MeIm by neat grinding, which is in accordance with previous report.^{27, 28} TGA measurement was further performed to explore the detailed formation process of Fe/Zn-(MeIm)₂ complex (Fig. 1b). The TG curve of mixed precursors (denoted as MIX) containing ZnCl₂, 2-MeIM, ferrous oxalate and

was getting molten and then Fe/Zn-(Melm)₂ complex formed. Crucially, the in-situ XRD pattern exhibits no diffraction peaks when the temperature reaches to 400 °C, implying no long-range periodic order, i.e., the Fe/Zn-(Melm)₂ complex is amorphous.²⁹ The amorphous Fe/Zn-(Melm)₂ complex would be relatively easy to decompose compared with crystalline MOF due to the less thermal stable amorphous structure.³⁰ The molten amorphous Fe/Zn-

Journal Name

 $(Melm)_2$ complex is very important for the fabrication of hierarchically porous Fe/N/C nanospheres, as it would be driven into the hierarchical pores of the NKM-5 hard template via caplillary force. After pyrolysis and etching the silica template, hierarchically porous nitrogen-doped-carbon nanospheres (Fe/N/C-HP) were obtained and single-atom Fe was in situ anchored by nitrogen to form Fe/N/C sites in the porous carbon matrix (as discussed later below).

The presence of Zn^{2+} is crucial in the preparation. With only 2-MeIM and NKM-5, after pyrolysis no carbon was left (Fig. S4) as 2-MeIM was totally decomposed. Pyrolysis of mixture of NKM-5, 2-MeIM and ZnCl₂ (i.e. without the addition of iron source and Phen) gave rise to hierarchically porous N-doped carbon nanospheres (denoted as HPNC) (Fig. S5-S6). The spherical morphology of HPNC indicates that the pyrolysis of Zn-(MeIm)₂ complex took place within the NKM-5 template, implying that the molten Zn-(MeIm)₂ complex was firstly driven into the pores of NKM-5 by capillary force. With further addition of ferrous oxalate and Phen, molten Zn-(MeIm)₂ complex with inclusion of Fe-Phen complex would be driven into NKM-5 and finally Fe/N/C-HP was fabricated (Fig. S7-S9). To clarify the role of Zn²⁺ in amorphous Fe/Zn-(MeIm)₂ complex, a control synthesis was performed with similar procedure to that of Fe/N/C- after high-temperature pyrolysis. This result is consistent with the TG analysis of MIX-no-Zn²⁺, and demonstrates again the necessity of Zn²⁺ which coordinates with 2-MeIM to form molten Zn-(MeIm)₂ complex.

2.2. Physical characterizations of Fe/N/C-HP catalyst

The morphology and structure of catalysts were investigated by SEM and transmission electron microscopy (TEM). SEM images (Fig. S8) demonstrate that Fe/N/C-HP retains the original spherical morphology of NKM-5 template. TEM images of Fe/N/C-HP display a hierarchically nanoporous structure (Fig. 2a, 2b and Fig. S9), indicating that the amorphous Fe/Zn-(MeIm)₂ complex is fully driven into the mesopores of NKM-5, and this pyrolysis Fe/Zn-(MeIm)₂ complex by template confinement approach significantly promote synthesis of hierarchically porous carbon spheres. Interestingly, carbon nanospheres are mutually linked, which can enhance the electron transport pathway between the carbon nanospheres and accelerate the electron transfer during the electrocatalytic process.²⁴ Moreover, the corresponding energy dispersive X-ray (EDX) element mapping images revealed that the C, N and Fe elements are homogeneously distributed throughout the whole carbon architecture (Fig. 2d). No visible Fe nanoparticles or clusters are



Fig. 2. (a-c) TEM images and (d) corresponding EDX-mapping Fe/N/C-HP, (e, f) TEM images and corresponding element mappings of Fe/N/C/NC.

HP but in the absence of Zn²⁺, and only extremely low carbon residual was obtained, which was denoted as Fe₃C@NC (Fig. S10). The TEM images of Fe₃C@NC (Fig. S11) show irregular shaped carbon matrix with Fe-based nanoparticles encapsulated in graphitic carbon shells

observed in the high resolution TEM images of the Fe/N/C-HP (Fig. 2c and Fig. S9c-9d), indicating that the Fe atoms are atomically dispersed on the nitrogen-doped carbon nanospheres, as also proved by XAFS measurement discussed below. The Fe content of

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Fe/N/C-HP is 0.73 wt% by inductively coupled plasma optical emission spectroscopy (ICP-OES).

For comparison, a control sample named Fe/N/C/NC was prepared without NKM-5 template. As shown in SEM images (Fig. S12) and TEM images (Fig. 2e-2f), Fe/N/C/NC exhibits a bulk and irregular shaped carbon structure, which are decorated with Fe nanoparticles wrapped inside the carbon nanotubes. Fe NPs catalyze the growth of nanotubes and the graphitization of carbon during the pyrolysis process.³¹ In the case of Fe/N/C-HP, the free migration and growth of Fe nanoparticles would be largely restricted by the interface confinement effect in mesopores of NKM-5, thus leading to an optimization of atomically dispersed Fe-Nx and formation of hierarchically porous structure, which indicates inorganic silica (NKM-5) can stabilize metal sites by interface confinement effect.

The XRD pattern (Fig. 3a) of Fe/N/C-HP exhibits two broad peaks with 20 values of 25° and 44°, which can be indexed to (002) and (101) plane of graphitic carbon, respectively, suggesting an amorphous nature of carbon. Notably, no peaks associated with Fe or Fe-based compounds could be detected, further confirming the atomically dispersed Fe-Nx in the Fe/N/C-HP. Weak XRD peaks corresponding to the Fe₃C phase as well as the increase of graphitic carbon peaks are observed for the Fe/N/C/NC, which confirms the presence of crystalline phase and higher degree of graphitic carbon. Further insights into the defect structures in the carbon lattice of the catalysts are investigated by Raman spectra analysis (Fig. 3b). Two prominent peaks at around 1340 and 1590 cm⁻¹ can be observed and are generally ascribed to the disordered defective sp³ carbon (D-



Fig. 3. (a) XRD spectra and (b) Raman spectra of Fe/N/C-HP and Fe/N/C/NC, (c) N₂-adsorption/desorption isotherms and (d) pore size distribution curves of Fe/N/C-HP and Fe/N/C/NC.

band) and graphitic sp²-carbon (G-band), respectively.³² The Raman spectra of Fe/N/C-HP and Fe/N/C/NC could be deconvoluted with five bands including D1, D2, D3, D4 and G bands, which represent disordered graphitic lattice (graphene layer edges), disordered graphitic lattice (surface graphene layers), amorphous carbon fraction of soot, sp²-sp³ bonds or C–C and C=C stretching vibrations of polyene-like structures and ideal graphitic lattice, respectively.³³ The relatively higher area ratio of I_{D1}/I_G for Fe/N/C-HP with respect to Fe/N/C/NC (1.61 vs 1.53) implies the formation of more disordered carbon with defects, upon which FeNx structures are more likely to form for Fe/N/C-HP and thus enhances ORR activity.³⁴⁻³⁵ The decreasing I_{D1}/I_{G} ratio of Fe/N/C-HP samples with different temperature implies less defects and an increase of graphitization with the increased annealing temperatures. (Fig. S13). From the results of XRD and Raman, the interface confinement of template NKM-5 are beneficial for forming Fe-Nx active site and promoting the defective structure.

N₂ adsorption-desorption tests were performed to evaluate the textural and porous properties of the catalysts (Fig. 3c and 3d). Fe/N/C-HP exhibits a hybrid type of I and IV adsorption-desorption isotherms with a sharp uptake at relatively low pressure $(P/P_0 = 0)$ 0.015) and a hysteresis loop at a higher pressure ($P/P_0 = 0.70-0.95$). The sharp increase at $P/P_0 < 0.05$ indicates the existence of abundant micropores in carbon materials (Fig. 3d). The hysteresis loop at high relative pressure ($P/P_0 = 0.70-0.95$) reveals the presence of mesopores, which can be attributed to the nanopores at a range of 10-30 nm derived after removing the NKM-5 template. Fe/N/C/NC exhibits a hybrid type of I and IV adsorption-desorption isotherms, which contains micropores and particle piled pore structure. Micropores structure for both Fe/N/C-HP and Fe/N/C/NC may partially attributed to the pore-formation function of Zn vapor at a high pyrolysis condition. It is worth mentioning that the presence of the NKM-5 template is essential for the generation not only mesopore but also micropore structure in the carbon matrix, as verified by the carbon counterpart obtained by carbonizing Fe/Zn-(MeIm)₂ complex without a template. The template effect of NKM-5 facilitates the formation of mesopores and the interface confinement effect of NKM-5 makes the volatile gaseous substances difficult to leave, which facilitates the formation of micropores. The Brunauer-Emmett-Teller (BET) surface areas and pore volumes of Fe/N/C-HP and Fe/N/C/NC are listed in Table S1. Notably, compared with Fe/N/C/NC (871 m² g⁻¹ and 0.69 cm³ g⁻¹), Fe/N/C-HP shows a higher specific surface area (1389 m² g⁻¹) and a higher pore volume (1.52 cm³ g⁻¹), indicating abundant mesoporous structure due to the introduction of NKM-5 template. The nearly 50% improvement in the BET surface area of Fe/N/C-HP over Fe/N/C/NC might be one of the reasons for the enhancement of the ORR performance of Fe/N/C-HP. As expected, Fe/N/C-HP mainly contain micropores and mesopores, which is favorable for the formation of high density of active sites Fe-Nx and enlarge the electrolyte/catalyst contact area and promotes the O_2 diffusion during the ORR. Overall, our data confirm that the nano-confined pyrolysis of Fe/Zn-(MeIm)₂ complex produces hierarchically porous nanospheres sample with high surface area and large pore volume. All of these features are expected to facilitate mass/electronic transfer, increase active-site exposure and contribute to excellent ORR performance.

Journal Name

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Fig. 4. (a) XPS survey spectra, (b) N 1s spectra, (c) the contents of different kinds of nitrogen contents in Fe/N/C-HP and Fe/N/C/NC (d) Fe K-edge XANES of Fe/N/C-HP, Fe foil, FeO, and Fe₂O₃, (e) FT k²-weighted EXAFS spectra of Fe/N/C-HP and Fe foil and (f) Corresponding FT-EXAFS fitting curves of Fe/N/C-HP.

To gain deep insight into the surface composition and electronic state of the samples, X-ray photoelectron spectroscopy (XPS) analyses were performed. As expected, the survey spectra of the Fe/N/C-HP and Fe/N/C/NC reveal the existence of C, N, O and Fe elements (Fig. 4a). The corresponding atomic percentages of the above elements are listed in Table S2. Interestingly, the N content of Fe/N/C-HP (9.4 at%) is much higher than that of Fe/N/C/NC (6.0 at%) as NKM-5 helps to reserve more N species during the confinement pyrolysis process, which may promote uniformly distributed Fe to coordinate with nitrogen. As displayed in Fig. 4b, N 1s spectra can be deconvoluted into four different bands at 397.7, 399.0, 400.2 and 402.5 eV, corresponding to pyridinic N, pyrrolic N, graphitic N and oxidized N, respectively. The higher contents of pyridinic N (35.5%) in the N 1s XPS spectra for Fe/N/C-HP (Fig. 4c) facilitates the formation of Fe/N/C active sites with a tailored electronic structure.36 It has been demonstrated experimentally and theoretically, that carbon atoms next to pyridinic N with Lewis basicity plays an important role to promote intrinsic ORR activity of Fe/N/C moieties through adsorbed oxygen molecules on Lewis base sites.³⁷ The high-resolution C 1s spectrum are shown in the Fig. S14. The sp³/sp² ratio of Fe/N/C-HP is higher than that of Fe/N/C/NC, further confirming its rich defect structure, which are expected to facilitate ORR activity by modulate and tune the electronic of the catalyst.³⁸ No signal of Si (103.4 eV for Si 2p) in Fe/N/C-HP series can be observed, indicating that Si element was totally removed after HF treatment (Fig. S15). The content of nitrogen decreases with increasing pyrolysis temperature from 750 to 1050 °C, indicating a conversion from pyridinic N to graphitic N species with the increasing pyrolysis temperature (Fig. S15c). The weak signals of Fe element in Fe/N/C-HP and Fe/N/C/NC are mainly due to their low content (Fig. S16).

Synchrotron-radiation-based X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were measured to investigate the electronic structure and coordination information of Fe atoms for Fe/N/C-HP electrocatalyst. The Fe K-edge XANES spectra (Fig. 4d) show that the absorption edge of Fe/N/C-HP locates between standard FeO and Fe₂O₃, but closer to the edge of Fe_2O_3 , indicating that the valence of Fe in Fe/N/C-HP close to +3.39, 12 Besides, the pre-edge peak at about 7113 eV was assigned to the Fe-N₄ square-planar configuration with axial ligands.¹² In the Fourier transformed EXAFS spectrum of Fe/N/C-HP (Fig. 4e), the main peak at about 1.5 Å could be assigned to Fe-N(O) coordination, and the absence of the Fe-Fe coordination peak at 2.2 Å indicates the atomic dispersion nature of Fe.³⁸ By fitting of the first coordination shell the coordination number of Fe-N(O) is 5.1±0.3 (Fig. 4f and Table S3), and it would be proposed that in Fe/N/C-HP, the single atomic Fe coordinates with four nitrogen to form Fe-N₄ sites and with one oxygen from the adsorption of O₂ molecule (Fig. 4f).40

To explore the generalization of this synthesis approach, a series of M/N/C-HP (M = Co, Ni, Cu and Mn) were prepared using the solvent-free nano-confined pyrolysis method. The XRD patterns of all M/N/C-HP shows two broad peaks (Fig. S17), corresponding to the (002) and (100) planes of graphite. No metal-related peaks are observed in the XRD patterns. TEM images (Fig. S18-S21) of M/N/C-HP ascertain no metal clusters or nanoparticles were present in hierarchically porous carbon nanospheres and EDX element mapping for M/N/C-HP further confirms a homogeneous dispersion of M and N over the N-doped carbon frameworks, which indicates the versatility and feasibility of this nano-confined pyrolysis approach for the preparation of hierarchically porous carbon nanospheres with Ncoordinated metal species.



Fig. 5. (a) LSV curves of Fe/N/C-HP, Fe/N/C/NC and Pt/C recorded in O₂-saturated 0.1 M KOH solution with a rotation rate of 1600 rpm, (b) $E_{1/2}$ and J_k at 0.9 V for Fe/N/C-HP, Fe/N/C/NC and Pt/C, (c) Tafel plots of Fe/N/C-HP, Fe/N/C/NC and Pt/C, (d) Electron transfer number and H_2O_2 yield plots of of the Fe/N/C-HP and Pt/C, (e) I–t chronoamperometric responses for Fe/N/C-HP and Pt/C at 1600 rpm with methanol injection and (f) I–t chronoamperometric responses for durability tests of Fe/N/C-HP and Pt/C in O₂-saturated 0.1 M KOH. ORR current density obtained from current divided by geometric area of electrode surface.

2.3 ORR electrocatalytic performance of Fe/N/C-HP

The ORR performance of Fe/N/C-HP is firstly evaluated by linear sweep voltammetry (LSV) in an O2-saturated 0.1 M KOH solutions with a scan rate of 5 mV s⁻¹ and a rotating rate of 1600 rpm. As indicated by the LSV tests in Fig. 5a, Fe/N/C-HP displays a superior ORR activity with a half-wave potential of 0.90 V, higher than that of the state-of-art commercial Pt/C ($E_{1/2}$, 0.85 V) and comparable to the most reported activities of various types of Fe/N/C catalysts⁴¹⁻⁴³ (Table S4). Similar comparisons are also performed for Fe/N/C-HP samples under different pyrolysis temperature (Fig. S22). The kinetic current density (J_k) of 5.3 mA cm⁻² at 0.9 V for Fe/N/C-HP exceeds that of Pt/C (1.1 mA cm⁻²) by a factor of ~5 (Fig. S23). The hierarchical pores structure of Fe/N/C-HP can accelerate the electron transfer, which manifests that Fe/N/C-HP has a better ORR kinetics. The kinetic performance is further evaluated by the Tafel plots (Fig. 5c). The Tafel slope of Fe/N/C-HP at low overpotential was determined to be 57.5 mV dec⁻¹, which is lower than that of Pt/C (65.3 mV dec-1), further suggesting a faster ORR kinetics on Fe/N/C-HP electrocatalyst. For comparison, Fe/N/C/NC exhibits a degraded ORR activity with an $E_{1/2}$ of 0.83 mV, which is 70 mV lower than that of Fe/N/C-HP (Fig. 5a). The slower ORR kinetics in Fe/N/C/NC is revealed by smaller J_k (0.7 mA cm⁻² at 0.9 V) and larger Tafel slope (70.9 mV dec⁻¹) (Fig. 5b, 5c). These results demonstrate the construction of hierarchically porous structure of Fe/N/C-HP can efficiently improve ORR activity and accelerate ORR kinetics. Further, the electrochemical double-layer capacitance (Cdl) is determined upon the cyclic voltammetry (CV) curves in a non-Faradic potential range (Fig. S24). Fe/N/C-HP has a much larger C_{dl} value of 7.3 mF than that of Fe/N/C/NC (3.6 mF), with corresponding larger electrochemical active surface area (ECSA) of 182.5 cm⁻² than that of

Fe/N/C/NC (90.0 cm⁻²), which could be likely a reason for the improved ORR performance.⁴⁴ The specific activity normalized to the corresponding ECSA is also used to evaluate the intrinsic activity of the resulting catalysts, and Fe/N/C-HP exhibits high specific activities of 5.7×10^{-3} mA cm⁻²_{ECSA} at 0.9 V for ORR, which can be comparable to other state-of-the-art ORR catalysts (such as np-MnO₂-ns catalyst with 8.4 ×10⁻³ mA cm⁻²_{ECSA} at 0.8 V vs RHE⁴⁵ and Cu SAs/N-C with 5×10^{-3} mA cm⁻² at 0.9 V vs RHE⁴⁶).



Fig. 6. (a) LSV curves of Fe/N/C-HP, Fe/N/C/NC and Pt/C recorded in O_2 -saturated 0.1 M HClO₄ solution with a rotation rate of 1600 rpm, (b) $E_{1/2}$ and J_k at 0.8 V for Fe/N/C-HP, Fe/N/C/NC and Pt/C, (c) Tafel plots of Fe/N/C-HP, Fe/N/C/NC and Pt/C, (d) Electron transfer number and H_2O_2 yield plots of the Fe/N/C-HP and Pt/C, (e) I–t chronoamperometric responses for Fe/N/C-HP and Pt/C at 1600 rpm with methanol injection and (f) I–t chronoamperometric responses for durability tests of Fe/N/C-HP and Pt/C in O_2 -saturated 0.1 M HClO₄. ORR current density obtained from current divided by geometric area of electrode surface.

The electron transfer mechanism of Fe/N/C-HP, RDE experiments at different rotating speeds are operated and the related Koutecky-Levich (K-L) plots are acquired (Fig. S25). The LSV curves present good linearity and the electron transfer number is calculated to be 4 in the potential range 0.3-0.6 V, manifesting a four-electron pathway, suggesting first-order reaction kinetics for ORR.47 Moreover, the electron transfer number is higher than that of Fe/N/C/NC (3.05-3.14). Then, the H₂O₂ yield of Fe/N/C-HP and Pt/C conducted by RRDE technique is calculated to be less than 5.0% with the electron transfer number (n) of nearly 4.00 within the potential range from 0.2 to 0.8 V, indicating an efficient four-electron oxygen reduction reaction for Fe/N/C-HP and Pt/C. The effect of different dosage of Fe precursor contents on the ORR activity of Fe/N/C-HP is also assessed. As shown in Fig. S26, the half-wave potential gradually increases along with increased Fe content and Fe/N/C-HP exhibits the highest $E_{1/2}$ (0.90 V). The performance of the counterpart of HPNC (prepared without iron precursor) is far worse, indicating the significance of Fe-Nx sites in ORR. As displayed in Fig. 5e, the ORR polarization curves of Fe/N/C-HP shows negligible decay in comparison with sharply decreased current density of Pt/C after injecting methanol, demonstrating the excellent methanol tolerance of Fe/N/C-HP. The long-term durability of catalysts is further evaluated by chronoamperometric measurement in O2-saturated 0.1 M KOH solution (Fig. 5f). After running for 40 000 s, the Fe/N/C-HP catalyst retains more than 94.8% of its relative current, while only 82.6% current retention is observed for Pt/C catalyst, showing the outstanding durability of Fe/N/C-HP in alkaline solutions.

The morphology and element composition of Fe/N/C-HP catalyst after the durability test in alkaline solution are investigated by TEM, HRTEM, EDX-mapping and XPS analysis. The TEM images (Fig. S27-28) of Fe/N/C-HP maintain the original carbon nanosphere structure after the stability test, emphasizing the impressive structural robustness after running for 40 000 s. The Fe, N and C elements are still homogeneously distributed over the hierarchically porous Ndoped carbon nanospheres in the element mapping for Fe/N/C-HP. The element contents derived from XPS survey were shown in Fig. S29. The carbon content of Fe/N/C-HP decreased from 85.0 to 80.8 at%, while the oxygen content increased from 5.2 to 12.5 at% before and after ORR test, which can be attributed to the weak oxidation of carbon. The amounts of N and Fe for pristine Fe/N/C-HP were 9.4 and 0.42 at%, whereas those of N and Fe for Fe/N/C-HP after ORR were 6.3 and 0.39 at%, respectively. The relative intensity of the N 1s peaks for pyridinic N, pyrrolic N, graphitic N and oxidized N components remained largely constant and there is no obvious Fe leaching after ORR durability. It should be noted that pyridinic N could anchor atomically dispersed Fe-based active site and prevent the leaching of Fe, which resultes in this outstanding ORR durability in 0.1 M KOH.⁴⁸⁻ 49

As shown in Fig. S30, all the prepared M/N/C-HP (M=Co, Cu, Mn and Ni) catalysts are used as ORR electrocatalysts, which exhibit high electrocatalytic activity for the ORR in alkaline media, revealing this application to develop highly efficient M/N/C materials as alternatives for oxygen electrodes or other related fields.

The ORR performance of Fe/N/C-HP in acidic electrolyte (0.1 M HClO₄) is also assessed using RDE technique (Fig. 6). Fe/N/C-HP exhibited an $E_{1/2}$ of 0.78 V, which is comparable to of Pt/C (0.83 V) and much better than that of Fe/N/C/NC (0.71 V). Fe/N/C-HP has a smaller Tafel slope of 56.6 mV dec⁻¹ compared to Pt/C (84.2 mV dec⁻¹), Fe/N/C/NC (73.2 mV dec⁻¹) (Fig. 6c), which reveals that Fe/N/C-HP has a better ORR kinetics. Furthermore, the favorable ORR kinetics of Fe/N/C-HP is also verified by higher J_k of 2.9 mA cm⁻² than those of Fe/N/C/NC (0.5 mA cm⁻²) at 0.8 V (Fig. 6b and Fig. S31). Furthermore,



Fig. 7. (a) Schematic illustration of an as-assembled Zn–air battery, (b) Photograph of the Fe/N/C-HP-based Zn–air battery with an open-circuit voltage of 1.484 V, (c) Discharge polarization curves and corresponding power density plots of the Zn–air batteries using Fe/N/C-HP and Pt/C as air electrode, respectively and (d) Long-time galvanostatic discharge curves of a Zn–air battery.

the C_{dl} were 8.5 mF for Fe/N/C-HP and 3.9 mF for Fe/N/C/NC, (Fig. S32) corresponding to the ECSA of 425.0 cm² for Fe/N/C-HP and 195.0 cm² for Fe/N/C/NC. Fe/N/C-HP exhibits specific activity of 1.3×10⁻³ mA cm⁻² higher than that of 0.8×10⁻⁴ mA cm⁻² at 0.8 V for Fe/N/C/NC and comparable to some reported values⁵⁰. The electron transferred number of Fe/N/C-HP, calculated from the slopes of K-L plots, is 3.73-3.78 at different rotating speeds (Fig. S33). Furthermore, the average H₂O₂ yield of Fe/N/C-HP is below 6.0% over the potential range from 0.2 to 0.8 V. These observations implied four-electron reduction path on Fe/N/C-HP for ORR in acidic electrolyte, matched well with the K-L plot results. Fe/N/C-HP samples under different pyrolysis temperature (Fig. S34) and Fe contents (Fig. S35) show that Fe/N/C-HP exhibits the most excellent ORR activity. This Fe/N/C-HP catalyst shows excellent methanol tolerance compared to Pt/C in acidic electrolyte. As for stability test, Fe/N/C-HP retains 95.4% of its initial ORR performance after 40 000 s, which is much better than that of Pt/C (73.5%). After ORR durability test in 0.1 M HClO₄, the TEM and HRTEM shows no obvious structure changes for the carbon nanosphere (Fig. S36). The XPS study shows that the C and O contents in the pristine Fe/N/C-HP are 85.0 and 5.2 at%, respectively (Fig. S37). The ratio changes to 72.1 and 20.8 at% after cycling, indicating that carbon oxidation or corrosion during the ORR durability test,⁵¹ which also leads to leaching of the elements involved in the structures of Fe and N in parallel to carbon oxidation.

It has been proposed that carbon oxidation would induce losing of Fe-N-C sites, leading to reduced ORR activity. $^{52\cdot53}$

To ascertain the nature of active sites for the excellent ORR, SCN⁻ poisoning experiment is employed to act as a probe to poison Fe/N/C catalysts.⁵⁴ Upon the addition of KSCN solution into 0.1 M HClO₄, the deactivation of Fe/N/C-HP in acidic media occurred with significantly decreased half-wave potential (Fig. S38), clearly manifesting that ionic iron coordinated with nitrogen embedded in carbon matrix are responsible for the excellent ORR performance of Fe/N/C-HP. The superior ORR performance of the Fe/N/C-HP could be ascribed to the following key aspects. Firstly, hierarchically porous NKM-5 confined pyrolysis could effectively trap large amount of nitrogen species to anchor atomically dispersed FeNx, holding great potentials in the excellent performance. Meanwhile, the increased micropores could host much Fe-Nx mojeties and afford more accessible active sites. Furthermore, Fe/N/C-HP with rich mesoporous structure derived from hierarchically porous silica could afford a facilitated mass transport of electrolytes and reactants during the ORR process. The linked carbon nanospheres are beneficial to electron transfer,55 which is revealed by larger current densities. All above profitable features endow the Fe/N/C-HP a promising ORR electrocatalyst with superior electrocatalytic activity and stability in both alkaline and acidic media.

To evaluate the practical application of the Fe/N/C-HP electrocatalyst in energy devices, a primary Zn-air battery was

constructed using Fe/N/C-HP on carbon paper as the cathode electrocatalyst (Fig. 7) and Zn foil as anode in a 6.0 M KOH electrolyte containing 0.2 M Zn(Ac)₂. Fe/N/C-HP exhibits a higher open-circuit potential (1.484 V) of the Zn-air battery than that of Pt/C (1.438 V), indicating the excellent catalytic performance of Fe/N/C-HP. Meanwhile, Fe/N/C-HP displays a higher peak power density of 181 mW cm⁻², higher than the value of 133 mW cm⁻² with Pt/C. Fe/N/C-HP exhibited stable performance in the long time galvanostatic discharge test under currents of 10 mA cm⁻² without noticeable voltage variation, indicating the excellent stability of Fe/N/C-HP in the Zn-air battery.

3. Conclusions

We developed a nano-confined pyrolysis approach for preparation of hierarchically porous FeNx doped carbon nanospheres. Two factors are crucial to the successful construction of the hierarchically porous carbon nanospheres, namely the confinement of NKM-5 and ligand molten-induced amorphous Fe/Zn-(MeIm)₂ complex. Molten Fe/Zn-(MeIm)₂ complex can contact well with NKM-5 and replicate its morphology. Furthermore, NKM-5 interfaces confinement effect can also inhibit Fe agglomeration under pyrolysis process and trap nitrogen to coordinate with Fe atoms. Thanks to the high N-doping level, hierarchically porous structure and good mass/proton transport, the catalyst exhibits excellent electrocatalytic activity for ORR with good stability and excellent tolerance to methanol. Meanwhile, the high-activity of Fe/N/C-HP electrocatalyst endowed the as-assembled Zn-air battery with excellent power density and discharge durability. We further demonstrate the general applicability of this synthetic strategy with respect to other atomically dispersed metal including Co, Cu, Ni and Mn. Taken into account different kinds of excellent electrocatalysts prepared by pyrolysis of specially designed organic/metal precursors or MOFs, this work may provide an alternative method to further endow hierarchical porosity and well-defined morphology to those carbon electrocatalysts for improving performance in energy conversion and storage applications.

Conflicts of interest

The authors declare no competing financial interests.

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