Zinc-Mediated Template Synthesis of Fe-N-C Electrocatalysts with Densely Accessible Fe-N_x Active Sites for Efficient Oxygen Reduction

Guangbo Chen, Pan Liu, Zhongquan Liao, Fanfei Sun, Yanghua He, Haixia Zhong, Tao Zhang, Ehrenfried Zschech, Mingwei Chen, Gang Wu, Jian Zhang,* and Xinliang Feng*

Owing to their earth abundance, high atom utilization, and excellent activity, single iron atoms dispersed on nitrogen-doped carbons (Fe-N-C) have emerged as appealing alternatives to noble-metal platinum (Pt) for catalyzing the oxygen reduction reaction (ORR). However, the ORR activity of current Fe-N-C is seriously limited by the low density and inferior exposure of active Fe-N_x species. Here, a novel zinc-mediated template synthesis strategy is demonstrated for constructing densely exposed Fe-N_x moieties on hierarchically porous carbon (SA-Fe-NHPC). During the thermal treatment of 2,6-diaminopyridine/ZnFe/SiO_2 complex, the zinc prevents the formation of iron carbide nanoparticles and the SiO_2 template promotes the generation of hierarchically pores for substantially improving the accessibility of Fe-N_x moieties after subsequent leaching. As a result, the SA-Fe-NHPC electrocatalysts exhibit an unprecedentedly high ORR activity with a half-wave potential (E_{1/2}) of 0.93 V in a 0.1 M KOH aqueous solution, which outperforms those for Pt/C catalyst and state-of-the-art noble metal-free electrocatalysts. As the air electrode in zinc–air batteries, the SA-Fe-NHPC demonstrates a large peak power density of 266.4 mW cm^{-2} and superior long-term stability. Therefore, the developed zinc-mediated template synthesis strategy for boosting the density and accessibility of Fe-N_x species paves a new avenue toward high-performance ORR electrocatalysts.

With rapid depletion of fossil fuels and growing environmental concerns, electrochemical energy storage and conversion technologies have emerged as promising pathways for developing clean energy devices.[^1-3] Electrochemical oxygen reduction reaction (ORR) plays a crucial role in next-generation energy storage and conversion systems, e.g., metal–air batteries[^4] and H_2-O_2 fuel cells.[^5,6] Up to now, platinum (Pt)-based catalysts still remain as benchmark electrocatalysts for catalyzing the ORR.[^7,8] Unfortunately, high cost, scarcity, and poor durability of Pt seriously hinder its widespread utilization in practical energy systems.[^9,10]

Among the various Pt-group-metal-free (PGM-free) catalysts, single iron atoms dispersed on nitrogen-doped carbon (Fe-N-C) electrocatalysts are the most promising candidates to replace Pt-based ORR catalysts.[^11-14] The single atomic (SA) iron coordinated nitrogen (Fe-N_x) moieties...
in the carbon matrix are commonly recognized as active centers for catalyzing sluggish ORR kinetics.\textsuperscript{[15–17]} Currently reported strategies for synthesizing Fe-N-C electrocatalysts unavoidably involve high-temperature pyrolysis of Fe- and N-containing precursors.\textsuperscript{[18,19]} However, during the thermal pyrolysis, Fe species tend to agglomerate and eventually form low-active Fe-based clusters and nanoparticles encapsulated in carbon shells (e.g., Fe,C@C NPs), which are difficult to be removed and thus seriously block the formation active Fe,N moieties (generally, SA Fe content in Fe-N-C is <1.0 wt%).\textsuperscript{[20,21]} Additionally, a large amount of Fe,N moieties encapsulated in the carbon matrix cannot participate in the ORR process as a result of their inaccessibility.\textsuperscript{[22]} The limited density of accessible Fe,N moieties seriously limits the ORR activity of the currently reported Fe-N-C electrocatalysts.

Here, we demonstrate a novel strategy for boosting the ORR activity of Fe-N-C electrocatalysts by construction of densely accessible Fe,N active sites in hierarchically porous carbon (SA-Fe-NHPC). The SA-Fe-NHPC was fabricated by the pyrolysis of nitrogen-rich 2, 6-diaminopyridine/Zn\textsuperscript{2+}/SiO\textsubscript{2} (DAP/ZnFe/SiO\textsubscript{2}, N/C = 3/5 in DAP) complex and subsequent etching treatment. The zinc can efficiently avoid the formation of Fe\textsubscript{3}C@C NPs during the high-temperature pyrolysis process and promote the generation of micropores. In addition, the SiO\textsubscript{2} were used as hard templates to fabricate mesoporous carbon nanostructure. Eventually, densely accessible Fe-N\textsubscript{x} active sites are achieved for SA-Fe-NHPC. As a result, the SA-Fe-NHPC shows a very large specific surface area of 1327 m\textsuperscript{2} g\textsuperscript{-1} and a high Fe content of 1.25 wt%. Benefiting from the high density and superb accessibility of the Fe-N\textsubscript{x} active sites, the SA-Fe-NHPC electrocatalyst performs a record ORR half-wave potential (E\textsubscript{1/2}) of 0.93 V (vs reversible hydrogen electrode (RHE)) in a 0.1 m KOH aqueous solution among the reported PGM-free electrocatalysts. Moreover, utilizing the SA-Fe-NHPC electrocatalyst as air electrode, the as-assembled Zn-air battery demonstrates a very high maximum power density of 266.4 mW cm\textsuperscript{-2} and outstanding stability over a period of 240 h.

As schematically illustrated in Figure 1a, the SA-Fe-NHPC was synthesized using a zinc-mediated pyrolysis process. First, DAP/ZnFe/SiO\textsubscript{2} solid composites were prepared by drying 15.0 g silica colloid solution (≈12 nm, 40%, Ludox HS40) containing 2.18 g DAP, 2.38 g Zn(NO\textsubscript{3})\textsubscript{2}⋅6H\textsubscript{2}O, and 0.40 g Fe(NO\textsubscript{3})\textsubscript{3}⋅9H\textsubscript{2}O (molar ratio of Zn/Fe = 8/1). The Zn and Fe ions easily coordinated with DAP molecules. Thereinto, the Zn nodes could serve as efficient space isolators to enlarge the distances of adjacent Fe atoms. Second, the obtained solid composites were thermally treated at 900 °C for 2 h under nitrogen atmosphere. At 900 °C, the Zn was easily vaporized and left rich micropores.\textsuperscript{[23]} Third, the carbonized sample was etched in hydrofluoric acid solution (10 wt%) for simultaneously removing the silica templates and unstable Fe-containing species (e.g., Fe NPs). After a second pyrolysis at 900 °C for 2 h in nitrogen atmosphere, the SA-Fe-NHPC electrocatalyst was eventually achieved. The SA-Fe-NHPC electrocatalyst can be synthesized with a high amount at the laboratory level (644 mg, Figure S1, Supporting Information). To probe the role of the Zn, the DAP/ZnFe/SiO\textsubscript{2} solid composites with different Zn contents (Zn/Fe molar ratio: 4/1, 6/1, 8/1, 10/1, and 12/1) were investigated for synthesizing SA-Fe-NHPCs. As depicted in Figures S2–S7 (Supporting Information), all the achieved SA-Fe-NHPCs displayed similar inter-connected porous nanostructures. The Fe contents were measured to be 1.07, 1.18, 1.25, 1.16, and 1.12 wt%, respectively, using inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Table S1, Supporting Information). For comparison, NHPC supported Fe-containing NPs (NP-Fe-NHPC) was synthesized in the absence of Zn(NO\textsubscript{3})\textsubscript{2}⋅6H\textsubscript{2}O. The Fe content in NP-Fe-NHPC was about 3.85 wt%. The NHPC was prepared without the utilization of Fe(NO\textsubscript{3})\textsubscript{3}⋅9H\textsubscript{2}O (Figure S8, Supporting Information). The FeNC was synthesized without the utilization of silica colloid.

The morphologies of the SA-Fe-NHPC were first examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As revealed in Figure 1b,c, abundant pores with an average diameter of ≈12 nm were observed on the SA-Fe-NHPC, which were consistent with the size of silica templates. Obviously, for the SA-Fe-NHPC, no NPs were detected in the TEM and high-angle annular dark-field scanning TEM (HAADF-STEM) images. Corresponding elemental mapping images (Figure 1d) and electron energy loss spectroscopy (EELS, Figure S9, Supporting Information) clearly indicated the homogeneous distribution of C, N, and Fe elements in SA-Fe-NHPC. Furthermore, the aberration-corrected HAADF-STEM image of SA-Fe-NHPC shows that the Fe atoms were atomically dispersed on the carbon support (Figure 1e). By contrast, plentiful NPs with a size of ≈20 nm existed in the NP-Fe-NHPC, which were confirmed to be Fe,C@C using the HRTEM (Figure S10, Supporting Information) and X-ray diffraction (XRD) analysis (Figure 2a). These results undoubtedly prove that the Zn can effectively avoid the formation of antiwashing Fe,C@C NPs.

To gain deep insight into the surface chemical composition and elemental bonding configuration of the SA-Fe-NHPC and NP-Fe-NHPC catalysts, X-ray photoelectron spectroscopy (XPS) analyses were conducted. The XPS survey spectra confirm the existence of C, N, and Fe in SA-Fe-NHPC and NP-Fe-NHPC (Figure S11, Supporting Information). The N content in SA-Fe-NHPC was determined to be as high as 5.60 wt%, thanks to the nitrogen-rich DAP precursor (Figure S12, Supporting Information). The high-resolution N 1s spectrum of SA-Fe-NHPC was deconvoluted into five types of N species, corresponding to pyridinic N (398.5 eV), Fe-N\textsubscript{c} (399.2 eV), pyrrolic N (400.3 eV), graphitic N (401.2 eV), and oxidized N (402.7 eV), respectively (Figure S13, Supporting Information).\textsuperscript{[24]} The high-resolution C 1s spectrum of SA-Fe-NHPC displays four peaks at 289.8, 287.8, 286.2, and 284.6 eV, which can be assigned to C=O, C–O, N, and C–C group, respectively (Figure S14, Supporting Information). The high-resolution Fe 2p XPS spectrum further reveals that no signal of metallic Fe was detected in the SA-Fe-NHPC. The Fe 2P\textsubscript{3/2} peak was at 711.6 eV, which situated between Fe\textsubscript{0} (710.7 eV) and Fe\textsuperscript{2+} (712.7 eV), suggesting that the Fe in SA-Fe-NHPC was ionic Fe\textsuperscript{3+} (0 < δ < 2) (Figure S15, Supporting Information).\textsuperscript{[25]} Then, synchrotron-radiation-based X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were carried out to investigate the electronic structure and coordination information of the SA-Fe-NHPC electrocatalyst. The C K-edge EXAFS spectrum of SA-Fe-NHPC confirmed the existence of C-N-C in
For the N K-edge spectrum of SA-Fe-NHPC, three obvious peaks were observed at 400.1, 402.5, and 408.4 eV, which correspond to a $\pi^*$-transition of the pyridinic N sites, $\pi^*$-transition of the graphitic N sites, and $\sigma^*$-transition of the C-N bonds, respectively (Figure 2b). For the Fe K-edge spectrum, the XANES profile of SA-Fe-NHPC in Figure 2c further confirmed that the Fe atoms in SA-Fe-NHPC were in a low-valent state. From the Fourier-transformed (FT) $k^3$-weighted EXAFS (Figure 2d), one main peak located at $\approx 1.5$ Å was observed, which was attributed to the Fe-N first coordination shell. Comparing with Fe foil, and NP-Fe-NHPC, the Fe-Fe coordination peak at $\approx 2.2$ Å was not detected on SA-Fe-NHPC, revealing the atomic dispersion nature of Fe. The Raman spectrum of the carbon lattice (Figure S16, Supporting Information). For the N K-edge spectrum of SA-Fe-NHPC, three obvious peaks were observed at 400.1, 402.5, and 408.4 eV, which correspond to a $\pi^*$-transition of the pyridinic N sites, $\pi^*$-transition of the graphitic N sites, and $\sigma^*$-transition of the C-N bonds, respectively (Figure 2b). For the Fe K-edge spectrum, the XANES profile of SA-Fe-NHPC in Figure 2c further confirmed that the Fe atoms in SA-Fe-NHPC were in a low-valent state. From the Fourier-transformed (FT) $k^3$-weighted EXAFS (Figure 2d), one main peak located at $\approx 1.5$ Å was observed, which was attributed to the Fe-N first coordination shell. Comparing with Fe foil, and NP-Fe-NHPC, the Fe-Fe coordination peak at $\approx 2.2$ Å was not detected on SA-Fe-NHPC, revealing the atomic dispersion nature of Fe. The Raman spectrum of
SA-Fe-NHPC shows two peaks at 1350 and 1590 cm$^{-1}$, which are assigned to disordered sp$^3$ carbon (D band) and graphitic sp$^2$ carbon (G band), respectively (Figure S17, Supporting Information).

Next, nitrogen-sorption analysis was applied to assess the porous properties of the SA-Fe-NHPC, NP-Fe-NHPC and FeNC catalysts (Figure 2e). Both SA-Fe-NHPC and NP-Fe-NHPC displayed a steep increase in $V_{\text{ads}}$ at a relatively low N$_2$ pressure ($P/P_0 = 0–0.015$) and a well-defined hysteresis loop at a higher N$_2$ pressure ($P/P_0 = 0.4–0.95$), reflecting the coexistence of micropores and mesopores.\[31\] The Brunauer–Emmett–Teller (BET) surface area and the total pore volume of SA-Fe-NHPC were measured to be 1327 m$^2$ g$^{-1}$ and 2.7 cm$^3$ g$^{-1}$, which are much larger than 971 m$^2$ g$^{-1}$ and 0.7 cm$^3$ g$^{-1}$ for NP-Fe-NHPC and 435 m$^2$ g$^{-1}$ and 0.2 cm$^3$ g$^{-1}$ for FeNC (Figure S18, Supporting Information). A detailed pore structure analysis revealed that SA-Fe-NHPC showed a more pronounced microporous/ mesoporous structure in comparison to that of NP-Fe-NHPC (Figure 2f). The specific mesopore and micropore surface areas of SA-Fe-NHPC are 896 and 297 m$^2$ g$^{-1}$, which are larger than 678 and 126 m$^2$ g$^{-1}$ for NP-Fe-NHPC.

The electrocatalytic ORR performance of SA-Fe-NHPC was investigated by cyclic voltammetry (CV, Figure S19, Supporting Information) and linear sweep voltammetry (LSV) in an O$_2$-saturated 0.1 m KOH solution. For comparison, a commercial Pt/C catalyst (20% Pt, Fuelcellstore), NP-Fe-NHPC, NHPC and FeNC were evaluated. All potentials were referenced to the RHE. As revealed in Figure 3a and Figures S20–S22 (Supporting Information), the SA-Fe-NHPC catalyst demonstrated the highest ORR activity with an onset potential of \( \approx 1.01 \) V. The $E_{1/2}$ of SA-Fe-NHPC was up to 0.93 V (Figure 3b), which was much higher than those for Pt/C (0.85 V), NP-Fe-NHPC (0.88 V), NHPC (0.84 V), FeNC (0.85 V, Figure S22, Supporting Information) and reported PGM-free electrocatalysts ($E_{1/2} < 0.91$ V, Table S2, Supporting Information). The corresponding Tafel slope of SA-Fe-NHPC was determined to be \( \approx 57.2 \) mV decade$^{-1}$, which was considerably lower than 83.2 mV decade$^{-1}$ for Pt/C, indicating that the SA-Fe-NHPC electrocatalyst manifested accelerated ORR kinetics (Figure S23, Supporting Information). The diffusion-limiting current density ($J_l$) of SA-Fe-NHPC was measured to be 6.0 mA cm$^{-2}$ at 0.7 V, outperforming the value for NP-Fe-NHPC (5.5 mA cm$^{-2}$), due to the abundant hierarchically porous structure for efficient O$_2$ diffusion and transportation.\[32\] Meanwhile, the kinetic current density ($J_k$) of SA-Fe-NHPC reached 57.2 mA cm$^{-2}$ at 0.85 V, which was 10.8 times higher than 5.3 mA cm$^{-2}$ for Pt/C (Figure 3b). To further probe the ORR kinetics, rotating disk electrode (RDE) measurement at different rotation speeds were operated and the related Koutecký–Levich (K-L) plots were acquired (Figure 3c). The inset in Figure 3c shows the linear and almost parallel K-L plots at different applied potentials, suggesting a first-order reaction kinetics toward the concentration of dissolved oxygen and a similar electron transfer number at the SA-Fe-NHPC electrode.\[33\] The electron transfer number was calculated to be 3.98 at 0.4 V, evidencing that SA-Fe-NHPC preferred a four-electron oxygen reduction process.\[34\] Moreover, this value was higher than those of Pt/C (3.96), NP-Fe-NHPC (3.92), and NHPC.
To quantitate the ORR pathway, a rotating ring-disk electrode (RRDE) technique was conducted to monitor the formation of H2O2 during the ORR process. The H2O2 yield of SA-Fe-NHPC was below 5% at the potential range from 0.4 to 0.9 V, indicating the superior selectivity of the oxygen reduction toward H2O (Figure 3d). As a comparison, the ORR activity of various SA-Fe-NHPCs with different Fe contents (1.07, 1.18, 1.25, 1.16, and 1.12 wt%) were investigated in an O2-saturated 0.1 M KOH aqueous solution. As shown in Figure S27 (Supporting Information), the half-wave potential of SA-Fe-NHPC gradually increased along with increased Fe content. The SA-Fe-NHPC exhibited the highest $E_{1/2}$ (0.93 V) for a Fe content of 1.25 wt%, proving the crucial role of the Fe-Nx moieties for catalyzing the ORR.

The electrocatalytic durability is another key criterion for accessing the ORR performance of an electrocatalyst. As shown in Figure 3e, after 10 000 cyclic voltammetry (CV) scans between 0.6 and 1.0 V at a scan rate of 50 mV s⁻¹ in 0.1 M KOH under O2 atmosphere, the $E_{1/2}$ of the SA-Fe-NHPC only decreased by 1 mV, unambiguously demonstrating its superior durability. In addition, methanol tolerance was evaluated using i–t chronoamperometry (CA) tests. As displayed in Figure 3f, in comparison with sharply decreased current density of Pt/C after injecting 2% (v/v) methanol, the current density of SA-Fe-NHPC showed negligible decay, reflecting its excellent methanol tolerance.

To evaluate its practical application of the SA-Fe-NHPC electrocatalyst in energy devices, a primary Zn–air battery was assembled utilizing SA-Fe-NHPC as the oxygen electrocatalyst on air electrode in a 6.0 M KOH electrolyte containing 0.2 M Zn(Ac)2 (Figure 4a). As depicted in Figure 4b and Figure S28 (Supporting Information), the open-circuit voltage of the SA-Fe-NHPC was as large as ≈1.52 V, which was close to the theoretical value of 1.65 V. The maximum power density of the SA-Fe-NHPC was up to 266.4 mW cm⁻² (Figure 4c), which considerably exceeded 154.1 mW cm⁻² for Pt/C and those for the previously reported oxygen electrocatalysts, e.g., 3D N and P codoped mesoporous carbon (55 mW cm⁻²), nanocarbon meso/micro-FeCo-Nx-CN (150 mW cm⁻²), atomic Co-Nx-C in hierarchical graphene (152 mW cm⁻²), Mn/Fe-HIB-MOF (195 mW cm⁻²), Fe-N4 SAs/NPC (232 mW cm⁻²) (Table S3, Supporting Information). Meanwhile, the SA-Fe-NHPC electrocatalyst based Zn–air battery delivered a specific capacity of 795.3 mAh gZn⁻¹ at 10 mA cm⁻², corresponding to ~96.9% utilization of the theoretical capacity (~820 mAh gZn⁻¹) (Figure 4d). In addition, the SA-Fe-NHPC electrocatalyst could stably work in a mechanically rechargeable battery by only refueling the consumed zinc anode and electrolytes at the end of each discharge. Significantly, no noticeable degradation was observed after 10 cycles over a period of 240 h at a current density of 20 mA cm⁻², highlighting the superior durability of the SA-Fe-NHPC electrocatalyst (Figure 4e and Figure S29, Supporting Information). Moreover, such Zn–air batteries steadily lighted up red light-emitting diodes (LEDs) in series more than ten days, promising their potential utilization for powering electronic devices (Figure S30, Supporting Information).

Additionally, the SA-Fe-NHPC electrocatalyst also demonstrated good ORR activity with an $E_{1/2}$ of 0.76 V in acidic solution (Figure S31 and Table S4, Supporting Information). When used for cathode catalyst in proton exchange membrane fuel cell (PEMFC), the SA-Fe-NHPC could generate a peak power density of 0.423 and 0.244 W cm⁻² under H2–O2...
and H₂–air condition, respectively (Figure S32, Supporting Information).

In conclusion, a hierarchically porous SA-Fe-NHPC electrocatalyst featuring with dense and highly accessible Fe-Nₓ active sites has been designed and synthesized using a zinc-mediated template synthesis strategy. The achieved SA-Fe-NHPC exhibited excellent ORR activity in alkaline solution, which is superior to those of commercial Pt/C and reported PGM-free electrocatalysts. Meanwhile, the high-activity of SA-Fe-NHPC electrocatalyst endowed the as-assembled Zn–air battery with superior discharge ability and durability. Therefore, the viable design of Fe-N-C electrocatalyst with densely accessible active sites not only provides a promising alternative to the Pt catalysts for ORR but also paves a new way for exploring highly active electrocatalysts for other energy-conversion-related catalytic reactions, for example, CO₂ reduction, water splitting, and N₂ fixation.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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accessible active sites, Fe-N-C catalysts, oxygen reduction reaction, zinc-mediated synthesis, Zn-air batteries

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