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Hierarchical 3D porous carbon with facilely accessible Fe–N₄ single-atom sites for Zn–air batteries†

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Here, we report a highly efficient ORR electrocatalyst with Fe–N₄ active sites uniformly dispersed on a three-dimensional (3D) interconnected porous nitrogen-doped carbon network synthesized by pyrolyzing SiO₂@ZIF-8 composites loaded with iron salts. The as-prepared single-atom Fe 3D-ordered mesoporous carbon (SA-Fe-3DOMC) possesses a high specific surface area of 1357.8 m² g⁻¹ and a high Fe loading of 0.84 wt% as well. Benefiting from these favourable structural properties, SA-Fe-3DOMC exhibits a superior ORR half-wave potential ($E_{1/2}$) of 0.901 V and negligible activity loss (only 3 mV) after 10 000 cycles in alkaline media, surpassing the state-of-the-art Pt/C electrocatalyst. Particularly, an integrated zinc–air battery with SA-Fe-3DOMC as the air electrode shows a remarkable peak power density (140 mW cm⁻²) and a high specific capacity (786.6 mA h g⁻¹), demonstrating great potential for practical application.

Zinc–air batteries (ZABs) have received significant attention as promising next-generation batteries because of their high power density, high specific energy, low cost, environmental friendliness and good safety.^{1–3} However, the oxygen reduction reaction (ORR) at the cathode is subject to sluggish kinetics and usually requires high overpotentials.⁴ In order to speed up the ORR and make ZABs more energy-efficient, suitable electrocatalysts are always needed.^{5–7} Although precious metals and their alloys remain as outstanding candidates for catalyzing the ORR, their practical applications have been significantly hampered by the prohibitive cost and scarcity of precious

metals.^{8–12} Therefore, it is important to develop high-performance inexpensive catalysts to replace precious metals.^{13,14}

To date, Fe single-atom catalysts (SACs) dispersed as Fe–N₄ active sites on a porous carbon matrix have been regarded as one of the most efficient ORR electrocatalysts owing to their high activity, durable stability and maximum atom utilization.^{15–17} In general, Fe SACs can be obtained by direct pyrolysis of mixtures of N- and C-containing precursors and Fe salts, followed by acid washing.^{18,19} However, iron species are prone to agglomerate during the pyrolysis process, forming iron-based nanoparticles or clusters that are difficult to remove, thus blocking the formation of Fe–N₄ active sites.²⁰ Moreover, inaccessible pores will be generated owing to the random mixing of the N–C precursors and Fe salts. This leads to some buried Fe–N₄ active sites that cannot be exposed at the three-phase interface, thus reducing the utilization of Fe SACs.^{21–24} Thus, an ideal Fe SAC should possess highly accessible Fe–N₄ active sites and a porous network that can facilitate the transport of electrons, oxygen and water.²⁵ A three dimensional (3D) ordered porous architecture with open channels would be suitable to maximize the accessibility of active sites, but suffers from the limitation of a low specific surface area and cannot support more Fe–N₄ active sites.^{26,27} Considering these issues collectively, a 3D-ordered large-pore structure with suitable micropores and mesopores will be highly desirable, which facilitates the exposure of active sites and mass transfer.^{28–30}

Herein, we have designed 3D-ordered porous nitrogen-doped carbon with accessible Fe–N₄ active sites as an efficient electrocatalyst for the ORR. Remarkably, the as-prepared SA-Fe-3DOMC possessed a high specific surface area of 1357.8 m² g⁻¹ and a high Fe loading (0.84 wt%). The electrochemical results demonstrated that SA-Fe-3DOMC exhibited excellent ORR catalytic activity and stability, with $E_{1/2}$ increased to 0.901 V while the current almost remained similar after 10 000 potential cycles from 0.6 V to 1 V in alkaline media. Furthermore, an integrated ZAB with SA-Fe-3DOMC as the air electrode showed a remarkable peak power density (140 mW cm⁻²) and a high

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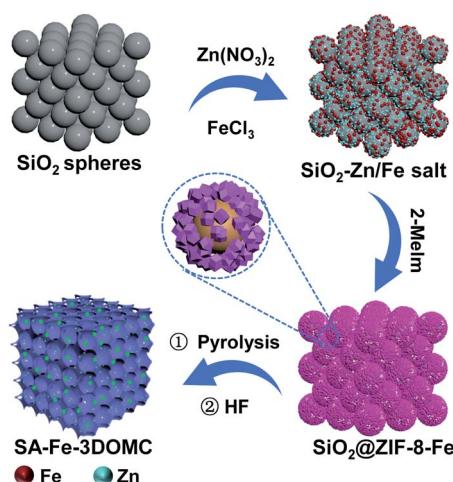
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specific capacity ($786.6 \text{ mA h g}^{-1}$), demonstrating great potential for practical application.

The synthetic procedure of the SA-Fe-3DOMC catalysts is illustrated in Scheme 1. Briefly, silica nanospheres with a size of 180–200 nm were first modified with Fe^{3+} ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and Zn^{2+} ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Fig. S1a, ESI†). The subsequent *in situ* growth of ZIF-8 embedded the silica nanospheres into the MOF precursors (Fig. S1b, ESI†).²⁶ After carbonization at 900°C and HF etching, SA-Fe-3DOMC was obtained, showing a honeycomb-like structure and uniform pores with a diameter ranging from 180 to 200 nm (Fig. 1a, b, S1c and d, ESI†), matching well with the size of silica templates. Consistently, a well-defined interconnected macroporous structure with a 10 nm-thick wall was identified by transmission electron microscopy (TEM) (Fig. 1c). Moreover, Fig. 1d reveals that no nanoparticles were detected in the high-angle annular dark field-scanning transmission electron microscope (HAADF-STEM) observation. Elemental mapping images clearly demonstrated the homogeneous distribution of C, N, O and Fe in SA-Fe-3DOMC (Fig. 1e), indicating that iron atoms exist in the carbon matrix as atomically dispersed active sites. Moreover, the HAADF-STEM image of SA-Fe-3DOMC exhibited that abundant and isolated Fe atoms with brighter spots were indeed atomically dispersed on the porous carbon matrix (Fig. 1f), which was a piece of strong evidence for the successful synthesis of single atoms.^{27,28}

The XRD patterns of N-C, SA-Fe-3DOMC and Fe-N-C-50 showed almost the same diffraction peaks centered at around 24.7° and 43.6° (Fig. 2a), which are assigned to the (002) and (101) lattice planes of graphitic carbon, respectively.^{31,32} Remarkably, no peaks belonging to Fe and Zn species were observed, confirming the absence of crystalline Fe and Zn particles in SA-Fe-3DOMC. The Fe loading amount of SA-Fe-3DOMC was measured to be 0.84 wt% by inductively coupled plasma-mass spectrometry (ICP-MS). The Raman spectra of the three samples exhibited two prominent peaks at 1340 cm^{-1} and 1590 cm^{-1} , which are ascribed to the D-band (sp^3 disordered carbon) and G-band (sp^2 graphitic carbon), respectively



Scheme 1 Schematic illustration of the synthesis of SA-Fe-3DOMC.

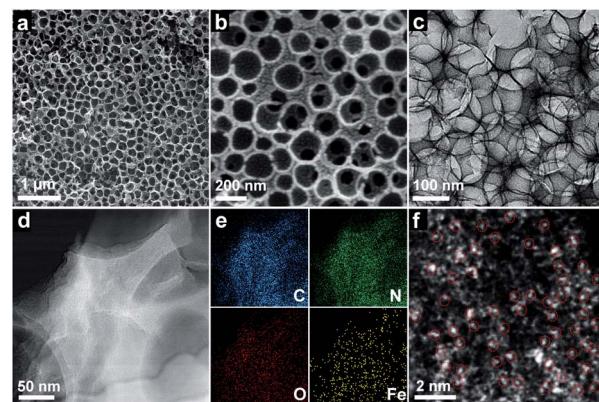


Fig. 1 (a and b) SEM images of SA-Fe-3DOMC. (c) TEM image of SA-Fe-3DOMC. (d) HAADF-STEM image of SA-Fe-3DOMC and (e) corresponding elemental images. (f) AC-HAADF-STEM image of SA-Fe-3DOMC.

(Fig. 2b).³³ The intensity ratio I_D/I_G values for N-C, SA-Fe-3DOMC and Fe-N-C-50 were calculated to be 0.96, 0.93 and 0.95, indicating that SA-Fe-3DOMC possessed a much higher graphitization degree than the other two counterparts.

The pore structures of the as-synthesized catalysts were further characterized by N_2 adsorption–desorption measurements. All catalysts presented a characteristic type IV isotherm, suggesting the presence of abundant mesopores in the samples. Furthermore, a rapid adsorption of N_2 at relatively low pressure ($P/P_0 < 0.1$) was observed, indicating that micropores can be speculated in the sample (Fig. 2c).^{34,35} With the increased number of Fe salts, the specific surface area dramatically decreased from $1681.6 \text{ m}^2 \text{ g}^{-1}$ for N-C to $1357.8 \text{ m}^2 \text{ g}^{-1}$ for SA-Fe-3DOMC and to $629.7 \text{ m}^2 \text{ g}^{-1}$ for Fe-N-C-50. Moreover, the

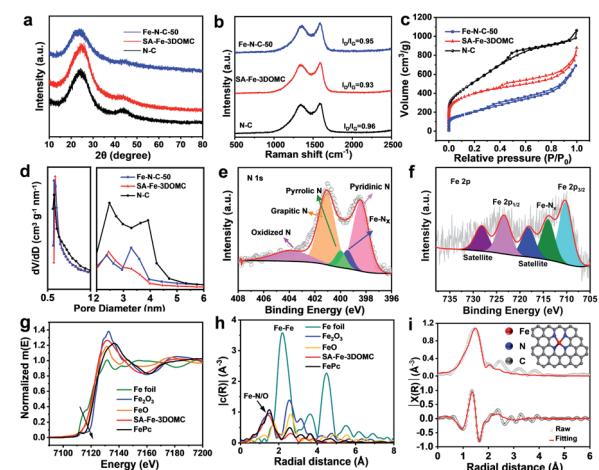


Fig. 2 (a) XRD spectra, (b) Raman spectra, (c) N_2 adsorption/desorption isotherms and (d) pore size distributions of N-C, SA-Fe-3DOMC and Fe-N-C-50. (e) The N 1s high resolution spectrum of SA-Fe-3DOMC. (f) Fe 2p high-resolution spectra. (g) Fe K-edge XANES spectra and (h) Fourier transforms of the Fe K-edge EXAFS oscillations of Fe foil, FeO, Fe_2O_3 , SA-Fe-3DOMC, and FePc. (i) FT-EXAFS curve fitting of SA-Fe-3DOMC in R space.

pore distribution revealed two sharp peaks at 0.565 nm and 2 to 4 nm (Fig. 2d), implying that a large number of micropores and mesopores were formed,³⁶ owing to the evaporation of Zn species and the catalytic effect of Fe salts, respectively.^{37,38} Notably, the higher specific surface area and abundant pores facilitate the exposure of more Fe–N_x active sites, resulting in better ORR catalytic performance.

The elemental chemical state of the obtained catalyst surface was analysed by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of SA-Fe-3DOMC presented showed the presence of C (89.28 at%), N (4.63 at%), O (5.04 at%), and Fe (1.05 at%) (Fig. S2a, ESI†). The C 1s spectrum of SA-Fe-3DOMC was resolved into C–C (~284.7 eV), C–N (~286.2 eV) and C–O (~289.0 eV), suggesting that heteroatom N was successfully doped into the porous carbon network (Fig. S3, ESI†).³⁹ The high-resolution N1s spectra of N–C, SA-Fe-3DOMC and Fe–N–C-50 can be deconvoluted into pyridinic-N (~398.5 eV), pyrrolic-N (~400.1 eV), graphitic-N (~401.1 eV) and oxidized-N (~403.9 eV). In addition, a peak at 399.6 eV assigned to Fe–N_x species was observed in both SA-Fe-3DOMC and Fe–N–C-50 (Fig. 2e, S2b and c, ESI†).²⁸ Furthermore, SA-Fe-3DOMC possessed the highest proportion of pyridinic N and graphitic N compared to the other two counterparts (Fig. S4, ESI†), which is beneficial for regulating the properties of the Fe–N–C catalyst.³⁹ The Fe 2p high-resolution spectra of SA-Fe-3DOMC and Fe–N–C-50 can be convolved into Fe 2p_{3/2} (710.0 eV) and Fe 2p_{1/2} (723.7 eV), with peaks around 725.5 eV and 716.1 eV classified as the satellite peaks of Fe, while the peak at 713.2 eV could be assigned to Fe–N_x species (Fig. 2f and S2d, ESI†).^{40,41} Linear fitting curve of Fe foil, FeO, Fe₂O₃ and SA-Fe-3DOMC were derived from corresponding Fe K-edge X-ray absorption near edge structure (XANES) position. The iron K-edge XANES position of SA-Fe-3DOMC was located close to that of FeO (Fig. 2g and S9, ESI†), indicating that the valence state of Fe in SA-Fe-3DOMC was close to +2.^{42,43} The Fourier-transform (FT) of k^3 -weighted extended X-ray absorption fine structure (EXAFS) revealed a predominant peak at 1.50 Å in R space for SA-Fe-3DOMC (Fig. 2h), ascribed to the Fe–N(O) coordination. No Fe–Fe coordination peak (at 2.2 Å) was observed for SA-Fe-3DOMC, further demonstrating the absence of metallic Fe.⁴⁴ The EXAFS fitting results were used to indicate the coordination environments of Fe in SA-Fe-3DOMC (Fig. 2i and Table S1, ESI†), which revealed that the Fe atoms in SA-Fe-3DOMC were coordinated with four N atoms, indicating a high probability that the active sites in SA-Fe-3DOMC could be Fe–N₄.⁴⁵

The electrocatalytic activity of NC, SA-Fe-3DOMC and Fe–N–C-50 was first evaluated by cyclic voltammetry (CV). Apparently, the CV curves of all samples showed obvious oxygen reduction peaks under O₂-saturated conditions (Fig. 3a, S5a and b, ESI†), and a more positive oxygen reduction peak of SA-Fe-3DOMC was observed, indicating a superior catalytic activity. Moreover, linear sweep voltammetry (LSV) curves recorded by using a rotating disk electrode (RDE) at 1600 rpm were used to investigate the ORR activities in O₂-saturated 0.1 M KOH solution. The SA-Fe-3DOMC catalyst exhibited the highest ORR catalytic activity with an onset potential (E_{onset}) of 0.994 V, a $E_{1/2}$ of 0.901 V and a diffusion-limited current densities of 5.696 mA

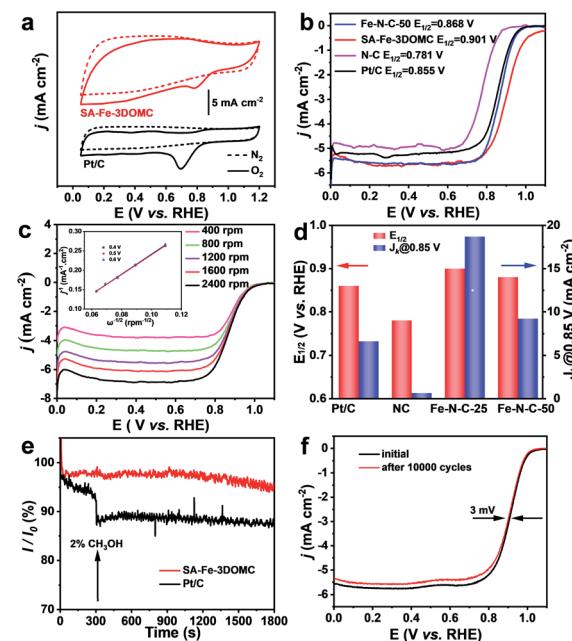


Fig. 3 (a) CV curves in O₂- and N₂-saturated 0.1 M KOH solution. (b) LSV of Pt/C, N–C, SA-Fe-3DOMC, and Fe–N–C-50 in O₂-saturated 0.1 M KOH at 1600 rpm. (c) RDE curves of SA-Fe-3DOMC from 400 rpm to 2400 rpm (inset: K–L plots at 0.4 V, 0.5 V and 0.6 V). (d) Comparison of kinetic current density (j_k) and $E_{1/2}$ for Pt/C, N–C, SA-Fe-3DOMC, and Fe–N–C-50. (e) Chronoamperometric curves of SA-Fe-3DOMC and Pt/C before and after the addition of 2% (v/v) methanol in O₂-saturated 0.1 M KOH. (f) ORR polarization curves of SA-Fe-3DOMC before and after 10 000 cycles.

cm⁻², which were much higher than those of commercial Pt/C (0.946 V, 0.855 V, and 5.228 mA cm⁻²), Fe–N–C-50 (0.955 V, 0.868 V, and 5.608 mA cm⁻²) and NC (0.876 V, 0.781 V, and 4.982 mA cm⁻²) (Fig. 3b). To further explore the ORR pathway of SA-Fe-3DOMC, LSV curves were recorded at different rotation speeds (from 400 to 2400 rpm). As depicted in Fig. 3c, the Koutecky–Levich (K–L) plots of SA-Fe-3DOMC showed good linearity and a similar slope, demonstrating that the ORR takes place on the SA-Fe-3DOMC catalyst in a similar way at different potentials. The average electron transfer number of SA-Fe-3DOMC calculated from the K–L plot at 0.4–0.6 V was about 3.7, reflecting an approximate 4e[–] oxygen reduction pathway (inset of Fig. 3c). RRDE measurements demonstrated very low H₂O₂ yields (3.4–5.1%) and electron transfer numbers in the range of 3.7–3.8 for the SA-Fe-3DOMC catalyst in the potential range from 0.2 to 0.8 V (Fig. S6a and b, ESI†). Fig. 3d further shows the kinetic current density (j_k) of N–C, SA-Fe-3DOMC, Fe–N–C-50 and commercial Pt/C. Remarkably, the j_k of SA-Fe-3DOMC reached as high as 18.70 mA cm⁻² at 0.85 V, and it was almost 2.8-fold that of commercial Pt/C (6.63 mA cm⁻²).

In addition, the methanol crossover effects on SA-Fe-3DOMC and Pt/C catalysts were measured in O₂-saturated 0.1 M KOH at 0.6 V. With the addition of 2% (v/v) methanol, a sharp decay in current density was immediately detected for Pt/C (Fig. 3e). In contrast, there was no noticeable variation in current density for SA-Fe-3DOMC, showing a better tolerance to methanol

crossover. The ORR stability of SA-Fe-3DOMC and commercial Pt/C was further investigated by an accelerated durability test (ADT). As illustrated in Fig. 3f, the $E_{1/2}$ of SA-Fe-3DOMC displayed a negligible negative shift of only 3 mV after 10 000 potential cycles from 0.6 V to 1 V. In comparison, the commercial Pt/C showed a severe loss of 12 mV (Fig. S7, ESI†). As shown in Fig. S8,† the morphology and corresponding elemental distribution of SA-Fe-3DOMC before and after 10 000 cycles remain almost unchanged, further confirming the robust properties of SA-Fe-3DOMC. These results suggested that the SA-Fe-3DOMC catalyst has superior electrocatalytic activity and durability in alkaline medium, making it very attractive as a cost-effective electrocatalyst alternative to replace Pt-based counterparts for the ORR.

To further reveal the potential of the SA-Fe-3DOMC electrocatalyst for practical applications, a liquid ZAB was assembled, where carbon paper loaded with SA-Fe-3DOMC and a gas diffusion layer was used as the air electrode (Fig. 4a). Such a battery afforded a stable open-circuit voltage (1.48 V), which was more positive than that of the Pt/C-based battery (1.37 V) (Fig. 4b), confirming outstanding catalytic performance. As shown in Fig. 4c, the battery with SA-Fe-3DOMC exhibited a peak power density of 140 mW cm⁻², which was superior to that with Pt/C (124.5 mW cm⁻²). A typical constant current discharge test also was performed at different current densities (Fig. 4d). Apparently, the voltage gap between SA-Fe-3DOMC and commercial Pt/C widened with the increase of current density, suggesting that the well-designed interconnected 3D nanoporous structure facilitated the mass transfer, especially at higher current densities.⁴⁶ When normalized to the consumed Zn during a long-term constant current discharge process at 10 mA cm⁻², the SA-Fe-3DOMC battery exhibited a much higher specific capacity with a value of 786.6 mA h g⁻¹, which means that the utilization of catalysts is equal to 95.9% since the theoretical capacity is 820 mA h g⁻¹ (Fig. 4e). Moreover, the SA-Fe-3DOMC-based battery can provide electrical energy for 8 light-emitting diodes (LEDs) (Fig. 4f), demonstrating great potential for practical applications.

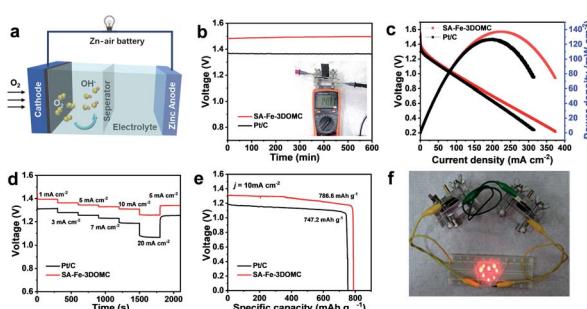


Fig. 4 (a) Schematic of ZABs using SA-Fe-3DOMC as the cathode. (b) Open-circuit plots of Pt/C and SA-Fe-3DOMC. (c) Discharge polarization curves and corresponding power density curves of ZABs respectively with Pt/C and SA-Fe-3DOMC as the cathodes. (d) Discharge curves of ZABs at different current densities. (e) Specific capacities of ZABs using SA-Fe-3DOMC and Pt/C as the cathode at 10 mA cm⁻². (f) A demonstration of an LED screen, powered by two ZAB sets.

In summary, we designed and synthesized a SA-Fe-3DOMC electrocatalyst with high ORR catalytic activity, using a SiO₂-embedded Zn-MOF assisted strategy. The achieved SA-Fe-3DOMC showed an excellent $E_{1/2}$ of 0.901 V and a high durability of only 3 mV decrease after 10 000 potential cycles, surpassing the state-of-the-art Pt/C in alkaline medium. For ZAB applications, the as-prepared SA-Fe-3DOMC electrocatalyst also exhibited an outstanding peak power density of 140 mW cm⁻² and a superior specific capacity of 786.6 mA h g⁻¹. Collectively, the hierarchical pores generated by SiO₂ and Zn species as porogens allowed the facile access of the single-atom active sites, providing effective strategies not only for seeking alternatives to Pt/C catalysts but also to develop more catalysts for various energy conversion devices, such as CO₂ reduction, water splitting, and N₂ fixation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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