Molten salt assisted fabrication of Fe@Fe₃₋₅₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋x oxygen electrocatalyst for high performance Zn-air battery

Wenjun Zhang a,b‡, Kaicai Fan c‡, Cheng-Hao Chuang d, Porun Liu c*, Jian Zhao b*, Dongchen Qi e, Lingbo Zong a*, Lei Wang a

a: Taishan Scholar Advantage and Characteristic Discipline Team of Eco Chemical Process and Technology, Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, State Key Laboratory of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, Shandong, China.
b: Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, Qingdao University of Science and Technology, Qingdao 266042, Shandong, China.
c: Centre for Clean Environment and Energy, School of Environment and Science, Griffith University, Queensland 4222, Australia.
d: Department of Physics, Tamkang University, Tamsui 251, New Taipei City, 251301, Taiwan.
e: School of Chemistry and Physics, Centre for Materials Science, Queensland University of Technology, Brisbane, Queensland 4001, Australia

*Corresponding authors.

E-mail addresses: lingbozong@qust.edu.cn (Lingbo Zong), p.liu@griffith.edu.au (Porun Liu); zhaojian@qust.edu.cn (Jian Zhao)

‡ These authors contributed equally to this work.
ABSTRACT

Non-noble-metal-based electrocatalysts with superior oxygen reduction reaction (ORR) activity to platinum (Pt) are highly desirable but their fabrications are challenging and thus impeding their applications in metal-air batteries and fuel cells. Here, we report a facile molten salt assisted two-step pyrolysis strategy to construct carbon nanosheets matrix with uniformly dispersed Fe$_3$N/Fe nanoparticles and abundant nitrogen-coordinated Fe single atom moieties (Fe@Fe$_{SA}$-N-C). Thermal exfoliation and etching effect of molten salt contribute to the formation of carbon nanosheets with high porosity, large surface area and abundant uniformly immobilized active sites. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, X-ray absorption fine spectroscopy, and X-ray photoelectron spectroscopy indicate the generation of Fe (mainly Fe$_3$N/Fe) and Fe$_{SA}$-N-C moieties, which account for the catalytic activity for ORR. Further study on modulating the crystal structure and composition of Fe$_3$N/Fe nanoparticles reveals that proper chemical environment of Fe in Fe$_3$N/Fe notably optimizes the ORR activity. Consequently, the presence of abundant Fe$_{SA}$-N-C moieties, and potential synergies of Fe$_3$N/Fe nanoparticles and carbon shells, markedly promote the reaction kinetics. The as-developed Fe@Fe$_{SA}$-N-C-900 electrocatalyst displays superior ORR performance with a half-wave potential ($E_{1/2}$) of 0.83 V versus reversible hydrogen electrode (RHE) and a diffusion limited current density of 5.6 mA cm$^{-2}$. In addition, a rechargeable Zn-air battery device assembled by the Fe@Fe$_{SA}$-N-C-900 possesses remarkably stable performance with a small voltage gap without obvious voltage loss after 500 hours of operation. The facile synthesis strategy for the high-performance composites represents another viable avenue to stable and low-cost electrocatalysts for ORR catalysis.

Keywords:
Molten salt; Oxygen reduction reaction; Long-term durability; Zn-air batteries
1. Introduction

The development and wholesale application of sustainable energy conversion and storage technologies, including metal-air batteries, are substantially dependent on the electrocatalysts towards oxygen reduction reaction (ORR). Nowadays, platinum group metal (PGM) electrocatalysts are the most active ORR electrocatalysts; however, the scarcity and exorbitant price greatly impede their scale-up production. Therefore, considerable noble-metal-free electrocatalysts are intensively pursued as alternatives for ORR.

Earth-abundant transition metal-based single atom catalysts (SACs) with fully exposed active sites, high atomic utilization and accelerated catalytic efficiency have been intensively studied in recent years [1]. Particularly, Fe-Nₓ-Cᵧ catalysts, where Fe-Nₓ moieties formed by coordination of isolated Fe with nitrogen on carbon support have emerged as promising electrocatalysts with encouraging ORR activities and stabilities [2]. Accordingly, a number of studies have been reported on metal-based electrocatalysts composite with carbon supports, such as carbon nanotubes (CNTs), graphene, and other carbonaceous materials [3–5]. Experiment and theoretical studies on metal nanoparticles stably anchored on FeSA-N-C matrix also reveal that the markedly enhanced ORR activity is attributed to the presence of Fe nanoclusters, which tailor the d-band centre of active Fe single atoms to a lower energy level and decrease the binding strength of OH* [6]. Meanwhile, it has been highlighted that the encapsulated metal architecture could activate the graphene shell as an exclusive ORR active site, i.e., the cobalt core in graphene shell-encapsulated Co nanoparticles functions as a donor and facilitate the charge transfer to the outer graphene shell to result in n-type nanographene, considerably reducing the work function of graphene and enhancing the active site density [7,8].

Recently, nitrogen incorporated into the interstices of metal lattice, i.e., transition metal nitrides (TMNs), can modify the electronic configuration of metal unit cell and lead to d-band shrinkage of metals and enhanced ORR activities [9–11]. It is commonly accepted that the thin
oxide shell on the surface of the metal nitride serves as the active sites for the ORR. Whereas highly delocalized states of active oxide are available at the metal nitride from the subsurface layer [12,13]. The conductive metal nitride core also efficiently mitigates the low conductivity of the metal oxide, and the thin oxidized layer defends the metal nitride particles from further oxidation without discernibly jeopardizing the electron transport [14]. Moreover, the electrocatalytic activities are dependent on the crystal structure to a certain degree. For example, various Co$_x$N/C have been fabricated and their ORR performances were delicately compared and Co$_4$N/C achieved best electrocatalytic performance [14]. However, there are few reports on achieving remarkable oxygen electrode electrocatalysts using the uniform dispersion of TMNs nanoparticles, while the compositions can be altered through a facile synthetic process. A rational design and fabrication of well-defined TMNs supported on highly porous carbon support is therefore favourable to gain the exposure of the active sites and considerably promote the electrochemical performance towards ORR.

Along with the highly efficient active species, the optimized pore structure and large surface area, which could facilitate the mass transfer of the oxygen and easy accessibility of active sites, are also particularly desirable to improve electrochemical activity [15,16]. Molten salt systems with ionized cations and anions endow a strong polarizing force, which is capable of breaking metallic, covalent or ionic bonds. Therefore, molten salt strategy has been exploited to obtain various nanomaterials, including precious metal, metal oxide and carbon materials with unique architectures [17]. Specifically, molten salt strategy can impede the loss of nitrogen species, as well as undesired aggregation of nanoparticles commonly occurred in a direct pyrolysis process. More importantly, the molten salts serving as confining agents are effective in fabricating well-dispersed single atom configures on the carbon support, which can contribute to the enhancement of catalytic activity [18,19]. Thus, carbon-based materials obtained through facile molten salt strategy generally possess various structural and
compositional advantages with uniformly distributed nanoparticles, abundant hierarchical pores and high specific surface areas, which not only render plentiful exposed defects and edges sites for heteroatom incorporation, but also facilitate the electron and mass transfer during electrochemical reactions [18–22]. Recently, defect rich graphene mesh was prepared through efficient thermal exfoliation of zeolite imidazolate framework nanoleaves using KCl and LiCl as the exfoliators and etching agents [19]. However, a notable loss of carbon and nitrogen species occurred due to vaporization of LiCl/KCl molten salts and decomposition of carbon materials through generating \( \text{Li}_x\text{C}_y \) and \( \text{LiKCO}_3 \) at high temperature (800 °C) [19].

Herein, a facile molten salt assisted two-step pyrolysis strategy is introduced to prepare highly porous carbon nanosheets with well-defined iron/iron nitride nanoparticles and uniformly distributed abundant atomically Fe-N sites (Fe@Fe\text{SA}-N-C-900). The synthesis involves the exfoliation of the precursors by small metal ions in LiCl/KCl molten salt simultaneously at 300 °C under \( \text{N}_2 \) atmosphere. Subsequent controlled carbonization was conducted to accomplish the formation of Fe\(_3\)N/Fe nanoparticles and atomically dispersed Fe-N\(_x\). The as-prepared Fe@Fe\text{SA}-N-C-900 possesses wrinkled nanosheet morphology with highly surface area and abundant porous structure. The as-obtained catalyst exhibits outstanding ORR activity and excellent stability. The experiments confirm that the well-dispersed Fe\(_3\)N/Fe nanoparticles, abundant Fe-N\(_x\) sites and highly porous structure synergistically contribute to the boosted electrochemical activity. The as-synthesized Fe@Fe\text{SA}-N-C-900 with encouraging performance is further studied as air cathode catalysts in Zn-air batteries, and the corresponding power density reaches 110 W cm\(^{-2}\). In addition, the assembled Zn-air batteries demonstrate extremely outstanding long-term durability of charge-discharge cyclability.

2. Materials and methods

2.1 Materials

All reagents (dicyandiamide, glucose, ferric chloride tetrahydrate, lithium chloride and
Potassium chloride) were obtained from Sinopharm Chemical Reagent Co., Ltd. 20 wt% Commercial Pt/C and 99.95% RuO2 were purchased from Alfa Aesar and were used without further purification.

2.2 Synthesis of Fe@FeSA-N-C and N-doped metal-free carbon nanosheets (N-C) electrocatalyst.

Typically, 0.0532 g FeCl2·4H2O, 0.5 g glucose and 0.5 g dicyandiamide were mixed with 1.125 g LiCl and 2.75 g KCl. The mixture was then dissolved in 10 mL Milli-Q water at 70 °C to achieve transparent solution under violent magnetic stirring. After that, the products were dried and collected at 100 °C for several hours when dicyandiamide and glucose experienced partly polymerization. To further improve the degree of polymerization, the as-prepared precursor was heated at 300 °C for 3 h under N2 atmosphere. After being washed with deionized water and freeze dried, the collected material was finally pyrolyzed (heating rate: 10 °C min⁻¹) with the protection of N2 flow (gas flow rate: 50 SCCM) for 1 h to obtain Fe@FeSA-N-C electrocatalysts. The N-doped metal-free carbon nanosheets (N-C) electrocatalyst was prepared with identical processes as Fe@FeSA-N-C sample without metal source (FeCl2·4H2O).

2.3 Physical characterizations

The morphology of the as-prepared electrocatalyst was analyzed by Scanning electron microscopy (SEM, FE-SEM, S4800, Hitachi). Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) were performed by a JEM-2100F. The aberration-corrected high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image was conducted on aberration-corrected Titan Cubed Themis G2 60-300 transmission electron microscope (Thermo Fisher Scientific). Powder X-ray diffraction (XRD) patterns of the as-developed samples were obtained with Rigaku-Dmax 2500 diffractometer with Cu-Kα radiation. The chemical states were investigated by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA). The specific surface area and pore distribution of the obtained
electrocatalysts were investigated using nitrogen adsorption-desorption analyzer (Micromeritics ASAP 2020 physisorption analyzer) at -196 °C. The specific surface area was calculated by multipoint BET analysis, and PSD curves were determined by the BJH method using adsorption/desorption branch. Raman spectroscopy was carried out on the confocal Raman microscope (LabRAM HR800) with an excitation wavelength of 532 nm. X-ray absorption near edge structure spectroscopy (XANES) measurements at C K-edge (280-320 eV) and N K-edge (395-420 eV) were conducted at the Soft X-Ray beamline of the Australian Synchrotron [23]. These measurements were carried out at room temperature under ultra-high vacuum (UHV) conditions with a base pressure of 5×10⁻¹⁰ mbar or better. All spectra were collected in total electron yield (TEY) mode. All XANES spectra were processed and normalized using the QANT software program developed at the Australian Synchrotron [24]. Fe k-edge XANES and extended X-ray absorption fine structure (EXAFS) were collected by Taiwan Light Source beamline 16A1 at Synchrotron Radiation Research Centre, which used a set of liquid nitrogen cooled Si (111) monochromator crystal. All data were recorded in fluorescence mode. All samples were prepared as pellets using mechanical grinding with the cellulose as the binder. The obtained EXAFS data were processed via the standard procedures with the Athena module implemented in the IFEFFIT software packages. The k³-weighted EXAFS spectra were acquired by subtracting post-edge background from the overall absorption and then normalizing with respect to the edge-jump step.

2.4 Electrochemical characterizations

Electrochemical workstation (CHI760E, Princeton) equipped with Pine’ rotational disk electrode (RDE, diameter of 5 mm), ring-disk electrode (RRDE, diameter of 5.61 mm) was used for the electrochemical measurements of the as-developed electrocatalysts. The glassy carbon electrode loaded with the resulted electrocatalyst and graphite rod were used as working electrode and counter electrode, respectively. Ag/AgCl electrode (saturated KCl) was used as
reference electrode for ORR test, and Mercury/Mercury oxide electrode (Hg/HgO) was used as reference electrode for OER test. The electrocatalyst ink was prepared by dispersing 5.0 mg of the as-developed electrocatalyst, 30.0 μL of Nafion and 240.0 μL of isopropanol into water (730.0 μL). The electrocatalyst loading capacity was 0.255 mg cm⁻².

For ORR measurements, 0.1 M KOH solution was served as the electrolyte. Before measurement, cyclic voltammetry was performed (50 mV s⁻¹) to activate the electrocatalysts. The Linear Scan Voltammetry (LSV) polarization curves were obtained from 1.2 to 0.2 V (vs. RHE) with the scan rate of 5 mV s⁻¹. All the LSV curves were corrected with 95% iR-correction. The electron transfer number (n) was calculated by the Koutecky-Levich equation:

\[
\frac{1}{j} = \frac{1}{j_K} + \frac{1}{J_L} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}
\]

\[B = 0.62nFC_0(D_0)^{2/3}v^{-1/6}\]

\[j_K = nFKC_0\]

Where \(j, j_K\) and \(j_L\) are the measured current density, dynamic current density and diffusion-limited current density, respectively. The diffusion-limited current mainly depends upon the parameters, i.e., number of electrons transferred (\(n\)), the Faraday constant \((F=96485 \text{ C mol}^{-1})\), the concentration of dissolved \(O_2\) in 0.1 mol KOH solution \((C_0=1.2 \times 10^{-3} \text{ mol L}^{-1})\), the diffusion coefficient \(O_2\) \((D_0=1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})\), the kinetic viscosity \((v = 0.01009 \text{ cm}^2 \text{ s}^{-1})\).

To investigate reaction selectivity, LSV was performed with RRDE. The ring potential was constant at 1.2 V (vs. RHE). The disk and ring currents were collected for calculating peroxide yield \((H_2O_2\%)\) and electron transfer number \((n)\). \(n\) and \(H_2O_2\%\) was calculated by the following equations:

\[n = \frac{4I_{\text{disk}}}{I_{\text{ring}}/N + I_{\text{disk}}}\]

\[H_2O_2\% = \frac{200I_{\text{ring}}/N}{I_{\text{ring}}/N + I_{\text{disk}}}\]
Here, $I_{\text{disk}}$ is the disk current, $I_{\text{ring}}$ is the ring current, $N (0.37)$ is the collection efficiency of RRDE.

For OER measurements, 1.0 M KOH solution was used as the electrolyte. Before measurement, cyclic voltammetry was performed (50 mV s$^{-1}$) to activate the electrocatalysts. LSV polarization curves were obtained from 1.2 to 1.85 V (vs. RHE) with the scan rate of 5 mV s$^{-1}$ and rotating speed of 1600 rpm. All the LSV curves were corrected with 95% $iR$-correction. The Faradaic efficiency (FE) of the as-developed electrocatalyst was performed using the RRDE technique in N$_2$ (O$_2$)-saturated 1.0 M KOH solution, and was calculated according to the following equation. Here, $C_e (0.37)$ is the oxygen collection coefficient, and $I_{\text{ring}}$ is the collection current on the Pt ring electrode at a constant potential of 0.4 V versus RHE.

$$\text{FE} = \frac{I_{\text{ring}}}{C_e I_{\text{disk}}}$$

2.5 Zn-air battery test

The electrocatalyst with best-performance was used to prepare air cathodes for Zn-air battery. The cathode electrocatalyst slurry was acquired by mixing 10 mg electrocatalyst in Nafion and isopropanol solution. Nickel foam with electrocatalyst slurry (loading amount: 1 mg cm$^{-2}$) was used as air cathode. A Zn plate was used as the anode. Air cathode and Zn plate anode were assembled into the home-made Zn-air battery (6 M KOH aqueous solutions as electrolyte).

3. Results and discussion
Fe@Fe₅₇₆-N-C porous carbon nanosheets were fabricated by a two-step pyrolysis process as depicted in Fig. 1. Typically, precursors were firstly synthesized through dissolving dicyandiamide, glucose and FeCl₂ with KCl and LiCl in water, and then dried and collected at 100 °C. Subsequently, the precursors were annealed at 300 °C to accomplish polymerization and carbonization between dicyandiamide and glucose, while molten LiCl and KCl served as exfoliator to achieve the formation of two-dimensional (2D) layered structure. The collected products after washing with water were denoted as Fe@Fe₅₇₆-N-C-300. Finally, Fe@Fe₅₇₆-N-C nanosheets were obtained after further pyrolysis at higher temperature under N₂ atmosphere.
Fig. 2. (a) Representative SEM image of Fe@Fe$_{SA}$-N-C-300. (b, c) SEM images of Fe@Fe$_{SA}$-N-C-900. (d) TEM image of Fe@Fe$_{SA}$-N-C-300. (e, f) TEM images of Fe@Fe$_{SA}$-N-C-900. (g) HAADF-STEM image and elemental mapping of maps of Fe@Fe$_{SA}$-N-C-900. (h) Aberration-corrected HAADF-STEM image of Fe@Fe$_{SA}$-N-C-900.

Fe@Fe$_{SA}$-N-C-300 was firstly characterized by scanning electron microscopy (SEM) as revealed in Fig. 2a, which possesses a noticeably flaky structure and different morphology to the precursors (Fig. S1). It clearly demonstrates an efficient thermal exfoliation of precursors in molten salt under inert atmosphere at 300 °C. SEM images of the obtained catalysts after the second step pyrolysis at 900 °C (Fe@Fe$_{SA}$-N-C-900) are shown in Fig. 2b and 2c. The nanosheets display a wrinkled lamellar morphology with rough surface and obviously
decreased thickness compared with Fe@Fe\textsubscript{SA}-N-C-300, and the morphology is similar to the ones prepared at 800 °C (Fe@Fe\textsubscript{SA}-N-C-800) and 1000 °C (Fe@Fe\textsubscript{SA}-N-C-1000) as presented in Fig. S2. The nanosheet structure has been formed with molten ions as thermal exfoliator during the initial pyrolysis step and preserved during the following higher temperature pyrolysis. The transmission electron microscopy (TEM) images are also presented to illustrate the detailed morphology transformation during pyrolysis process. As presented in Fig. 2d, there is no nanoparticle in the carbon nanosheet with flat and smooth surface was observed after the first pyrolysis at 300 °C. In contrast, for Fe@Fe\textsubscript{SA}-N-C-900 (Fig. 2e), wrinkle carbon nanosheets with abundant nano-sized holes are observed, which contribute to the exposure of various defects that could significantly improve the utilization of active sites [25]. Furthermore, the well crystallized nanoparticles were encapsulated by carbon nanosheets and uniformly dispersed on the porous carbon substrate (Fig. 2f and Fig. S3). The lattice fringes with the interplanar spacing of 2.1 Å match well with Fe\textsubscript{3}N (111) as revealed by the inset in Fig. 2f, which is further indicated by X-ray diffraction (XRD, see below). Additionally, the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the associated elemental mapping images (Fig. 2g) confirm homogeneously distributed C, N and Fe atoms in the obtained Fe@Fe\textsubscript{SA}-N-C-900 electrocatalyst. The aberration corrected HAADF-STEM image displays that Fe@Fe\textsubscript{SA}-N-C-900 are featured with atomically dispersed Fe species in the carbon matrix (Fig. 2h). TEM images of catalysts prepared at various pyrolysis temperatures are also exhibited in Fig. S4. As revealed, the nanoparticles are formed when the pyrolysis temperature increased to 800 °C, and the well-defined nanoparticles retained and distributed uniformly on the carbon nanosheets when the pyrolysis temperature raised to 1000 °C. The results indicate the effectiveness of the two-step pyrolysis strategy in preparing highly porous nanosheet structure with uniformly dispersed crystallized nanoparticles, and the inherent large numbers of nanosized pores would induce various defects and expose active sites.
The crystal structures of the as-synthesized Fe@Fe\textsubscript{SA}-N-C-900 were then characterized by XRD. As presented in Fig. 3a, a wide peak at around 26° attributing to the diffraction of (002) plane of graphitic carbon can be distinguished [26]. It is notable that the well-defined peaks centred at 44.7°, and 43.4° match well with the diffraction peaks of Fe (110) and Fe\textsubscript{3}N (111). To further investigate the formation of Fe\textsubscript{3}N during high temperature pyrolysis treatment, the XRD patterns of Fe@Fe\textsubscript{SA}-N-C-800 and Fe@Fe\textsubscript{SA}-N-C-1000 were compared. As shown, no peak centred at 43.4° can be observed for Fe@Fe\textsubscript{SA}-N-C-800, indicating only metallic Fe nanocrystals were generated at the pyrolysis temperature of 800 °C. When the pyrolysis temperature increased, the XRD peak assigning to Fe\textsubscript{3}N appeared at 900 °C, and its relative intensity increased when the pyrolysis temperature reached 1000 °C. It should be noted the crystallized nanoparticles appeared when the pyrolysis temperature was higher than 700 °C (Fig. S5), which is in good accordance with the observation from TEM images. The results reveal that Fe\textsubscript{3}N formed and its amount gradually increased as the raise of pyrolysis temperature. Thus, the chemical environment of Fe in the crystals can be modulated accordingly.

To characterize the relative number of defects possessed in the carbon nanosheets, Raman spectra of Fe@Fe\textsubscript{SA}-N-C obtained at different pyrolysis temperatures were compared. As demonstrated in Fig. 3b, all Raman spectra display two prominent peaks at 1340 and 1590 cm\textsuperscript{-1}, corresponding to the D-band (defective sp\textsuperscript{3} carbon) and G-band (graphitic sp\textsuperscript{2} carbon) [19,27]. As presented, the intensity ratio of the D band and G band (I\textsubscript{D}/I\textsubscript{G}) declines from 1.01 to 0.97 with the raise of pyrolysis temperature, indicating the formation of a higher ordered graphitic structure at a higher temperature. This feature alludes to a graphitization mechanism in which a significant amount of doped nitrogen was removed from the carbon support and the intrinsic holes were comparatively diminished in number and size at higher pyrolysis temperatures. Proper number of foreign anion dopant and edge-rich holes or defects are supposed to promote
the exposure of efficient active sites and are desirable to boost the performance towards specific electrochemical reactions [28,29]. \( \text{N}_2 \) adsorption-desorption analysis was further performed to assess the porosity of \( \text{Fe@Fe_{SA}-N-C} \) as shown in Fig. S6a. All these samples display a type-IV isotherm, demonstrating a prominent mesoporous characteristic. Brunauer-Emmett-Teller (BET) surface area of \( \text{Fe@Fe_{SA}-N-C-900} \) was calculated to be 284.98 m\(^2\) g\(^{-1}\), which is higher than 149.91 m\(^2\) g\(^{-1}\) and 225.19 m\(^2\) g\(^{-1}\) for \( \text{Fe@Fe_{SA}-N-C-800} \) and \( \text{Fe@Fe_{SA}-N-C-1000} \), respectively. Additionally, the detailed pore structure analysis (Fig. S6b) confirms that all these three samples possess a distinct mesoporous structure, which are assumed to be efficiently constructed by the \( \text{Li}^+ \) cations in molten salt when the precursors were polymerized and carbonized at 300 °C. Notably, the pore size experienced gradual decrease with the raise of pyrolysis temperature, while \( \text{Fe@Fe_{SA}-N-C-900} \) held the highest specific surface area. This is primarily attributed to the drastic release of nitrogen gas at higher temperature, which generates more pores apart from the existing mesopores created by molten salt [30]. In contrast, enhanced graphitized degree at higher temperature (i.e., 1000 °C) predominantly induced a smaller specific surface area and lower nitrogen dopant level (\( \text{Fe@Fe_{SA}-N-C-1000} \)). These porosities of samples are in good accordance with the graphitization degree indicated in Raman spectra of the samples. Together with HR-TEM, Raman spectra and \( \text{N}_2 \) adsorption/desorption isotherm results indicate that \( \text{Fe@Fe_{SA}-N-C-900} \) possesses abundant mesopores and high surface area, which are expected to improve the exposure of accessible active sites and enhance diffusion of reactants towards active sites during the electrocatalytic reactions [31].
The chemical compositions of Fe@Fe$_{SA}$-N-C were subsequently investigated through X-ray photoelectron spectroscopy (XPS). XPS survey spectra (Fig. S7a) reveal the presence of N, C and Fe, which correspond to the EDS mapping results. It is noteworthy that N content gradually decreases from 1.94% to 0.96% as the rise of the pyrolysis temperature (Table S1), consisting with the proposed nitrogen removal during high temperature pyrolysis. The high-resolution Fe 2$p$ XPS spectra (Fig. 3c) confirm the presence of two prominent bands at 711 eV and 724 eV, which can be ascribed to Fe 2$p_{3/2}$ and Fe 2$p_{1/2}$, respectively. Deconvolution analysis reveal that the Fe 2$p_{3/2}$ peak can be further fitted into three peaks centred at around 707.6 eV, 711.1 eV and 713.8 eV, which can be ascribed to Fe$^0$, Fe$^{2+}$ and Fe$^{3+}$ species. As
shown, two peaks assigning to Fe$^{2+}$ and Fe$^{3+}$ evidence the existence of Fe-coordinated nitrogen configuration (Fe-N$_x$), which is consistent with HAADF-STEM image and the N 1s spectra of Fe@Fe$_{SA}$-N-C (Fig. 3d and Table S2) with an observed peak of iron-nitrogen moieties (Fe-N) located at around 399.4 eV. The other three peaks observed in the N 1s spectra of Fe@Fe$_{SA}$-N-C are assigned to pyridinic N (398.3 eV), pyrrolic N (400.4 eV) and graphitic N (401.5 eV), respectively. It is formerly manifested that the pyridinic N would enhance the oxygen adsorption and reduction processes via the electron modulation on adjacent carbon atoms [32], and Fe-N$_x$ moieties are highly active species towards ORR [33,34].

Fig. 4. (a) C K-edge and (b) N K-edge XANES of Fe@Fe$_{SA}$-N-C-900. (c) XANES spectra and (d) The Fourier transform (FT) of Fe K-edges EXAFS spectra of Fe foil, FePc, FeO and Fe@Fe$_{SA}$-N-C-900. (e and f) Wavelet transform (WT) contour plots of the $K^2$-weighted Fe K-edge EXAFS of Fe@Fe$_{SA}$-N-C-900 (e) and Fe foil (f).

To reveal the local atomic coordination property and electronic structure of Fe@Fe$_{SA}$-N-C-900, X-ray absorption spectroscopy measurements (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were measured. The C K-edge XANES spectrum of Fe@Fe$_{SA}$-N-C-900 as shown in Fig. 4a presents three distinguished peaks at 285.4 eV ($\pi^*$ C=C), 288.3 eV ($\pi^*$ C-N-C) and 292.9 eV ($\sigma^*$ C-C)
It possesses similar features to highly graphitized carbon, evidencing an retained the electronic structure and high electron conductivity of carbon matrix even after introduction of Fe and N atoms [36]. The N K-edge XANES spectrum (Fig. 4b) shows three peaks [a], [b] and [c] located at around 398.4, 399.6, and 400.9 eV, which can be ascribed to $\pi^*$-transition of the pyridinic N, pyrrolic N, and graphitic N, respectively [37,38]. The measured chemical state of carbon and nitrogen are consistent with the obtained XPS data. To probe the atomic coordination of Fe, Fe K-edge EXAFS of Fe@Fe$_{SA}$-N-C-900 sample and several reference samples, including Fe foil, FeO and iron phthalocyanine (FePc) were measured. As presented in Fig. 4c, the near edge adsorption threshold of Fe@Fe$_{SA}$-N-C-900 is similar to that of FePc, but the adsorption edge locates at higher energy than FeO, which reveals that the average valence state of Fe is larger than 2+. Considering the metallic nature of Fe and Fe$_3$N, the higher valence state of Fe can be ascribed to the formation of Fe-N$_x$, corresponding to the obtained HAADF-STEM data [6]. In the pre-edge region, a peak at ~7116 eV is presented in Fe@Fe$_{SA}$-N-C-900, which can be assigned to the $1s \rightarrow 3d$ transition along with simultaneous charge transfer of ligand-to-metal, illustrating the dominant coordinated geometry around Fe was close to a square-planar structure. The Fourier transform (FT) of Fe K-edge EXAFS spectrum of Fe@Fe$_{SA}$-N-C-900 (Fig. 4d) presents an obvious Fe-Fe bond centred at 2.5 Å and a distinguished Fe-N$_x$ coordination peak located at ~1.5 Å, strongly suggesting a coexisting of Fe$_3$N/Fe nanoparticles and atomically dispersed Fe atoms in Fe@Fe$_{SA}$-N-C-900 [39]. Meanwhile, there is a slight shift in the Fe-N (1.5 Å) coordination peak for Fe@Fe$_{SA}$-N-C-900 compared to the Fe atom with four-coordinated nitrogen in FePc (1.6 Å), demonstrating the strong interaction between Fe and N atoms associated with the axial-coordinated N-ligands [40]. Furthermore, it should be noted that the Fe-Fe bond (2.5 Å) in Fe@Fe$_{SA}$-N-C-900 sample is longer than that of Fe foil (2.2 Å), confirming that some Fe atoms are present in form of iron nitrides [41]. These EXAFS results solidly confirmed the Fe$_3$N/Fe nanoparticles distribute on
the isolated Fe-based Fe-SA-N-C matrix. In addition, the wavelet transform (WT) of Fe K-edge EXAFS oscillations was conducted to investigate the chemical coordination of Fe in Fe@Fe-SA-N-C-900. As revealed in Fig. 4e, there are two intensity maximum at around 3 and 6 Å⁻¹ corresponding to the Fe-N and Fe-Fe coordination, respectively, revealing that the Fe coordination environments of Fe@Fe-SA-N-C-900 were significantly different with the Fe foil (Fig. 4f).

Fig. 5. (a) ORR polarization curves of Fe@Fe-SA-N-C-900, N-C and Pt/C. (b) Corresponding Tafel plots (c) RDE polarization curves of Fe@Fe-SA-N-C-900 under various rotation speeds. Insert: Koutecky-Levich (K-L) plots. (d) RRDE polarization curve of Fe@Fe-SA-N-C-900 recorded with a rotating disc speed of 1600 rpm and scan rate of 5 mV s⁻¹. (e) Chronoamperometric curves of Pt/C and Fe@Fe-SA-N-C-900 recorded at 0.67 V (vs. RHE), and with a rotating disc speed of 1600 rpm. (f) Chronoamperometric response of Pt/C, Fe@Fe-SA-N-C-900 upon addition of methanol.

ORR activities of Fe@Fe-SA-N-C electrocatalyst were systematically investigated by the rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) measurements in an O₂-saturated alkaline solution. The cyclic voltammogram (CV) curves of Fe@Fe-SA-N-C-900 and
commercial 20 wt% platinum (Pt/C) benchmark (Fig. S8) reveal well-defined cathodic ORR peaks at the potentials between 0.75 and 0.90 V vs. reversible hydrogen electrode (RHE) in the O\textsubscript{2}-saturated 0.1 M KOH solution, whereas they are not observed in N\textsubscript{2} saturated solution. Particularly, Fe@Fe\textsubscript{SA}-N-C-900 presents a sharp irreversible reduction peak at 0.81 V vs. RHE in O\textsubscript{2} saturated solution, while Pt/C shows a slightly larger one (0.83 V), which manifests that Fe@Fe\textsubscript{SA}-N-C-900 has decent electrocatalytic activity towards ORR comparable to that of Pt/C. Linear scanning voltammetry (LSV) curves (Fig. 5a) recorded on the RDE indicate that Fe@Fe\textsubscript{SA}-N-C-900 possesses exceptional ORR performance with more positive half-wave potential \((E_{1/2})\) of 0.83 V and larger diffusion limited current density \((j_d)\) of 5.6 mA cm\textsuperscript{-2} than Fe-free sample (N-C, SEM and TEM images shown in Fig. S9 and S10) \((E_{1/2}=0.74V, j_d=3.1\) mA cm\textsuperscript{-2}) and comparable to Pt/C \((E_{1/2}=0.82 V, j_d=5.8\ mA cm^{-2})\). Tafel slope is another vital parameter to evaluate the reaction rate of the electrocatalyst and a lower Tafel slope typically manifests a higher ORR activity. As presented in Fig. 5b, Fe@Fe\textsubscript{SA}-N-C-900 has a Tafel slope of 59.6 mV dec\textsuperscript{-1}, which is comparable to Pt/C (57.5 mV dec\textsuperscript{-1}), highlighting favourable ORR kinetics. These results demonstrate outstanding ORR activity of Fe@Fe\textsubscript{SA}-N-C-900 and indicate that metallic iron-based nanoparticles and single-atom Fe\textsubscript{SA}-N-C are significantly beneficial for facilitating the electrocatalytic reaction. Fe@Fe\textsubscript{SA}-N-C samples obtained at different pyrolysis temperature were also tested and compared with N-C to illustrate the splendid contribution of the Fe\textsubscript{3}N to the excellent ORR activity as depicted in Fig. S11. In previous work, the outstanding ORR performance of metal nitride is attributed to the unique nitride-core oxide-shell structure, the crystal structure of metal nitride through modifying the nitrogen incorporation is manifested to regulate the electrochemical activity towards ORR [12-14]. Here, the crystalline phase of the nanoparticles was adjusted by rationally controlling the pyrolysis temperature, and Fe@Fe\textsubscript{SA}-N-C-800 and Fe@Fe\textsubscript{SA}-N-C-1000 possess noticeably inferior activities towards ORR compared to Fe@Fe\textsubscript{SA}-N-C-900. Thus, it is reasonable to
propose that the distinct chemical environment of Fe in Fe$_3$N/Fe crystals prepared at 900 °C yields efficient active species and promoted ORR activity. After all, it is still difficult to quantitatively evaluate the exact contribution of the active site (Fe$_3$N/Fe or single atomic Fe) to the observed excellent catalytic activities as the synergistic effects between different active species, the results convincingly highlight the existence of multiple active species, including Fe$_3$N/Fe nanoparticles and single-atomic Fe$_{SA}$-N-C configuration. Amongst, Fe$_3$N/Fe with unique chemical and electronic structure is vital to account for the efficient active species, contributing to the excellent electrocatalytic activity towards ORR as discussed. Moreover, abundant accessible catalytic sites and a large catalytically active surface area of the catalyst significantly contribute to the rapid charge transfer and the improvement of the electrochemical kinetics. Thus, the electrochemical surface areas (ECSA) were evaluated by double layer capacitance ($C_{dl}$). As shown in Fig. S12, the $C_{dl}$ of Fe@Fe$_{SA}$-N-C-900 reaches 10.66 mF cm$^{-2}$, surpassing the values of the Fe@Fe$_{SA}$-N-C-800 (1.39 mF cm$^{-2}$) and Fe@Fe$_{SA}$-N-C-1000 (4.11 mF cm$^{-2}$). The large ECSA can be ascribed to the highly porous architecture of catalysts obtained through the two-step pyrolysis strategy.

To further assess the ORR kinetics of Fe@Fe$_{SA}$-N-C-900, LSV curves obtained at different rotating speeds from 400 to 2500 rpm were conducted and the corresponding Koutecky-Levich (K-L) plots are presented in Fig. 5c. Accordingly, K-L plots exhibit good linearity and parallelism, manifesting first-order reaction kinetics towards the concentration of dissolved oxygen. The electron transfer number ($n$) is determined to be approximately 3.93 for Fe@Fe$_{SA}$-N-C-900 (Fig. 5c inset), evidencing a four-electron pathway for ORR. Furthermore, RRDE measurement was further conducted to examine the ORR pathways through evaluating the generation of H$_2$O$_2$ during ORR process (Fig. 5d). The H$_2$O$_2$ yield of Fe@Fe$_{SA}$-N-C-900 is less than 5% at the potential range from 0.2 to 0.9 V, and the corresponding electron transfer number is calculated to be around 4 (Fig. S13). Therefore, the four-electron transfer kinetics of
the oxygen reduction to H$_2$O by the as-prepared Fe@Fe$_{SA}$-N-C-900 electrocatalyst is firmly identified. In addition to the activity, the stability and methanol tolerance of the electrocatalyst were assessed. Chronoamperometric measurements (Fig. 5e) at a constant voltage of 0.67 V reveal that the Pt/C catalyst experienced a noticeable degree of attenuation with only ~ 74% retention of current density after 40,000 s, whereas Fe@Fe$_{SA}$-N-C-900 experienced almost no decrease of current density after continuous reaction. In addition, the chronoamperometric current response to methanol (Fig. 5f) show that the current density of Pt/C experienced a sharp decline after injecting methanol, while ORR activity of Fe@Fe$_{SA}$-N-C-900 was perfectly preserved. The TEM images (Fig. S14) of Fe@Fe$_{SA}$-N-C-900 recorded after the ORR stability test revealed the morphology was preserved, demonstrating outstanding robustness of the catalysts. In addition, the chemical composition after ORR stability test was characterized by the high-resolution Fe 2p and N 1s spectra. As shown in Fe 2p XPS spectra (Fig. S15a), the Fe$^0$ and Fe$^{δ+}$ retained after electrochemical reaction while broadening of the signals have been observed [42,43]. One the other hand, in the N 1s XPS spectra, the pyrrolic-N peak decreased obviously while pyrrolic-N and pyridonic-N peaks remained. The variation in the composition of nitrogen species could be resulted from the reaction between carbon atoms next to pyridinic-N with OH species generating pyridonic-N speices [32]. The validated impressive robustness and excellent tolerance to methanol of Fe@Fe$_{SA}$-N-C-900 is essential to the commercial application in the energy conversion devices.

Meanwhile, TMNs with high electrical conductivity possess excellent oxygen evolution reaction (OER) performance, which is superior to that of the corresponding oxides, hydroxide and sulfide [44]. Therefore, the OER performance of the as-synthesized Fe@Fe$_{SA}$-N-C-900 was evaluated to explore its bifunctional electrocatalytic activity towards ORR and OER. As the LSV curves indicated in Fig. S16a, Fe@Fe$_{SA}$-N-C-900 delivers a current density of 10 mA cm$^{-2}$ ($E_{10}$) at 1.62 V (vs. RHE), demonstrating an excellent OER activity. Moreover, as revealed
in Fig. S16b, the corresponding Tafel slope $\text{Fe@Fe}_{\text{SA}}$-N-C-900 is determined to be 57 mV dec$^{-1}$, which was similar to RuO$_2$ (52 mV dec$^{-1}$) and much smaller than N-C sample (223.5 mV dec$^{-1}$), demonstrating a superior reaction kinetics for OER (Table S3). The number of transferred electrons and Faradaic efficiency during OER are essential factors to determine the reaction kinetics and were measured by RRDE strategy. As shown in Fig. S16c, the current density on the ring electrode ($j_{\text{ring}}$) is negligible compared to the disk current density ($j_{\text{disk}}$) in the whole tested potential range, suggesting the desirable four-electron pathway for OER [45]. To verify that the observed disk current density originates exclusively from water oxidation rather than from side reactions, the OER Faradaic efficiency of Fe@Fe$_{\text{SA}}$-N-C-900 was further assessed (Fig. S16d). When a constant current of 300 µA was applied to the disk electrode to produce oxygen, an oxygen reduction current of 110 µA on the ring electrode from O$_2$ reduction was detected. Therefore, a high Faradic efficiency (~100%) was achieved, demonstrating that the observed catalytic current is completely assigned to four electron oxidations of water rather than other side reaction [44]. The fabulous robustness of Fe@Fe$_{\text{SA}}$-N-C-900 is then suggested by the chronoamperometry technique at the potential of 1.62 V as shown in Fig. S17, in which the current density of Fe@Fe$_{\text{SA}}$-N-C-900 retains ~100% after 30,000 s cycle testing, exceeding the benchmark RuO$_2$. The robustness of the electrocatalyst for OER was then evaluated by TEM and XPS measurements. As the TEM image revealed in Fig. S18, Fe@Fe$_{\text{SA}}$-N-C-900 still maintained the relatively intact morphologies after the long-term stability test. In addition, Fe 2p XPS spectra of the sample (Fig. S19a) confirm the existence of $\text{Fe}^0$ and $\text{Fe}^{8+}$ after OER test with broadening signal [45,46]. Slight variation in the N speciation in the sample has been recorded in the N 1s XPS spectra (Fig. S19) indicating an overall durability.
Fig. 6. (a) Polarization curves of Fe@Fe$_{SA}$-N-C-900 and Pt/C + RuO$_2$ showing the potential gap ($\Delta E$) for ORR and OER, Scan rate, 5 mV s$^{-1}$. (b) Power density and discharge polarization of Zn-air battery assembled with Fe@Fe$_{SA}$-N-C-900 air cathode. (c) Discharge/charge cycling curve of rechargeable Zn-air battery assembled with Fe@Fe$_{SA}$-N-C-900 air cathode.

The potential gap $\Delta E$ between $E_{1/2}$ for ORR and $E_{10}$ for OER is normally applied to evaluate the bifunctional properties of an oxygen electrocatalyst, and a smaller value of $\Delta E$ implies less efficiency loss. The value of $\Delta E$ for Fe@Fe$_{SA}$-N-C-900 is 0.79 V, which is smaller than that of many nonprecious metal electrocatalysts reported so far (Fig. 6a and Table S4). Comprehensively, the excellent bifunctional catalytic performances of Fe@Fe$_{SA}$-N-C-900 towards OER and ORR strongly suggest its practical applicability in rechargeable Zn-air batteries. As the power density and discharging polarization of the Zn-air battery assembled with Fe@Fe$_{SA}$-N-C-900 air cathode (Fig. 6b), the highest power density is 110 mW cm$^{-2}$,
surpassing the one assembled with Pt/C+RuO₂ benchmark catalyst (Fig. S20). The discharge current of the Fe@Fe₃N/Fe-N-C-900 is also obviously higher than that for the Pt/C+RuO₂-based battery. Galvanostatic charge/discharge cycle tests (Fig. 6c) were employed to evaluate the efficiency and stability of Zn-air battery. After a continuous 500 cycles charges/discharge cycles over a period of 500 h, the Zn-air battery assembled by Fe@Fe₃N-N-C-900 retained its performance with a lower charge-discharge gap (0.73 V) than Pt/C+RuO₂ (Fig. S21), indicating the exceptional electrocatalytic performance of the prepared Fe@Fe₃N-N-C-900 as bifunctional oxygen electrocatalyst.

4. Conclusions

In summary, we report a facile molten salt assisted two-step pyrolysis strategy to prepare well-defined Fe₃N/Fe nanoparticles and abundant nitrogen-coordinated Fe single atom moieties uniformly distributed in carbon nanosheets matrix (Fe@Fe₃N-N-C). The highly porous carbon nanosheet generated when the carbon precursors were thermally exfoliated and etched by the potassium ions and lithium ions under inert atmosphere at 300 °C. The as-prepared Fe@Fe₃N-N-C-900 electrocatalyst is featured with a large surface area, abundant exposed active sites and accessible porosity for enhanced mass transfer. It should also be noted that rational modulation of the crystalline structure of Fe₃N/Fe nanoparticles is essential and experimentally realized, thus the modified surface electronic structure facilitates the reduction of oxygen. Therefore, the composite structure remarkably boosts the reaction kinetics in ORR for Fe@Fe₃N-N-C-900 electrocatalyst, rendering superior ORR activity and extremely high stability. When constructed cathodes electrode of Zn-air battery with Fe@Fe₃N-N-C-900, it exhibits excellent performance with a small voltage gap and excellent stability. This study illustrates an effective strategy to prepare outstanding, low-cost porous carbon nanosheets based composites with abundant electrochemical active sites for electrochemical energy conversion devices.
Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This work was supported financially by the National Natural Science Foundation of China, China (Grant No. 51702180, 51772162), the Taishan Scholar Advantage and Characteristic Discipline Team of Eco Chemical Process and Technology, the Scientific and Technical Development Project of Qingdao, China (Grant No.18-2-2-52-jch). The XAS measurements were undertaken on the SXR, XAS beamlines at the Australian Synchrotron, part of Australia's Nuclear Science and Technology Organization (ANSTO), as well as the 16A1 beamline at Taiwan Light Source, part of Synchrotron Radiation Research Center.
References


Carbon nanosheets with Fe₃N/Fe nanoparticles and Fe single atom moieties (Fe@Fe₃A-N-C), which presented exceptional ORR and OER activity, were fabricated through molten salt assisted two-step pyrolysis strategy.

Molten salt assisted fabrication of Fe@Fe₃A-N-C oxygen electrocatalyst for high performance Zn-air battery

Wenjun Zhang⁵, Kaicai Fan⁴, Cheng-Hao Chuang⁴, Porun Liu⁴*, Jian Zhao⁵*, Dongchen Qi², Lingbo Zong⁴*, Lei Wang⁴

a: Taishan Scholar Advantage and Characteristic Discipline Team of Eco Chemical Process and Technology, Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, State Key Laboratory of Eco-chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, Shandong, China.
b: Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, Qingdao University of Science and Technology, Qingdao 266042, Shandong, China.
c: Centre for Clean Environment and Energy, School of Environment and Science, Griffith University, Queensland 4222, Australia.
d: Department of Physics, Tamkang University, Tamsui 251, New Taipei City, 251301, Taiwan.
e: School of Chemistry and Physics, Centre for Materials Science, Queensland University of Technology, Brisbane, Queensland 4001, Australia

*Corresponding authors.

E-mail addresses: lingbozong@qust.edu.cn (Lingbo Zong), p.liu@griffith.edu.au (Porun Liu);
zhaojian@qust.edu.cn (Jian Zhao)

‡ These authors contributed equally to this work.
Fig. 1. Schematic of Fe@Fe$_{SA}$-N-C nanosheets electrocatalyst synthesis.
Fig. 2. (a) Representative SEM image of Fe@Fe\textsubscript{SA}-N-C-300. (b, c) SEM images of Fe@Fe\textsubscript{SA}-N-C-900. (d) TEM image of Fe@Fe\textsubscript{SA}-N-C-300. (e, f) TEM image of Fe@Fe\textsubscript{SA}-N-C-900. (g) HAADF-STEM image and elemental mapping of maps of Fe@Fe\textsubscript{SA}-N-C-900. (h) Aberration-corrected HAADF-STEM image of Fe@Fe\textsubscript{SA}-N-C-900.
Fig. 3. (a) XRD patterns and (b) Raman spectra of Fe@Fe$_{SA}$-N-C-800, Fe@Fe$_{SA}$-N-C-900 and Fe@Fe$_{SA}$-N-C-1000. (c) Fe 2p and (d) N 1s spectra of Fe@Fe$_{SA}$-N-C-800, Fe@Fe$_{SA}$-N-C-900 and Fe@Fe$_{SA}$-N-C-1000.
Fig. 4. (a) C K-edge and (b) N K-edge XANES of Fe@Fe$_{{\text{SA}}}$-N-C-900. (c) XANES spectra and (d) The Fourier transform (FT) of Fe K-edges EXAFS spectra of Fe foil, FePc, FeO and Fe@Fe$_{{\text{SA}}}$-N-C-900. (e and f) Wavelet transform (WT) contour plots of the $K^2$-weighted Fe K-edge EXAFS of Fe@Fe$_{{\text{SA}}}$-N-C-900 (e) and Fe foil (f).
Fig. 5. (a) ORR polarization curves of Fe@Fe<sub>SA</sub>-N-C-900, N-C and Pt/C. (b) Corresponding Tafel plots (c) RDE polarization curves of Fe@Fe<sub>SA</sub>-N-C-900 under various rotation speeds. Insert: Koutecky-Levich (K-L) plots. (d) RRDE polarization curve of Fe@Fe<sub>SA</sub>-N-C-900 recorded with a rotating disc speed of 1600 rpm and scan rate of 5 mV s<sup>-1</sup>. (e) Chronoamperometric curves of Pt/C and Fe@Fe<sub>SA</sub>-N-C-900 recorded at 0.67 V (vs. RHE), and with a rotating disc speed of 1600 rpm. (f) Chronoamperometric response of Pt/C, Fe@Fe<sub>SA</sub>-N-C-900 upon addition of methanol.
Fig. 6. (a) Potential gap (ΔE) of Fe@Fe\textsubscript{SA}-N-C-900 and Pt/C+RuO\textsubscript{2}, Scan rate, 5 mV s\textsuperscript{−1}. (b) Power density and discharge polarization of Zn-air battery based on Fe@Fe\textsubscript{SA}-N-C-900 air cathode. (c) Discharge/charge cycling curve of rechargeable Zn-air battery based on Fe@Fe\textsubscript{SA}-N-C-900 air cathode.

A facile molten salt assisted two-step pyrolysis strategy was introduced.

The constructed carbon nanosheet anchors Fe\textsubscript{3}N/Fe and isolated Fe-N\textsubscript{x} configurations.

Fe@Fe\textsubscript{SA}-N-C-900 possesses exceptional ORR activity and stability.

The modulated crystal structure of Fe\textsubscript{3}N/Fe contributes to the enhanced ORR activity.

The Zn-air battery device achieves remarkable stability with a small voltage gap.