Shrimp-shell derived carbon nanodots as precursor to fabricate Fe, N-doped porous graphitic carbon electrocatalyst for efficient oxygen reduction and zinc-air battery†

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In this work, shrimp-shell derived N-doped carbon nanodots (N-CNs) as carbon and nitrogen **sources** are assembled into particle-like aggregates by a simple polymerization reaction of pyrrole in the presence of Fe³⁺ to form Fe contained N-CNs/polypyrrole (PPY) composite (Fe-N-CNs/PPY). The resulting composite is thermally treated through a facile pyrolysis approach in N₂ atmosphere to obtain Fe, N-doped porous graphitic carbon (Fe-N-PGC) material. The results demonstrate that the pyrolytically converted carbon material at 800 °C (Fe-N-PGC-800) exhibits an approximately mesoporous structure with a pore size distribution centered at **~1.97 nm and ~2.8 nm** and a surface area of 806.7 m² g⁻¹. As electrocatalyst for oxygen reduction reaction (ORR) in alkaline media, Fe-N-PGC-800 shows superior ORR catalytic activity with an onset potential of -0.017 V and a limiting current density of 5.42 mA cm⁻² (at -0.4 V, vs. Ag/AgCl), which is superior to that of commercial Pt/C catalyst (onset potential of -0.018 V and limiting current density of 5.21 mA cm⁻² at -0.4 V, vs. Ag/AgCl). Additionally, Fe-N-PGC-800 also exhibits good ORR activity in acidic media with an onset potential of 0.53 V and a limiting current density of 5.58 mA cm⁻² (at 0.1 V, vs. Ag/AgCl), comparable to that of most reported Fe-based N-doped carbon electrocatalysts. An air cathode made from Fe-N-PGC-800 indicates high performance and superior cycling durability in zinc-air battery (gravimetric energy density of 752 Wh kg⁻¹), comparable to that of commercial Pt/C-based battery (gravimetric energy density of 774 Wh kg⁻¹). This work demonstrates the feasibility of utilizing biomass as starting material to fabricate **Fe, N-doped** carbon materials as high performance ORR electrocatalysts for a practical application in ORR-relevant energy devices.

Introduction

It is critically important to develop non-precious metal electrocatalysts with high oxygen reduction reaction (ORR) performance for potential applications in ORR-relevant energy devices such as fuel cells and metal-air batteries.¹⁻⁵ Although Pt-based materials as electrocatalysts have demonstrated the best ORR catalytic activity to date, the high cost and source scarcity of Pt-based electrocatalysts with poor tolerance to small fuel molecules (e.g. methanol) in ORR have greatly limited their large-scale practical applications.¹⁻⁷ Therefore, much effort has been devoted to developing cheap, abundant and high-efficiency ORR catalyst materials to replace Pt-based electrocatalysts.⁶⁻⁹ Among varieties of ORR catalysts reported

to date, transition metal contained N-doped carbon materials (M@N-C, M=Fe, Co etc.) have demonstrated great potential as promising candidates for ORR in both alkaline and acidic conditions.¹⁰⁻¹⁷ Besides of experimental evidences, theoretical calculations results also reveal that the O=O bond on N-coordinated metal active sites of M@N-C can be effectively weakened, thus leading to high efficient O₂ reduction.¹ Although lots of achievements have been gained, it is still highly needed for exploring more transition metal contained N-doped carbon materials in respect to structure, composition, catalytic activity and cost for practical applications in future ORR-relevant energy devices.

Recently, N-doped carbon materials containing different formed Fe **active** species have been extensively investigated, demonstrating great potential as promising candidates for ORR due to their intrinsically high catalytic activity.^{5,10-12,16-24} In reported literatures to date, varieties of Fe-based N-doped carbon materials with different structures and compositions have been developed, such as Fe, N-doped carbon materials,^{17,25} Fe nanoparticle@N-doped carbon core-shell structures,^{5,20} iron oxide nanoparticles@N-doped carbon composites,^{11,24} and iron carbide (Fe₃C) nanocrystals encapsulated in N-doped carbon nanostructures.^{12,16,18,22,26} No matter what the structure and composition are, the

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forementioned Fe-based N-doped carbon materials as electrocatalysts all exhibit superior ORR catalytic activities in alkaline or both alkaline and acidic conditions.^{5,10-12,16-26} However, the origin of ORR catalytic activity of these Fe-based N-doped carbon electrocatalysts is still under debate. It has been generally accepted that Fe-N_x moieties in Fe, N-doped carbon structures are considered as major catalytic active sites to promote ORR performance,^{1,17,23,25} whereas a synergetic coupling effect between N-doped carbon and iron oxide nanoparticles may contribute high ORR catalytic activity of iron oxide@N-doped carbon composites.^{11,24} A recently experimental observation reveals the presence of three Fe-N₄ like ORR catalytic centers with distinctly different Fe-N switching behaviors in Fe, N-doped carbon structure, contributing the ORR catalytic activities governed by the dynamic structure associated with the Fe^{2+/3+} redox transition.²⁷ For Fe/Fe₃C nanocrystal@N-doped carbon core-shell materials, some **related** studies have demonstrated that the encapsulated Fe/Fe₃C nanocrystals in carbon structures cannot directly contact with the electrolyte, but possibly activate the surrounding graphitic layers to enable the outer surface of the carbon active toward ORR.^{5,12,16,20,22} Although the ORR active mechanisms have not been very clear, it is believed that the superior ORR catalytic activity of these Fe-based N-doped carbon materials is ascribed to not only their intrinsically catalytic active sites also their structure properties such as high surface area and porous structure. It has been demonstrated that high surface area and porous structure of electrocatalysts are favorable for the exposure of catalytic active sites and the ORR-related mass transport, thus improving ORR performance.^{16,28} Up to now, almost all reported Fe-based N-doped carbon materials are synthesized by using fossil oil derived chemicals as carbon and nitrogen sources,^{5,10-12,16-24} which enhances undoubtedly the cost of practical applications. Therefore, it is highly desirable for utilizing inexpensive and abundant precursors as carbon and nitrogen sources to fabricate high performance Fe-based N-doped carbon electrocatalysts for ORR and ORR-related energy

devices.

Biomass (e.g., grass, soy milk)-derived N-doped carbon nanodots (N-CNs) not only possess small nanodot sizes and surface rich O-containing functional groups, but also contain naturally doped nitrogen atoms in carbon structures, which have indicated good ORR performance as electrocatalysts.²⁹⁻³¹ Further, it should be feasible using biomass-derived N-CNs as carbon and nitrogen source to fabricate Fe-based N-doped carbon materials for ORR and corresponding energy devices (e.g., zinc-air battery). As far as we know, related studies have not been reported yet in literatures. Herein, Fe contained N-CNs/polypyrrole (PPY) composite (Fe-N-CNs/PPy) was first fabricated by a simple polymerization reaction of pyrrole in the presence of Fe³⁺ and shrimp-shell derived N-CNs. Subsequently, Fe-N-CNs/PPy composites were pyrolytically treated at different temperatures in N₂ to obtain Fe, N-doped porous graphitic carbon (Fe-N-PGC) materials, as shown in Fig.1. As ORR electrocatalyst, Fe-N-PGC obtained at 800 °C (Fe-N-PGC-800) exhibits superior catalytic activity with close four-electron-transfer pathway in both alkaline and acidic conditions. Additionally, the Fe-N-PGC-800 also demonstrates great potential as air cathode material in zinc-air battery with high performance and cycling durability.

Experimental section

Material synthesis

Preparation of N-doped carbon nanodots (N-CNs): N-doped carbon nanodots (N-CNs) were synthesized by one-step hydrothermal method using shrimp shells as starting material without any synthetic chemicals.³² The shrimp shells were first dried at 80 °C for 12 h, and then ground into powder form as reaction precursor. Subsequently, 6.0 g shrimp shell powder was added to 60 mL of deionized water, and then transferred into a 100 mL of Teflon-lined autoclave and kept at 180 °C for 15 h. After hydrothermal reaction, the obtained mixture was adequately filtrated to remove large size residues by simple filtration approach (two times using 0.45 μm Millipore filter;

Fig.1 Schematic illustration of the preparation process of Fe-N-PGC using shrimp-shell derived N-doped carbon nanodots as precursor.

one time using 0.22 μm Millipore filter). The obtained solution was further treated by centrifugation at 14,000 rpm for 15 min, and the supernate was then collected for further characterization and use. The product yield of N-CNs is $\sim 15\%$ and the concentration of N-CNs solution is $\sim 15 \text{ mg mL}^{-1}$.

Preparation of Fe-N-CNs/PPy and Fe-N-PGC samples: In a typical synthesis, 20 mL of 15 mg mL^{-1} N-CNs solution and 0.6 mL of pyrrole were first mixed under stirring for 10 min, and then added to 25 mL of deionized water followed by ultrasonication for 15 min and vigorous stirring for 30 min. Subsequently, 25 mL of 0.24 M FeCl_3 solution was dropwise added to the above solution under continuous stirring at room temperature. After continuous stirring of 4 h for complete polymerization, the obtained product (Fe-N-CNs/PPy) was separated by filtration and washed adequately with ethanol and water. The resultant product (Fe-N-CNs/PPy) was dried at 80°C for overnight in N_2 atmosphere for further use.

Fe, N-doped porous graphitic carbon (Fe-N-PGC) samples were fabricated by pyrolysis of the polymerized product (Fe-N-CNs/PPy) at different temperatures ($600, 700, 800, 900^\circ\text{C}$) for 1 h with a heating rate of 5°C min^{-1} in N_2 atmosphere. To remove ORR-nonreactive substances, an acid preleaching procedure was performed for the pyrolytic product in 0.5 M H_2SO_4 solution at 80°C for 5 h, followed by centrifugation collection and thoroughly washing with deionized water. Then, the acid preleached sample was again pyrolyzed in N_2 atmosphere as the same procedure as first pyrolysis process for 2 h to obtain Fe-N-PGC products with different temperatures. The pyrolytic product was denoted as Fe-N-PGC-X (X represents pyrolysis temperature of $600, 700, 800, 900^\circ\text{C}$, respectively).

Preparation of N-CNs-800, N-CNs/P-800 and Fe-P-800 samples: The N-CNs-800 was simply obtained by pyrolysis of the dried N-CNs (obtained by freeze drying the N-CNs solution for 24 h) at 800°C for 3 h with a heating rate of 5°C min^{-1} in N_2 atmosphere. To obtain the N-CNs/P-800 sample, 0.6 mL of pyrrole and 20 mL of 15 mg mL^{-1} N-CNs solution were added into 50 mL of deionized water solution. Subsequently, 200 μL of 36% HCl and 3.0 mL of 30% H_2O_2 were quickly added into the above solution under vigorous stirring. After constant stirring of 4 h for complete polymerization, the product was separated by filtration and washed with ethanol and water. The hybrids were heated to 800°C at a heating rate of 5°C min^{-1} and held at the temperatures for 3 h in N_2 atmosphere. The Fe-P-800 sample was synthesized by the same process as Fe-N-PGC-800 sample except for using 70 mL of deionized water solution to replace 20 mL of N-CNs and 50 mL of deionized water solution.

Characterization

The crystalline structures of samples were identified by X-ray diffraction analysis (XRD, Philips X'pert PRO) using Nifiltered monochromatic $\text{CuK}\alpha$ radiation ($\lambda\text{K}\alpha 1 = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. The morphology and structure of samples were characterized by field emission scanning electron microscopy (FESEM, Quanta 200FEG) and transmission electron

microscopy (TEM, JEOL 2010) with an energy dispersive X-ray spectrometer (EDS Oxford, Link ISIS). X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al $\text{K}\alpha 1, 2$ monochromatized radiation at 1486.6 eV X-ray source. All binding energies were carefully aligned referenced to the C 1s peak (284.6 eV) arising from the surface hydrocarbon of sample. The surface area and porosity of samples were measured by a Surface Area and Porosity Analyzer (Tristar3020M). Fourier transform infrared (FT-IR) spectroscopy of the sample was recorded on a Perkin-Elmer TGA7 infrared spectrometer to identify the functional groups of the sample.

Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments, Inc., Shanghai, China) coupled with a PINE rotating disk electrode (RDE) system (Pine Instruments Co. Ltd. USA). A standard three-electrode electrochemical cell equipped with gas flow system was employed during measurements. Prior to measurements, rotating disk electrode (RDE, 5.0 mm in diameter) was first polished with 5.0, 3.0 and 0.05 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for 1 min, respectively. The cleaned electrode was dried with a high-purity nitrogen steam. The Fe-N-PGC catalyst ink was prepared by dispersing catalyst powder (5.0 mg) into a mixture including 100 μL of Nafion solution (0.5 wt.%) and 900 μL of ethanol, followed by ultrasonic treatment for 2 min. After that, 12 μL of catalyst ink was then cast onto glassy carbon (GC) electrode surface, leading to a catalyst loading amount of $305 \mu\text{g cm}^{-2}$. For comparison, a commercial Pt/C catalyst ink was also made as the same procedure as Fe-N-PGC catalyst ink.

The ORR performance of catalysts was investigated by cyclic voltammogram (CV) and linear sweep voltammogram (LSV) measurements in O_2 (or N_2)-saturated 0.1 M KOH solution. CV curves were measured at a scan rate of 50 mV s^{-1} . LSV curves were measured at a scan rate of 10 mV s^{-1} under different disk rotation rates of 400, 625, 900, 1225, 1600 and 2025 rpm. All the potentials in this work were recorded with respect to the Ag/AgCl reference electrode. The electron transfer number (n) per oxygen molecule in an ORR process was calculated by the Koutecky-Levich (K-L) equation:⁹

$$J^{-1} = J_k^{-1} + (B\omega^{1/2})^{-1} \quad (1)$$

$$B = 0.62nF(D_0)^{2/3}v^{-1/6}C_0 \quad (2)$$

$$J_k = nFkC_0 \quad (3)$$

where J is the measured current density during ORR, J_k is the kinetic current density, ω is the electrode rotating angular velocity ($\omega = 2\pi N$, N is the linear rotation speed), B is the slope of K-L plots, n represents the electron transfer number per oxygen molecule, F is the Faraday constant ($F =$

Fig. 2 (a) TEM image of N-CNs (insets of nanodot size distribution and HRTEM image of an individual nanodot). (b) FT-IR spectrum of N-CNs. (c) High resolution N 1s XPS spectrum of N-CNs. (d) SEM image of Fe-N-CNs/PPy.

96485 C mol^{-1} , D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinetic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$), C_0 is the bulk concentration of O_2 ($1.2 \times 10^{-3} \text{ mol L}^{-1}$). The ORR performance of catalysts was also evaluated in O_2 (or N_2)-saturated 0.1 M HClO_4 solution with other test conditions kept the same. In 0.1 M HClO_4 solution, the diffusion coefficient D_0 is $2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and the bulk concentration of O_2 , C_0 is $1.5 \times 10^{-3} \text{ mol L}^{-1}$. For comparison, N-CNs derived carbon material was fabricated by direct pyrolysis of freeze dried N-CNs in the absence of pyrrole and Fe^{3+} in N_2 at 800°C for 2 h (denoted as N-CNs-800); N-CNs/pyrrole composite without Fe^{3+} was pyrolyzed in N_2 at 800°C for 2 h to obtain N-doped carbon material (denoted as N-CNs/P-800); Fe^{3+} triggered polypyrrole without N-CNs was pyrolyzed in N_2 at 800°C for 2 h to obtain Fe-contained N-doped carbon material (denoted as Fe-P-800).

The measurements of zinc-air batteries were performed on home-built electrochemical cells.¹⁶ All data were collected from the as-fabricated cell with a CHI 760D (CH Instruments, Inc., Shanghai, China) electrochemical workstation at room temperature. Briefly, zinc foil was used as anode and catalysts loaded on the gas diffusion layer (Teflon-coated carbon fiber paper with a geometric area of 1.0 cm^2 , catalyst loading amount of 2.0 mg cm^{-2}) was used as the air cathode. The electrolyte was 6.0 M KOH.

Results and discussion

Recently, Fe-based N-doped carbon materials fabricated by a simple pyrolysis approach have been widely investigated as ORR electrocatalysts.^{5,10-12,16-26} However, utilization of different carbon sources as precursors results in the formation of various Fe active species (e.g., zero-valent Fe, iron oxides, and iron carbide) in graphitic carbon structures, thus leading to dramatically different ORR performance.^{5,10-12,16-26} In this work,

Fig. 3 (a) XRD patterns of Fe-N-PGC-600, Fe-N-PGC-700, Fe-N-PGC-800 and Fe-N-PGC-900. (b) TEM image of Fe-N-PGC-800. (c) EDX elemental mapping images of Fe-N-PGC-800. (d) High resolution N 1s XPS spectrum of Fe-N-PGC-800. (e) High resolution Fe 2p XPS spectrum of Fe-N-PGC-800. (f) N_2 adsorption-desorption isotherm of Fe-N-PGC-800 and corresponding pore size distribution.

as shown in Fig. 1, we utilize shrimp-shell derived N-doped carbon nanodots as carbon and nitrogen source to fabricate Fe, N-doped porous graphitic carbon (Fe-N-PGC) materials as ORR electrocatalysts by a simple combined approach of polymerization and pyrolysis. Fig. 2a shows the TEM image of shrimp-shell derived N-CNs. As shown, the hydrothermally fabricated carbon nanodots possess a size distribution of $1.5\sim 5.5 \text{ nm}$ (inset in Fig. 2a), exhibiting a lattice spacing of 0.26 nm which is smaller than the interlayer distance between graphene layers in graphite (inset in Fig. 2a).³³ The FT-IR analysis indicates that shrimp-shell derived carbon nanodots contain rich surface O and N functional groups such as O-H, N-H, C=O/C=N, C-O/C-N, similar with previous reports (Fig. 2b).^{30,33} Further, XPS survey spectra of the N-CNs confirm the presence of C, N and O elements with a nitrogen content of 14.4% (Fig. S1, ESI†). The high resolution N 1s spectrum of the N-CNs reveals the existence of three types of doped N atoms, namely, pyridinic-N (398.7 eV), pyrrolic-N (399.7 eV) and graphitic-N (400.8 eV) (Fig. 2c).^{30,34} The N-CNs with small nanodot sizes and surface rich O- and N-containing functional groups can be fully utilized as carbon and nitrogen source to fabricate high performance ORR electrocatalysts.^{29,30,35} After assembly of N-CNs by polymerization reaction of pyrrole in the presence of Fe^{3+} , particle-like aggregates can be obtained (Fe-N-CNs/PPy), as shown in Fig. 2d. Further, Fe-N-CNs/PPy can be pyrolytically transformed into Fe-based graphitic carbon material for ORR.

The Fe-N-CNs/PPy was treated by a pyrolysis approach at different temperatures to obtain Fe, N-doped porous graphitic carbon materials (Fe-N-PGC-X, X represents pyrolysis temperature of 600, 700, 800 and 900 °C, respectively). Fig. 3a shows the XRD patterns of pyrolytic samples at different temperatures. As shown, all pyrolytic samples exhibit strong inter-plane (002) diffraction at around 24.7° and relatively weak inner-plane (101) diffraction at around 43.7°, ascribed to graphitic carbon.²⁸ No diffraction peaks of Fe-related species such as zero-valent iron, iron carbide and iron oxides can be observed in the XRD patterns, indicating that the acid leaching process removes almost most of unstable Fe-related species (e.g., iron oxides) in this work (Fig. S2, ESI†). After pyrolysis treatment, the SEM images of samples at different temperatures show similar carbon aggregation morphologies (Fig. S3, ESI†). A detailed structure information on pyrolytic sample was obtained by TEM characterization. As shown in Fig. 3b and inset, a stacking layered structure of graphitic carbon can be clearly observed with highly distorted lattice (take Fe-N-PGC-800 as an example). Moreover, no Fe-related particles were found, consistent with XRD results. The energy-filtered TEM (EFTEM) imaging confirms the presence of C, N, O and Fe elements in Fe-N-PGC-800 with homogeneously distributed characteristics (Fig. 3c). Importantly, the elemental mapping signals of homogeneously distributed Fe and N in graphitic carbon structure are highly overlaid with each other, implying the presence of Fe, N doping in graphitic carbon structure.^{16,35,37} These Fe, N-doped graphitic carbon structures have demonstrated superior ORR catalytic activity.^{16,35,37} Fig. S4 (ESI†) shows a surface survey XPS spectra of Fe-N-PGC-800, further indicating the presence of C (87.73%), O (6.96%), N (4.95%) and Fe (0.36%) elements. The high resolution N 1s spectrum (Fig. 3d) can be divided into four peaks at 398.5, 399.6, 400.8, and 404.6 eV, corresponding to pyridinic-N (25.0%), pyrrolic-N (22.9%), graphitic-N (40.4%), and quarternary N⁺-O⁻ (11.7%).^{17,37} It has been generally accepted that pyridinic-N and pyrrolic-N can serve as metal-coordination sites owing to their lone-pair electrons, whereas pyridinic-N and graphitic-N are responsible for oxygen reduction.³⁸ By comparing the high resolution N 1s spectrum of N-CNs and Fe-N-PGC-800 (Fig. 2c and Fig. 3d), it can be clearly seen that pyrrolic-N is predominant in shrimp-shell derived N-doped carbon nanodots, while pyridinic-N and graphitic-N are dominant in Fe-N-PGC-800, indicating high temperature pyrolysis treatment facilitating the transformation of N doping type. The pyridinic-N and graphitic-N are of high content in Fe-N-PGC-800, possibly leading to high ORR catalytic activity. The composition analysis of all pyrolytic samples by XPS technique indicates that N doping concentration in graphitic carbon is decreased with pyrolysis temperature, as shown in Table. S1 (ESI†). At higher pyrolysis temperature (e.g., 900 °C), the significantly decreased N doping level in graphitic carbon may be unfavourable for high ORR catalytic activity owing to the decreased catalytic active sites resulted from N doping. Besides, the high resolution C 1s XPS spectrum of Fe-N-PGC-800 exhibits the presence of C=C-C and C-N/O (Fig. S5, ESI†).³² The high resolution Fe 2p spectrum (Fig. 3e) shows five peaks

Fig. 4 (a) Cyclic voltammetry (CV) curves of Fe-N-PGC-800 and commercial Pt/C catalysts in N₂- or O₂-saturated 0.1 M KOH solution; the scan rate of 50 mV s⁻¹. (b) Linear sweep voltammogram (LSV) curves of N-CNs-800, N-CNs/P-800, Fe-P-800, Fe-N-PGC-800 and commercial Pt/C catalysts in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. (c) Linear sweep voltammogram (LSV) curves of Fe-N-PGC-800 obtained at different rotating rates in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹. (d) Koutecky-Levich (K-L) plots of Fe-N-PGC-800 derived from Fig. 4c at different potentials. (e) Electron transfer number (*n*) of Fe-N-PGC-800 derived from Fig. 4d at different potentials. (f) Tafel plots of Fe-N-PGC-800 and commercial Pt/C catalysts.

at 710.9, 713.5, 718.5, 724.7, and 730.5 eV. Among them, the peak at 718.5 eV is a satellite peak; the peaks at 710.9 and 713.5 eV can be ascribed to the binding energies of the 2p_{3/2} orbits of Fe²⁺ and Fe³⁺ species, respectively, whereas the peaks at 724.7 and 730.5 eV are corresponding to the binding energies of the 2p_{1/2} bands of Fe²⁺ and Fe³⁺, respectively.^{16,17} Additionally, the peak at 710.9 eV in the Fe 2p_{3/2} XPS spectrum may be also due to Fe-N bonding resulted from Fe ions coordinated to N.^{16,17} Fig. 3f shows the N₂ adsorption-desorption isotherm of Fe-N-PGC-800. The Brunauer-Emmett-Teller surface area and total pore volume of Fe-N-PGC-800 are 806.7 m² g⁻¹ and 0.205 cm³ g⁻¹, respectively. The pore size distribution (inset of Fig. 3f) of Fe-N-PGC-800 is mainly centered at ~1.97 nm and ~2.8 nm, exhibiting an approximately mesoporous structure. Also, the surface area and total pore volume (Fig. S6 and Table S2, ESI†) of Fe-N-PGC-600, Fe-N-PGC-700 and Fe-N-PGC-900 are 677.3 m² g⁻¹ and 0.198 cm³ g⁻¹, 786.8 m² g⁻¹ and 0.203 cm³ g⁻¹, and 837.7 m² g⁻¹ and 0.242 cm³ g⁻¹, respectively. Apparently, an increase in pyrolysis temperature leads to the increase of surface area and pore volume of pyrolytic sample, which is very beneficial for the exposure of catalytic active sites.¹⁶ The pore size

distribution curves (Fig. S6b, ESI[†]) indicate that Fe-N-PGC-600 and Fe-N-PGC-700 mainly display microporous structures with pore size distribution concentrated at ~ 1.4 nm and ~ 1.6 nm, respectively, while Fe-N-PGC-800 and Fe-N-PGC-900 exhibit mesoporous structures (inset of Fig. 3f and Fig. S6b, ESI[†]). Obviously, the pyrolytic samples obtained at 800 °C and 900 °C possess mesoporous structures with high surface area and large pore volume, which are favorable for ORR-related mass transport and catalytic active site exposure, thus high ORR catalytic performance.¹⁶

To evaluate the ORR electrocatalytic activity, cyclic voltammetry (CV) measurements were first performed for Fe-N-PGC-800 and commercial Pt/C catalysts in O₂- and N₂-saturated 0.1 M KOH solution under identical experimental conditions. As shown in Fig. 4a, no O₂ reduction peaks can be observed in N₂-saturated 0.1 M KOH solution for both two catalysts, while O₂ reduction peaks at -0.18 V and -0.17 V appear for Fe-N-PGC-800 and commercial Pt/C in O₂-saturated 0.1 M KOH solution, respectively. Very approximate O₂ reduction potentials of Fe-N-PGC-800 and Pt/C indicate that Fe-N-PGC-800 possesses superior ORR catalytic activity. To obtain a meaningful comparison, N-CNs without Fe³⁺ and pyrrole, N-CNs/pyrrole composite without Fe³⁺ and Fe³⁺ triggered polypyrrole without N-CNs were pyrolyzed at 800 °C to obtain corresponding carbon products, denoted as N-CNs-800, N-CNs/P-800 and Fe-P-800, respectively. Fig. 4b shows the linear sweep voltammetric (LSV) responses of N-CNs-800, N-CNs/P-800, Fe-P-800, Fe-N-PGC-800 and commercial Pt/C catalysts in an O₂-saturated 0.1 M KOH solution under a rotation rate of 1600 rpm. As shown, the onset potentials are -0.17 V, -0.09 V, -0.09 V, -0.017 V and -0.018 V for N-CNs-800, N-CNs/P-800, Fe-P-800, Fe-N-PGC-800 and Pt/C, respectively, and the half-wave potential is -0.27 V, -0.19 V, -0.185 V, -0.15 V and -0.16 V for N-CNs-800, N-CNs/P-800, Fe-P-800, Fe-N-PGC-800 and Pt/C, respectively. In general, the N-CNs-800 sample shows good ORR catalytic activity.³² When introduced the pyrrole or Fe, the ORR catalytic activity of corresponding catalyst was obviously improved. The role of pyrrole can contribute N doping sites in resulting carbon structure, while the introduction of Fe element can help to form Fe, N doped active sites.¹⁶ These all are favourable for improving electrocatalytic activity of the electrocatalyst. Comparatively, the Fe-N-PGC-800 sample possessing Fe, N doped active sites and porous structure exhibits smaller overpotential value close to that of commercial Pt/C catalyst, indicating its highly intrinsic ORR catalytic activity. More importantly, the Fe-N-PGC-800 also shows higher limiting current density (5.42 mA cm⁻² at -0.4 V), superior to commercial Pt/C catalyst (5.21 mA cm⁻² at -0.4 V), further manifesting a superior ORR activity of Fe-N-PGC-800. In this work, Fe-N-PGC samples at different pyrolysis temperatures were also evaluated for comparative purpose. The LSV responses (Fig. S7, ESI[†]) demonstrate that the Fe-N-PGC samples at lower and higher pyrolysis temperatures (e.g., Fe-N-PGC-600 and Fe-N-PGC-900) possess decreased ORR catalytic performance. The pyrolytic sample obtained at 600 °C possesses relatively low surface area and microporous structure (Fig. S6 and Table S2, ESI[†]) may be

Fig. 5 (a) Crossover effect measurements of Fe-N-PGC-800 and commercial Pt/C catalysts. (b) Durability tests of Fe-N-PGC-800 and commercial Pt/C catalysts at an applied potential of -0.35 V and a rotation rate of 1600 rpm. (c) Linear sweep voltammogram (LSV) curves of Fe-N-PGC-800 and commercial Pt/C catalysts in O₂-saturated 0.1 M HClO₄ solution at a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. (d) Linear sweep voltammogram (LSV) curves of Fe-N-PGC-800 obtained at different rotating rates in O₂-saturated 0.1 M HClO₄ solution at a scan rate of 10 mV s⁻¹. (e) K-L plots of Fe-N-PGC-800 derived from Fig. 5d at different potentials. (f) Electron transfer number (*n*) of Fe-N-PGC-800 derived from Fig. 5e at different potentials.

unfavourable for the exposure of more catalytic active sites and mass transport, thus decreasing ORR activity. However, although the sample obtained at 900 °C exhibits larger surface area and mesoporous structure, significantly decreased N doping level in graphitic carbon (Table S1, ESI[†]) may result in the decrease of catalytic active sites caused by Fe-N bonding (the absolute Fe content in graphitic carbon should be constant under the given experimental conditions). In this work, the Fe-N-PGC samples obtained at 700 °C and 800 °C exhibit very close ORR catalytic performance possibly attributed to their suitable Fe, N doping level and advantageous graphitic carbon structure (such as large surface area and porous structure), favourable for creating more catalytic active sites, catalytic active site exposure and ORR-relevant mass transfer.¹⁶ Fig. 4c shows the LSV curves of Fe-N-PGC-800 obtained from an O₂-saturated 0.1 M KOH solution under different rotation rates. With increasing rotation rate, an increase in the cathodic current demonstrates a mass transfer controlled process.³⁹ The linearity of Koutecky-Levich (K-L) plots for Fe-N-PGC-800 derived from Fig. 4c indicates first-order reaction kinetics with regard to the concentration of dissolved oxygen and similar transferred electron numbers at different potentials (Fig. 4d). The average value of transferred

Fig. 6 (a) Open circuit voltage measurements of zinc-air batteries with Fe-N-PGC-800 and Pt/C as the cathode catalysts. (b) Typical galvanostatic discharge curves of zinc-air batteries with Fe-N-PGC-800 and Pt/C as cathode catalysts at current densities of 10 mA cm^{-2} . (c) A polarization curve ($V \sim i$) and corresponding power density plot of the battery using Fe-N-PGC-800 as the cathode catalyst compared with the battery using commercial Pt/C catalyst (d) Long-term galvanostatic discharge curves of zinc-air batteries until complete consumption of Zn anode. The specific capacity was normalized to the mass of consumed zinc.

electron number (n) at $-0.35 \text{ V} \sim -0.60 \text{ V}$ was calculated to be 3.98 (Fig. 4e), approximate to the theoretical value of Pt/C catalyst ($n=4.0$, Fig. S6a, ESI[†]), indicating a near four electron ORR process. Under identical experimental conditions, the average values of transferred electron number (n) were calculated to be 3.72, 3.96 and 3.15 for Fe-N-PGC-600, Fe-N-PGC-700 and Fe-N-PGC-900, respectively (Fig. S8b-d, ESI[†]), further confirming the important role of a suitable pyrolysis temperature to fabricate highly catalytic active ORR catalyst. The Tafel plots shown in Fig. 4f exhibit Tafel slopes of 66.8 mV dec^{-1} and 69.7 mV dec^{-1} for Fe-N-PGC-800 and Pt/C catalysts, respectively, demonstrating a superior kinetic process of Fe-N-PGC-800 for ORR.

The resistance to fuel molecule interference and durability are important parameters to evaluate an ORR catalyst for practical application. Fig. 5a shows the influence of methanol addition in O_2 -saturated 0.1 M KOH solution on the instant current curves of Fe-N-PGC-800 and Pt/C catalysts under identical experimental conditions. Apparently, no important influence can be found for Fe-N-PGC-800 when 3.0 M methanol introduced, while methanol addition results in significantly decreased instant current for Pt/C catalyst, indicating a high tolerance of Fe-N-PGC-800 to methanol crossover effect. Fig. 5b shows the durability test of Fe-N-PGC-800 and Pt/C catalysts. As shown, only 9.8% decrease in the initial activity was observed from Fe-N-PGC-800 after 11 h run, but almost 30% decrease was achieved from Pt/C catalyst, confirming a high applicable stability of Fe-N-PGC-800. Recently, Fe-based N-doped carbon materials have demonstrated great potential as ORR electrocatalysts used for both alkaline and acidic conditions.^{16,17,22} To explore the

applicability, the ORR performance of Fe-N-PGC-800 was also evaluated in 0.1 M HClO_4 electrolyte under a rotation rate of 1600 rpm in this work. As shown in Fig. 5c, the LSV curves demonstrate that Fe-N-PGC-800 possesses a good ORR catalytic activity with an onset potential of 0.53 V , half wave potential 0.29 V and a large limiting current density of 5.91 mA cm^{-2} at 0 V (limiting current density of 5.84 mA cm^{-2} for Pt/C at 0 V). Fig. 5d shows the LSV curves of Fe-N-PGC-800 with different rotation rates in an O_2 -saturated 0.1 M HClO_4 electrolyte. Also, the cathodic currents obviously increase with rotation rates under given experimental conditions, indicating a mass transfer controlled process.³⁹ Based on the $K-L$ plots (Fig. 5e) derived from Fig. 5d, the average value of transferred electron number (n) was calculated to be 3.66 at $0.15 \text{ V} \sim 0.35 \text{ V}$, suggesting that the Fe-N-PGC-800 possesses an approximate four electron ORR process in acidic media (Fig. 5f). The electrocatalytic activity measurements mentioned above demonstrate that Fe-N-PGC-800 possesses high ORR activity in both alkaline and acidic conditions, which can be ascribed to the formed Fe-N_x moieties in graphitic carbon structure contributing catalytic active sites and the structure characteristics of high surface area and porous structure favourable for catalytic active site exposure and ORR-related mass transfer.^{16,17,27}

It is critically important for an ORR electrocatalyst to evaluate its practical applicability in a real energy device. In this work, a zinc-air battery device assembled with zinc foil anode and Fe-N-PGC-800 loaded cathode was tested in 6.0 M KOH electrolyte. As shown in Fig. 6a, the open-circuit voltage was determined to be 1.45 V for Fe-N-PGC-800, comparable to that (1.49 V) of commercial Pt/C catalyst. Also, the Fe-N-PGC-800 catalyst exhibits high voltage of 1.32 V at the discharge current density of 10 mA cm^{-2} , almost identical with commercial Pt/C catalyst (1.34 V), further indicating a high ORR catalytic performance of Fe-N-PGC-800 in a zinc-air battery device (Fig. 6b). In the discharge process at different current densities, Fe-N-PGC-800 shows a high discharge current density of 112 mA cm^{-2} at 1.0 V , slightly lower than that (120 mA cm^{-2}) of commercial Pt/C catalyst (Fig. 6c). At current density of 200 mA cm^{-2} , the power densities are 140 mW cm^{-2} and 150 mW cm^{-2} for Fe-N-PGC-800 and commercial Pt/C catalysts, corresponding to the voltage values at 0.70 V and 0.75 V , respectively (Fig. 6c). Further, the specific capacities of Fe-N-PGC-800 and commercial Pt/C catalysts normalized to the mass of consumed zinc were calculated to be 578 mAh g^{-1} and 596 mAh g^{-1} , respectively, at the discharge current density of 10 mA cm^{-2} , corresponding to the gravimetric energy densities of 752 Wh kg^{-1} for Fe-N-PGC-800 and 784 Wh kg^{-1} for commercial Pt/C. The zinc-air battery performance of Fe-N-PGC-800 is comparable to most results obtained from currently reported Fe-based N-doped carbon catalysts.^{5,16,40,41} Therefore, the Fe-N-PGC-800 in this work possesses great potential in future zinc-air battery devices.

Conclusions

In summary, Fe, N-doped porous graphitic carbon materials were successfully fabricated using shrimp-shell derived N-doped carbon nanodots as carbon and nitrogen source by a combined approach of polymerization and pyrolysis. As electrocatalyst, the pyrolytic product obtained at 800 °C (Fe-N-PGC-800) exhibited superior ORR catalytic activity closely comparable to the state-of-the-art Pt/C catalyst in alkaline media, and good ORR catalytic activity in acidic media. As a high efficient oxygen reduction electrocatalyst, the Fe-N-PGC-800 also demonstrated a great potential as air cathode material in zinc-air battery device with high performance and excellent cycling durability. The findings in this work demonstrated the feasibility of using cheap and abundant biomass as starting material to fabricate high performance oxygen reduction electrocatalysts for zinc-air battery applications.

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