Template-free synthesis of non-noble metal single-atom electrocatalyst with N-doped holey carbon matrix for highly efficient oxygen reduction reaction in zinc-air batteries

Suyuan Zhang, Weiguang Yang, Yulin Liang, Xue Yang, Minna Cao, Rong Cao

Abstract

M-N-C single-atom electrocatalysts recently have received significant attention because of high catalytic activity and maximal atom utilization. Here, it is firstly reported that macrocycle cucurbit[6]uril (CB[6]) self-assembly was employed as precursor to fabricate M-N-C single-atom electrocatalysts for the Zn-air battery (ZAB). This template-free method using CB[6] self-assembly acquires the holey N-doped matrixes with hierarchical micro/mesoporous structure. The Fe loaded N-doped holey carbon single-atom electrocatalyst (Fe-NHC) exhibited high activity with the half-wave potential (E_1/2) of 0.89 V versus reversible hydrogen electrode (RHE) for oxygen reduction reaction (ORR) in alkaline condition, which was better than those of Co or Ni loaded catalyst and commercial Pt/C, especially M-N-C single-atom catalysts. This work provided a promising strategy to design stable and highly efficient catalyst for long-life electrochemical storage devices.

1. Introduction

The electrochemical storage and conversion are crucial technologies for exploiting clean energy economy and have attracted worldwide interest. Electrochemical storage devices like Zn-air battery (ZAB) with high energy density, low cost and environmental friendliness became the promising appliances for emerging electronic applications [1,2]. However, the widespread applications of ZAB were heavily impeded due to poor cycling life and inferior energy conversion efficiency. The oxygen reduction reaction (ORR), as the crucial reaction of the device, bears sluggish kinetics with large amounts of catalysts needed to facilitate the reaction [3,4]. Although Pt has long been the most efficient catalyst for ORR, the rare reserves, high price and unfavorable stability restricted relative applications. To meet the requirements of practical application, tremendous efforts have been made for developing low-platinum or platinum-free ORR catalysts with high catalytic activity and durability [5,6].

Among numerous substitution candidates, transition metals and their derivatives have been regarded as the most promising alternatives to commercial Pt/C, especially M-N-C single-atom catalysts. The single-atom catalysts possess the isolated M-N-C configuration and maximal atom utilization, which presents high activities for electrocatalytic reactions [7]. To improve the performance of single-atom catalysts, the support is crucial requiring exposure and stabilization of sufficient atomically dispersed M-N sites as well as ample electrode/electrolyte interface. N-doped holey carbon materials possessing high surface area and abundant defects are suitable matrixes for loading isolated single-atom sites. Usually, tedious pre-treatments or post processing like template methods, acid etching, hydrothermal treatments or special gas (ammonia, hydrogen, etc.) treatment were employed to achieve structures with high surface area and defects which caused extra costs and works [8-10]. Besides, some porous precursors were used to get the

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Keywords:
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A B S T R A C T

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porosity of carbonaceous samples while the collapse and transform of precursors during carbonization need to be overcome. Recently, the supramolecules were tried to obtain porous carbon matrix for various application with considerable performance [11–13]. Employing the strategy, the single-atom electrocatalysts with N-doped holey carbon substrate acquire improved property promisingly.

Herein, we synthesize a series of M-N-C (M = Fe, Co and Ni) single-atom electrocatalysts derived from macrocyclic cucurbit[6]uril (CB[6]) self-assembly and equipped for ZABs. By pyrolyzing the mixture of Fe (Co, Ni) chloride and CB[6], the catalysts possessed holes spread over the whole carbon substrate. The calculated distributions of pores were verified by the high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images. The investigation on the effects of various metal species showed the Fe loaded N-doped holey carbon single-atom electrocatalyst (Fe-NHC) exhibited an unexpected catalytic performance for ORR in alkaline condition, which is better than commercial Pt/C and Co or Ni loaded samples. Moreover, the isolated Fe metal sites have been fully confirmed by aberration-corrected high angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) and Fe K-edge X-ray absorption fine structure (XAFS) spectra. Besides, the high energy density, power density and long-term discharge or cyclic stability for ZAB were achieved with Fe single-atom catalyst. This work holds great promise for fabricating catalysts with high surface area from macrocycle self-assembly in enabling reversible energy storage and conversion devices.

2. Experimental section

2.1. Reagents and chemicals

FeCl₂·6H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O and ethanol were purchased from Sinopharm Chemical Reagent Co., China. The CB[6] was prepared according to previous reported process [14]. Nafion (5 wt.% in lower aliphatic alcoholic) were purchased from Sigma-Aldrich (Shanghai, China). 20 wt.% Pt/C were acquired from Alfa Aesar (China) Chemical Co., Ltd. Deionized (DI) water from Milli-Q System (Millipore, Billerica, MA) was used in all experiments. All chemicals were used without further purification unless otherwise noted.

2.2. Preparation of CB[6]-derived M-N-C catalyst (Fe-NHC, Co-NHC, Ni-NHC)

In a typical procedure, 2 mg FeCl₂·6H₂O was added into 2 mL deionized water and absolutely soluble with ultrasonic treatment to get aqueous solution. Then 300 mg CB[6] and 3 mL deionized water were added into FeCl₂ aqueous solution followed by magnetic stirring for 6 h. Next, the mixture was lyophilized and moved to furnace. With the heating rate of 5 °C/min, the sample was kept at 900 °C for 3 h under N₂ atmosphere, and then naturally cooled to room temperature. The resultant powder (about 30 mg) was collected and put into 30 mL 1 M HCl aqueous solution followed by stirring for 12 h. Lastly, the sample was washed with water three times and ethanol once before drying in vacuum. The sample was denoted as Fe-NHC.

The similar processes were employed by replacing FeCl₂·6H₂O with CoCl₂·6H₂O and NiCl₂·6H₂O in the same mass. Samples were denoted as Co-NHC and Ni-NHC, respectively.

2.3. Electrochemical measurements

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) measurements were investigated using IM6ex (Zahner, Germany). Typical preparation of electrode was as follow: 5 mg of catalyst were dispersed in 1 mL isopropl alcohol and ultrasonicated for 2 h. Then, 40 μL 5 wt.% Nafion was added and ultrasonicated for 30 min. Lastly, 10 μL of the resulting ink was added dropwise onto the surface of a rotation disk electrode (RDE) with a glassy carbon disk of 5 mm diameter and dried at ambient condition. The Ag/AgCl with saturated KCl solution electrode and a 1 cm × 1 cm platinum mesh were served as the reference electrode and the counter electrode, respectively. The potential value was normalized with respect to the reversible hydrogen electrode (RHE) unless otherwise mentioned. Both CV and LSV tests were carried out in N₂ or O₂-saturated 0.1 M KOH with scan rates of 50 and 10 mV/s for CV and LSV, respectively. CA test was performed with potential fixed at 0.6 V.

For rotating ring-disc electrode (RRDE) measurements, the disk electrode was scanned at a rate of 5 mV/s and the ring electrode potential was set to 1.5 V. The HO₂% of catalysts was determined from the following equation:

\[
\text{HO}_2^- (\%) = 200 \times \frac{I_R/N}{I_R/N + I_D} \quad (1)
\]

The n is calculated from the following equation:

\[
n = 4 \times \frac{I_D}{I_R/N + I_D} \quad (2)
\]

where \(I_D\) is the disk current, \(I_R\) is the ring current, and \(N\) is the ring collection efficiency measured to be 0.397.

For ZAB test, a polished zinc plate (3.3 cm × 8 cm) and a hydrophobic carbon paper (3.3 cm × 5 cm) loaded with 0.5 mg catalyst on a 1 cm × 1 cm area were selected as anode and cathode respectively. 15 mL mixed electrolyte solution containing 6 M KOH/0.2 M zinc acetate was filled in the chamber of battery.

2.4. Characterisation

Scanning electron microscopy (SEM) images were taken with field-emission Scanning Electron Microscope (JSM-6700 F). Transmission electron microscopy (TEM) measurements were performed using a field-emission microscope (FEI Tecnai G20) operated at 200 kV. AC-HAADF-STEM and Energy-Dispersive X-ray spectroscopy (EDS) of samples were performed with FEI Theims Z high-resolution transmission electron microscope. Powder X-ray diffraction (XRD) patterns are recorded on a Miniflex 600 diffractometer using Cu Kα radiation (\(\lambda = 0.154 \text{ nm}\)). The Raman spectra were performed on a Labram HR800 Evolution over a range of 500–3500 cm⁻¹. N₂ adsorption-desorption isotherms were performed using a Micromeritics ASAP 2460 instrument to give Brunauer–Emmett–Teller (BET) surface area and pore size. The pore size distribution curves were analyzed with Non-local density functional (NLDF) method. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, HORIBA Jobin Yvon, France) was performed to determine the concentrations of Fe, Co and Ni. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Kα source (15 kV, 10 mA). The XAFS at the Fe K-edge were measured at the BL14W1 beamline station of the Shanghai Synchrotron Radiation Facility, China.

3. Results and discussion

3.1. Structural analysis of the catalysts

The typical synthesis procedures of CB[6]-derived M-N-C electrocatalysts were presented in Fig. 1a. The catalysts were synthesized by pyrolyzing the mixture of CB[6] and Fe (Co, Ni) chloride at 900 °C. CB[6] is a kind of rigid macrocyclic molecule consisting of C, H, N, O and possessing high N content (34 wt.%). Besides, the assembled backbone of CB[6] presented evenly distributed pores on the c axis. These features promoted the obtained pyrolytic N-doped holey structure with high specific surface area. The original CB[6] assembly possessed the rod-like shape as SEM presented (Fig. S1). After pyrolysis and acid etching, the SEM and TEM images revealed that the resultant CB[6]-
derived M-N-C catalysts were preserved with rod-like morphology, demonstrated the robustness of CB[6] self-assembly backbone (Figs. 1b, e and S2). As the HAADF-STEM images of CB[6]-derived M-N-C catalysts shown (Figs. 1c and S3), the holey structures over the whole carbon matrixes were clearly observed [15]. For Fe-NHC, the EDS elemental mapping images indicated that Fe, N dopants were homogeneously dispersed over the carbon matrix (Fig. 1d). Besides, the similar distributions of Fe, N and C were also observed for high magnitude images of HAADF-STEM and EDS elemental mapping (Fig. S4), in which there were no Fe-based NPs detected. Moreover, the homogeneously dispersed Co, N dopants or Ni, N dopants over the carbon matrix were also observed for Co-NHC and Ni-NHC and no metal-based NPs detected (Figs. S5 and S6). To confirm the existence of metal single atoms in CB[6]-derived M-N-C sample, AC-HAADF-STEM was carried out. The AC-HAADF-STEM images further corroborate the formation of Fe (Co, Ni) single atoms (Figs. 1f and S7a, c). As marked by red circle, numerous of highly dispersed bright dots with size less than 0.5 nm could be attributed to heavier metal atoms due to Z-contrast (Figs. 1g and S7b, d) [16–18].

As shown in Fig. 2a, there were no peaks related to the metallic phase found for Fe-NHC, Co-NHC and Ni-NHC in PXRD patterns. CB[6] with carbonyl-fringed portals is attractive for ions binding through the ion–dipole effect, which are beneficial to dispersing metal chlorides of mixed precursors and thereby forming scattered metal sites for pyrolyzed samples [19,20]. TEM and PXRD analysis results confirmed that no detective agglomeration of metal species occurred in the pyrolysis procedure. The broad peaks around 25° and 43° were ascribed to (002) and (100) planes of graphitized carbon [21]. Raman spectra were performed to characterize the carbon structure of the catalysts (Fig. 2b), in which the D band indicated the existence of defects or disordered in carbon structures and G band indicated the graphitic carbon [22]. Additionally, a band detected simultaneously at 2500–3200 cm$^{-1}$ belongs to the 2D band meant layered graphene-like architectures existed after pyrolysis [23].

N$_2$ adsorption-desorption analysis showed all the samples displayed typical type-IV isotherms with hysteresis loops in the P/P$_0$ range of 0–1.0, suggesting the existence of hierarchical micro/mesoporous structure (Fig. S8) [24]. The presence of micropores endowed substrate with higher specific surface area and mesopores were recognized to generate an ample electrode/electrolyte interface for ion or charge accumulation performance during the ORR [25,26]. These holey structures derived from pyrolyzed CB[6] backbones also created more defects, acting as active sites and anchoring metal atoms to generate an ample electrode/electrolyte interface for ion or charge accumulation performance during the ORR [25,26]. The BET surface areas were 729, 889 and 686 m$^2$/g for Fe-NHC, Co-NHC and Ni-NHC, respectively. NLDFT analysis also confirmed that carbon matrixes mainly included micropores and mesopores over the range of 1.0–2.0 nm and 2.5–10 nm respectively (Fig. 2c and Table S1). The calculated pore distribution of CB[6]-derived M-N-C catalysts was in agreement with the holey structures owning diameter less than 10 nm distinguished in the HAADF images (Figs. S3 and 2c, inset).

The surface structure and composition of the obtained catalysts were investigated by XPS. The full spectra and high resolution C 1s, N 1s, Fe (Co, Ni) 2p spectra confirmed the presence of C, N, O, and Fe (Co, Ni) (Figs. 2d, S9–S11). The Fe (Co, Ni) 2p spectra revealed the weak peak intensity due to low metal content of samples. ICP-AES indicated that the weight fraction of Fe in the Fe-NHC was 0.47 wt.%, Co in the Co-
NHC was 0.55 wt.% and Ni in the Ni-NHC was 0.42 wt.%. The N 1s spectra of samples can be well-fitted by four types of nitrogen species corresponding to pyridinic N (398.3 eV), pyrrolic N or M-N (399.4 eV), graphitic N (400.9 eV) and oxidized N (402.6 eV), respectively (Fig. 2d) [29]. Relative contents of different types of N were presented and substantial portion of graphitic N (43.1%–47.4%) were identified, which played a crucial role in oxygen reduction (Fig. S12 and Table S2) [30]. Besides, the pyrrolic N and pyridinic N were also detected, which were deemed to make the adsorption of O\textsubscript{2} easier and promoted the first electron transfer step for ORR [31].

To precisely investigate the electronic structure and coordination environment of Fe atoms, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were recorded at the Fe K-edge. The near-edge profile of Fe-NHC sample was compared to those of contrast Fe foil, Fe\textsubscript{2}O\textsubscript{3} and iron phthalocyanine (FePc) model samples. As shown in Fig. 2e, the position of absorption edge for Fe-NHC was similar to that of Fe\textsubscript{2}O\textsubscript{3}, which was situated between Fe\textsuperscript{2+} (FeO) and Fe\textsuperscript{3+} (Fe\textsubscript{2}O\textsubscript{3}). It suggested that the Fe single atoms in Fe-NHC might be a state between +2 and +3 [32]. Fourier-transform (FT) EXAFS curve of the Fe-NHC in Fig. 2f presented a primary scattering peak located at 1.6 Å (uncorrected for phase shift). The peaks of Fe–O (1.4 Å, uncorrected), Fe–O–Fe (2.6 Å, uncorrected) and Fe–Fe (2.2 Å, uncorrected) scattering detected in Fe\textsubscript{2}O\textsubscript{3} or Fe foil were not observed in Fe-NHC, indicating the absence of metallic Fe and oxide Fe species [33,34]. Instead, the identified peaks were close to peaks of Fe-N scattering path for FePc. The corresponding fitting curves were presented with fitting results (Fig. S13 and Table S3), which further verified the isolated Fe atom sites are coordinated with the adjacent nitrogen atoms from pyrrolytic matrix. To specifically discriminate the coordination atoms in the Fe species, the wavelet transform (WT) analysis of Fe-NHC, Fe foil and Fe\textsubscript{2}O\textsubscript{3} was carried out, as shown in Fig. 2g-i. For Fe\textsubscript{2}O\textsubscript{3}, intensity maximums at ca. 2.3 Å\textsuperscript{-1} and ca. 7.0 Å\textsuperscript{-1} were ascribed to Fe–O scattering and Fe–O–Fe scattering, respectively. The Fe foil showed an intensity maximum at ca. 8.1 Å\textsuperscript{-1}, corresponding to the Fe–Fe scattering [35]. These scatters were not detected in Fe-NHC, replaced by the observed intensity maximum at ca. 3.2 Å\textsuperscript{-1} ascribed to Fe-N scattering indicating the isolated Fe sites. The unique chemical state of Fe was in agreement with HAADF-STEM observation results of atomically dispersed Fe atoms.

3.2. Catalytic performance of CB[6]-derived M-N-C for ORR

To investigate the effects of metal species on ORR catalytic activities, the electrocatalytic behaviors of the CB[6]-derived M-N-C catalysts were first evaluated with CV measurements in both O\textsubscript{2}-saturated and N\textsubscript{2}-saturated 0.1 M KOH solution (Fig. 3a). All the catalysts represented the well-defined cathodic peaks detected in O\textsubscript{2}-saturated electrolyte which were not observed in N\textsubscript{2} atmosphere. It indicated the ORR catalytic activities of CB[6]-derived M-N-C catalysts in alkaline solution. Among these samples, Fe-NHC possessed the most positive peak potential at 0.81 V, which was more positive than those of Co-NHC (0.78 V) and Ni-NHC (0.71 V). To further investigate the ORR activities, LSV curves were recorded of catalysts and contrastive commercial Pt/C catalyst as shown in Fig. 3b. Fe-NHC represented the most positive onset potential.
**(Fig. 3.** (a) CV curves of CB[6]-derived M-N-C catalysts in N₂-saturated (solid line) and O₂-saturated (dash line) 0.1 M KOH solution with a sweep rate of 50 mV/s. (b) LSV curves of CB[6]-derived M-N-C catalysts and Pt/C in O₂-saturated 0.1 M KOH solution with a sweep rate of 5 mV/s. (c) Calculated CDL and (e) varying n and HO₂% of CB[6]-derived M-N-C catalyst. (f) The durability of CB[6]-derived M-N-C and Pt/C for ORR at a constant potential of 0.6 V.)

(E_{onset} = 0.94 V) and half-wave potential (E_{1/2} = 0.89 V), as well as the highest diffusion-limiting current density (j_0 = 5.6 mA/cm²), better than Co-NHC (E_{1/2} = 0.84 V), Ni-NHC (E_{1/2} = 0.79 V) and commercial Pt/C (E_{1/2} = 0.83 V) (Table S4). The CB[6]-derived M-N-C catalysts presented various E₁/₂ with metal species following the positive order of Fe > Co > Ni, which meant the decisive impact of different metals on the active sites. Among the reported non-noble metal single-atom electrocatalyst, Fe-based samples usually exhibited the highest ORR activities in alkaline condition in terms of E₁/₂ and j₀ [36]. Research has unravelled the ORR catalytic activities trend of Fe, Co, Ni single-atom electrocatalyst. Single Fe atoms sites with proper electronegativity promote the nearly same free and adsorption states of O₂ 2p state, which is the optimal one for catalysing ORR [37]. Fig. 3c presented the corresponding Tafel slope calculated for CB[6]-derived M-N-C catalysts and commercial Pt/C. Fe-NHC with the smallest Tafel slope (53.7 mV/dec) was lower than that of commercial Pt/C (74.7 mV/dec), which manifested a good kinetic process for the ORR on Fe-NHC electrocatalyst.

Besides, the electrochemical surface areas (ECsAs) of the CB[6]-derived M-N-C catalysts were also evaluated by the double-layer capacitance (Cdl) with CVs measurement (Fig. S14). The approximately rectangular-type CV curves revealed the Cdl nature of the electrocatalysts. As shown in Fig. 3d, the Cdl value can be calculated in terms of the slope of current density vs. scan rate in this region. The Fe-NHC exhibited the maximum value of Cdl (19.68 m F/cm²), which was higher than those of Co-NHC (16.96 m F/cm²) and Ni-NHC (11.61 m F/cm²). In view of this, metal species influence the exposed active sites and the most active sites were exposed for Fe-NHC which was benefit to the best ORR catalytic performance. Furthermore, to clarify the ORR pathway, the transfer number (n) and peroxide yield (HO₂%) for CB[6]-derived M-N-C catalysts were accurately calculated by the RRDE measurements (Fig. S15). As shown in Fig. 3e, when the potential ranged between 0.2 to 0.85 V, the n value of Fe-NHC was 3.85–3.98 which was higher than those of Co-NHC (3.73–3.92) and Ni-NHC (2.89–3.38). Moreover, the HO₂% remained below 10 % for Fe-NHC, suggesting its dominant four-electron pathway towards ORR.

To evaluate the durability of catalysts, CA test was performed as shown in Fig. 3f. After electrolysis for 9 h, both Fe-NHC and Co-NHC catalysts presented outstanding durable performance with current loss less than 5 %. As compared, the contrastive Pt/C lost about 29 % of initial current. To be noticed, Ni-NHC with poor activity still presented less loss of current (11 %), which indicated the intrinsic better durability of CB[6]-derived M-N-C catalysts than Pt/C. Poor methanol tolerance was known to be an inevitable issue for energy conversion devices involving ORR. The varying of currents for Fe-NHC and Pt/C were also tested after adding 3 M methanol into electrolyte (Fig. S16). The drastic change happened for Pt/C reflecting the sensitivity of Pt/C to methanol crossover [38]. As contrast, no obvious change occurs for Fe-NHC, suggesting excellent methanol tolerance of catalyst.

### 3.3. Test for performance of assembled rechargeable zinc-air batteries

Due to the ORR performance of Fe-NHC sample, a home-made ZAB device was assembled as illustrated in Fig. 4a to evaluate the application of catalysts. The Fe-NHC catalyst and contrast Pt/C + Ir/C catalysts were used for air electrode, respectively. As presented in Fig. 4b, the maximum power density of the ZAB employing Fe-NHC catalyst was as high as 157 mW/cm², better than that of Pt/C + Ir/C catalyst (120 mW/cm²). Fig. 4c presented the open-circuit potential (OCP) and rate tests for discharge of assembled ZABs. The battery assembled with the Fe-NHC catalyst exhibited an OCP about 1.426 V (Fig. S17). Through increasing galvanostatic discharge currents density from 0.1 to 200 mA/cm², discharge rate performance could be manifested. It is obvious that the voltage platform of the ZAB with Fe-NHC catalyst descends gently whereas that of ZAB with the Pt/C + Ir/C catalyst drops acutely especially for current densities over 20 mA/cm². Besides, a clear voltage loss was observed for Pt/C + Ir/C catalyst with the increasing discharge current and duration at 100 mA/cm².

The long-time discharging stability of the ZAB with Fe-NHC catalyst was demonstrated at a discharging current density of 20 mA/cm² and 10 mA/cm² (Figs. 4d and S18). No obvious voltage drop was observed for Fe-NHC catalyst with discharging current density of 20 mA/cm² until 70 h which further confirmed the outstanding stability of the Fe-NHC catalyst in ZAB. The energy density of ZAB with Fe-NHC catalyst is as high as 907.04 Wh/kgZn. As contrast, the ZAB employing Pt/C + Ir/C catalyst presented continuous voltage loss and the corresponding energy density was 745.62 Wh/kgZn. As shown in Fig. 4d inset, two ZABs in series using Fe-NHC catalyst on the air electrodes can easily power up a blue light emitting diode (ca. 2.6 V).

As Oxygen Evolution Reaction (OER) catalytic activity was also
presented for Fe-NHC (Fig. S19), the galvanostatic charge-discharge test
was used to examine the rechargeable ZAB with current of 10 mA/cm².
For Fe-NHC catalyst, battery was able to work continuously over 60 h
cycling without observed loss of the voltage gap for charge/discharge
potentials (Fig. 4e). As contrast, the voltage gap of Pt/C + Ir/C catalyst
dramatically increased after 4 h test. On the whole, Fe-NHC was a
promising alternative catalyst with better activity and stability to
replace precious metal-based catalysts in rechargeable ZABs.

4. Conclusions

In this work, the supramolecular CB[6] self-assembly was reported as
carbonaceous precursors to fabricate a series of M-N-C single-atom
electrocatalysts with hierarchical micro/mesoporous structure.
Employing this versatile template-free method, the catalysts acquire
holey substrate possessing high specific surface area and N-doping,
which create abundant defects and anchor atomic metal sites for ORR
catalytic performance. The atomic dispersed Fe sites of the Fe-NHC
electrocatalyst were confirmed by AC-HAADF-STEM and XAFS mea-
surements. Moreover, the Fe-NHC catalyst with better activities and
stabilities than commercial Pt/C was demonstrated by RDE tests and
ZAB performance tests. This work gives a good guidance for designing
and fabricating single-atom catalysts with porous substrates and further
applied for reversible energy storage and conversion devices.

CRediT authorship contribution statement

Suyuan Zhang: Conceptualization, Methodology, Data curation,
Writing - original draft. Weiguang Yang: Methodology, Validation.
Yulin Liang: Data curation, Methodology. Xue Yang: Methodology,
Validation. Minna Cao: Conceptualization, Funding acquisition,
Writing - review & editing. Rong Cao: Supervision, Conceptualization,
Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

References

A zeolitic-imidazole frameworks-derived interconnected macroporous carbon
matrix for efficient oxygen electrocatalysis in rechargeable zinc-air batteries, Adv.
X.Y. Lu, Harnessing the interplay of Fe-Ni atom pairs embedded in nitrogen-doped
carbon for bifunctional oxygen electrocatalysis, Nano Energy 71 (2020), 104597,
free ORR electrocatalysts for fuel cell past, present, and future, Adv. Mater. 31
Q. Huang, Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction
ash6125.


