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Article

Fabricating high-loading Fe-N₄ single-atom catalysts for oxygen reduction reaction by carbon-assisted pyrolysis of metal complexes

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ARTICLE INFO

Article history:

Received 19 April 2020

Accepted 11 June 2020

Available online 22 September 2020

Keywords:

Fe-N₄ single-atom catalysts

Oxygen reduction reaction

High-loading

Coordinated effect

Four-electron transfer process

ABSTRACT

Iron-based single-atom catalysts with nitrogen-doped carbon as support (Fe-SA/NPC) are considered effective alternatives to replace Pt-group metals for scalable application in fuel cells. However, synthesizing high-loading Fe-SA catalysts by a simple procedure remains challenging. Herein, we report a high-loading (7.5 wt%) Fe-SA/NPC catalyst prepared by carbon-assisted pyrolysis of metal complexes. Both the nitrogen-doped porous carbon (NPC) support with high specific surface area and *o*-phenylenediamine (*o*-PD) play key roles in the preparation of high-loading Fe-SA/NPC catalysts. The results of X-ray photoelectron spectroscopy, high-angle annular dark-field scanning transmission electron microscopy, and X-ray absorption fine structure spectroscopy experiments show that the Fe atoms are anchored on the carbon carriers in a single-atom site configuration and coordinated with four of the doped nitrogen atoms of the carbon substrates (Fe-N₄). The activities of the Fe-SA/NPC catalysts in the oxygen reduction reaction increased with increasing iron loading. The optimized 250Fe-SA/NPC-800 catalyst exhibited an onset potential 0.97 V of and a half-wave potential of 0.85 V. Our study provides a simple approach for the large-scale synthesis of high-loading single-atom catalysts.

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1. Introduction

Owing to their ultra-high atomic utilization, superb catalytic ability in several reactions, single-atom catalysts (SACs, in which the metal atoms are isolated and highly dispersed on an appropriate substrate) are among the most promising materials for electrocatalysis, and have attracted huge interest from the scientific community [1–8]. The successful preparation of SACs with high-density active sites is the prerequisite and key task of fundamental studies and practical applications. However, the atoms of SACs are prone to agglomerate into clusters or even particles during the preparation and catalytic process, due

to the sharp increase in surface free energy with decreasing size [5,9–11]. So far, considerable efforts have been devoted to rationally preparing these catalysts, and various SACs, such as Au [12–14], Fe [10,15–22], Co [2,23,24], Cu [25–28], Zn [29–31], Pt [3,32–35], Pd [36,37], Rh [38], and Ru [39,40] have been produced.

Fe-based single-atom (Fe-SA) catalysts, containing non-precious metals, are widely believed to be effective alternatives to replace Pt-group metals for scalable applications in fuel cells [20,41]. Fe-N_x moieties, such as edge-hosted and in-plane FeN₄, are the principal active sites of Fe-SA catalysts for the electrochemical oxygen reduction reaction (ORR)

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This work was supported by the Natural Science Foundation of Guangdong province, China (2018A0303130101).

DOI: 10.1016/S1872-2067(20)63689-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 5, May 2021

[17,41–43]. A higher loading of Fe-N_x is needed to achieve a better ORR performance. To date, various strategies have been proposed to fabricate Fe-SA materials, such as spatial confinement [10,16,17,20,22, 44–48] and coordination synthesis [11,19,49]. Only a few high loading (>5 wt%) Fe-SA catalysts have been obtained. Yi *et al.* [50] used an ionothermal process to prepare isolated Fe atoms on porous porphyrinic triazine-based substrates at 600 °C, and the content of Fe was up to 8.3 wt%. Cheng *et al.* [51] carried out the pyrolysis of a mixture of porcine hemin and dicyandiamide at 900 °C and obtained a high-loading Fe-SA catalyst with 7.7 ± 1.3 wt%. Hu *et al.* [21] recently presented a cascade anchoring strategy for the synthesis of atomic Fe-N_x moieties embedded in a nitrogen-doped carbon substrates at 800 °C, with a metal loading of 8.9 wt%. In these synthetic methods, the porphyrin and glucose coordinating agents prevent metal agglomeration. Dicyandiamide and melamine decompose to carbon nitrogen species and capture metal atoms to form M-N_x moieties. Moreover, oxygen-rich carbon supports with high specific surface area can be doped with nitrogen, which also provides abundant anchoring sites to stabilize the metal atoms. Nevertheless, we believe that new coordinating agents and carbon supports still need be developed to obtain high-loading SACs.

Herein, we developed a simple and straightforward route to prepare high-loading Fe-SA catalysts by carbon-assisted pyrolysis of metal complexes, involving the pyrolysis of a carbon-hosted Fe-*o*-phenylenediamine (Fe-*o*-PD) complex in the presence of melamine. In this procedure, nitrogen-doped porous carbon (NPC) is a porous biomass-based carbon material with abundant nitrogen defects, high surface area, and good dispersion [52]. *o*-Phenylenediamine (*o*-PD), as a bidentate ligand with two amino groups, can easily coordinate transition metals to form square-planar four-coordinated complexes [53]. In addition, *o*-PD has been recently employed as N-doped carbon precursor due to the transition metal catalysis under high temperature treatment [54]. Therefore, the above features endow NPC and *o*-PD with a promising potential for the synthesis of high-loading Fe-SA materials. By adjusting the amount of Fe precursor, the highest Fe loading in Fe-SA catalysts could reach up to 7.5 wt%. The 250Fe-SA/NPC-800 material achieved superior electrochemical performance in the ORR, with a high onset potential of 0.97 V and half-wave potential of 0.85 V in 0.10 M KOH, which are comparable to those of the commercial Pt/C catalyst.

2. Experimental

2.1. Materials

Potassium oxalate monohydrate (K₂C₂O₄·H₂O, AR) was bought from Sinopharm chemical reagent Co. Ltd. Glucose anhydrous (C₆H₁₂O₆) was obtained from Shanghai Boao Biotechnology Co., Ltd. Melamine (C₃H₆N₆, 99%) and *o*-PD (C₈H₈N₂, 98%) were purchased from Aladdin Chemistry Co. Ltd. Iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, AR) and hydrochloric acid (HCl, AR) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd and Guangzhou chemical reagent factory, re-

spectively. All chemicals were used without further purification.

2.2. Preparation

The preparation of nitrogen doped porous carbon (NPC) implicated one-step pyrolysis according to the previous reports with some modifications. In a specific procedure, 4 g glucose, 8 g C₃H₆N₆ and 14.4 g K₂C₂O₄·H₂O were ground intensely until the mixture became uniform. Subsequently, the white mixture was transferred into the tubular furnace, calcining at 800 °C (ramping rate 3 °C min⁻¹) for 1 h under Ar ambient. After cooling to room temperature, the residuals were treated with 1 M HCl, washed with distilled water until neutral pH and dried in an oven at 70 °C for 12 h to achieve NPC.

90 mg NPC were dispersed into 20 mL ethanol by ultrasonication for 30 min to give Suspension A. *x* mg Fe(NO₃)₃·9H₂O and *o*-PD with molar ratio of 1:10 were dissolved in 30 mL methanol with ultrasonication for 30 min to form Solution B. Solution B was then slowly dripped into Suspension A with vigorous stirring for 1 h and then evaporated at 70 °C to disperse the Fe-*o*-PD complex on NPC substrates. The recovered black solid was mingled with melamine at a mass ratio of 1:5 by grounding and calcined at 350 °C for 2 h and then at *T* °C (700–900 °C) for 2 h under Ar ambient with ramping rate of 2 °C min⁻¹. After cooling down to the room temperature, the samples were obtained without further treatment, denoted as *x*Fe-SA/NPC-*T* (where *x* represents the amount of Fe(NO₃)₃·9H₂O, *T* represents the calcination temperature). In case of the formation of nanoparticles, the corresponding samples were denoted as 375Fe-NP/NPC-800 and 250Fe-NP/NPC-900. For comparison, some control samples were prepared with the same procedure of 250Fe-SA/NPC-800 without adding *o*-PD or NPC, the final productions were denoted as 250Fe-NP/NPC-800 and 250Fe-NP-800.

2.3. Characterizations

Power X-ray diffraction patterns of the as-prepared catalysts were obtained by a Bruker D8 X-ray diffractometer operating at 40 mA and 40 kV with Cu K_{α1} radiation (λ = 0.15418 nm). Scanning electron microscopy (SEM-Merlin, Zeiss) and transmission electron microscopy (TEM-1400plus, JEOL) were used to observe the morphologies and microstructure of the samples. AC-HAADF-STEM images were acquired by a Transmission Electron Microscope with A Probe Corrector (Titan Cubed Themis G2 300, FEI, USA). The surface area and pore size distribution were measured on the Multi-station full-automatic specific surface area and aperture test system (ASAP 2640, Mike, Inc. USA) at 77 K. Previous to the test, the samples were dried at 70 °C overnight under vacuum, and then degassed at 423 K for 12 h. X-ray photoelectron spectroscopy (XPS) was characterized by a Thermo Electron ESCALAB250 XPS Spectrometer (X-ray Source: Al). Raman spectra were recorded on a Lab RAM Aramis Micro Raman spectrometer (H. J. Y Inc., France). The metal loading of the catalysts was measured on ICP-OES 720ES (Agilent, USA).

2.4. Electrochemical tests

The electrochemical performances of oxygen reduction reaction (ORR) were tested on an electrochemical workstation (Zennium, Zahner) at ambient conditions. Gold wire and saturated calomel electrode (0.245 V vs RHE) were served as the counter and reference electrodes, respectively. A glass carbon (GC) electrode with a diameter of 3 mm was considered as working electrode. In this study, all potentials were measured against the SCE with the conversion E (vs. RHE) = E (vs. SCE) + 0.0591 × pH + 0.24 V. The catalyst ink was obtained by mixing of 10 mg sample and 1 mL Nafion solution (0.84 wt% Nafion) and sonicating for 1 h, and then 10 μL as-prepared uniform catalyst ink was dripped on the surface of GC electrode, dried at room temperature naturally. Before electrochemical tests, all of the electrolytes were continuously purged with N₂ or O₂ for >20 minutes. CV curves were conducted at the potential window from 0.0 to 1.223 V with a scan rate of 20 mV s⁻¹ in the N₂-saturated 0.1 M KOH electrolyte until the curves remained stable. The LSV polarization curves were carried out at a scan rate of 5 mV s⁻¹ and a rotation speed of 1600 rpm in O₂-saturated 0.1 M KOH solution to measure the onset potential and half-wave potential of the catalysts. Other LSV polarization curves were recorded at rotation speeds range from 400 to 2025 rpm. According to the K-L equation the slope of K-L plot could be used to deduce the electron transfer number in the reaction process. the equation takes the following form:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6}$$

Herein, J refers to the measured current density, J_K and J_L are the kinetic and diffusion-limiting current densities, respectively. ω is the electrode rotation rate, n is transferred electron number, F is the Faraday constant (96485 C mol⁻¹), C_0 is the bulk concentration of O₂ (1.2×10⁻⁶ mol cm⁻³), D_0 is the diffusion coefficient of O₂ in 0.10 M KOH (1.9×10⁻⁵ cm² s⁻¹) and ν is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹).

The percentage of H₂O₂ formation was calculated with the following equations:

$$H_2O_2 (\%) = 100 \times \frac{\frac{4-n}{2}}{\frac{4-n}{2} + \frac{2n-4}{4}}$$

The electron transfer number of the 250Fe-SA/NPC-800 was about 3.6 calculating from the K-L equation. So the percentage of H₂O₂ formation of the 250Fe-SA/NPC-800 was calculated to be 20%.

3. Results and discussion

Nitrogen-doped carbon-supported single-atom Fe (Fe-SA/NPC) catalysts with different Fe loadings were prepared by simple carbon-assisted pyrolysis of metal complexes. A schematic illustration of the formation of Fe-SA/NPC catalysts is shown in Scheme 1. NPC with high specific surface area (1267 m²·g⁻¹), obtained by the pyrolysis of potassium oxalate, glucose, and melamine [52], was dispersed in ethanol to form a

homogeneous suspension. An ethanol solution of iron(III) nitrate nonahydrate and *o*-PD was added dropwise into the NPC suspension with vigorous stirring for 1 h. Then, the mixture was evaporated at 70 °C to disperse the Fe-*o*-PD complex on the NPC substrate. The recovered black powders were mixed with a certain amount of melamine and pyrolyzed at 700–900 °C under argon ambient with a flow rate at 50 mL·min⁻¹. The obtained samples were denoted as *x*Fe-SA/NPC-*T* (where *x* represents the added amount of Fe(NO₃)₃·9H₂O and *T* denotes the calcination temperature). When nanoparticles were formed, the corresponding samples were denoted as 375Fe-NP/NPC-800 and 250Fe-NP/NPC-900. For comparison, some control samples were prepared with the same procedure used for 250Fe-SA/NPC-800, without adding either *o*-PD or NPC, and the final products were denoted as 250Fe-NP/NPC-800 and 250Fe-NP-800. Further details are reported in the Supporting Information (SI).

Power X-ray diffraction (XRD) measurements were performed to investigate the crystalline structure of the samples. Two broad diffraction peaks at approximately 26.5° and 44.0° were observed for the NPC sample (Fig. 1(A)), which originate from the (002) and (100) crystal planes of graphitic carbon, respectively [11]. Interestingly, after loading the Fe species onto the carbon substrates, the samples exhibited similar XRD patterns to NPC. No peaks associated with FeC_x, FeO_x, and Fe were detected until the added amount of Fe(NO₃)₃·9H₂O was higher than 375 mg, indicating that the Fe species could be highly dispersed on the carbon substrates by adding the appropriate amount of Fe precursor. To study the effect of each component on the synthesis of 250Fe-SA/NPC-800, two control samples were synthesized without either NPC or *o*-PD. In contrast, the XRD patterns of 250Fe-NP-800 and 250Fe-NP/NPC-800 both display a few diffraction peaks corresponding to Fe₂O₃ and FeC₃ (Fig. S1(A), see electronic supporting information, the same below), revealing that some Fe₂O₃ and FeC₃ crystals were formed. These results highlight the crucial roles of the NPC and *o*-PD components in the preparation of SACs with high Fe loadings. In the pyrolysis procedure, *o*-PD, as a good ligand, not only isolated Fe atoms through the coordinated effect of the amino group, but was also converted to N-doped carbon in a process catalyzed by Fe species. More specifically, during the carbonization process, *o*-PD was transformed into a stable polymeric intermediate when the temper-

Scheme 1. Schematic illustration of the formation of *x*Fe-SA/NPC-*T* samples; yellow and blue-grey balls represent melamine and the Fe-*o*-PD complex, respectively.

Fig. 1. XRD patterns (A) and Raman spectra (B) of NPC, xFe-SA/NPC-800, and 375Fe-NP/NPC-800 samples.

ature reached the appropriate range ($T \approx 200\text{ }^{\circ}\text{C}$), and ultimately formed N-doped carbon materials serving as substrates for loading single metal atoms [54]. Due to its huge specific surface area, NPC promoted the high dispersion of Fe-*o*-PD complexes, thus avoiding the interatomic contact between Fe atoms during the pyrolysis process. At the same time, the individual Fe atoms were captured by some doped nitrogen atoms, and achieved a monatomic distribution state. In addition, melamine could increase the nitrogen doping content of the carbon framework during the heating process. The influence of the pyrolysis temperature on the evolution of the catalyst was also explored. Upon at $700\text{ }^{\circ}\text{C}$, although no peaks corresponding to Fe-based species were detected, the peak of the (100) crystal plane of graphitic carbon exhibited a very weak intensity, due to imperfect graphitization that would reduce the electrical conductivity and ORR stability of the sample. For pyrolysis temperatures up to $900\text{ }^{\circ}\text{C}$, some crystal peaks originating from metallic iron and iron carbides were observed (Fig. S1(B)), which can be ascribed to the fact that a high temperature promotes the agglomeration of metal atoms. Thus, $800\text{ }^{\circ}\text{C}$ was considered as the optimal synthesis temperature.

Raman spectra were recorded to obtain a better understanding of the defect properties of the carbon substrate (Fig. 1(B)). The two peaks located around 1350 cm^{-1} and 1570 cm^{-1} were assigned to the D and G bands of graphitic carbon, respectively. The I_D/I_G values of all Fe-SA samples were higher than the corresponding ratio of the NPC support, suggesting that a more defective structure was formed in the carbon substrates, mainly because of the introduction of larger amounts of N and Fe atoms in the graphitic structure of the carbon support [16,55–58].

In order to further examine the microstructure of the Fe-SA samples, we obtained scanning electron microscopy and transmission electron microscopy images. The 250Fe-SA/NPC-800 sample exhibited a stacked fold-like nanosheet morphology (Fig. 2(A)). The TEM image (Fig. 2(B)) also displays a thin folded nanosheet structure. No visible nanoparticle of iron-based materials were observed on the carbon nanosheets in the SEM and TEM images, in agreement with the absence of crystal peaks of iron-based materials in the XRD

patterns. In comparison, the energy-dispersive X-ray spectroscopy (EDX) mapping (Fig. 2(D)) shows that the C, N, and Fe elements were uniformly distributed, implying that Fe-containing species were potentially loaded on the carbon substrates in the form of ultra-small clusters or even single atoms. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used as a powerful tool to provide visual insight on whether the metal atoms were individually dispersed over the substrates. As shown by the HAADF-STEM images of 250Fe-SA/NPC-800 in Fig. 2(C), the presence of atomically distributed Fe atoms was clearly observed as bright dots on the N-doped carbon nanosheets (with the Z-contrast difference reflecting differences in atomic mass). However, many well-defined nanoparticles emerged in the TEM and STEM images of 375Fe-NP/NPC-800 (Fig. S2), showing that the iron species would be close to each other and agglomerate into nanoparticles if the iron precursor content is higher than an upper limit. Using inductively coupled plasma

Fig. 2. Morphology characterization of 250Fe-SA/NPC-800 sample. (A) SEM image; (B) TEM image; (C) High-resolution AC-HAADF-STEM image; (D) Low-resolution AC-HAADF-STEM image with corresponding EDX mapping.

optical emission spectroscopy (ICP-OES), the Fe content in 250Fe-SA/NPC-800 was determined to be 7.5 wt%, exceeding that of many reported Fe-SA catalysts (Table S1).

X-ray photoelectron spectroscopy tests were carried out to investigate the surface chemical composition and valence state of the Fe-SA samples. C, N, O, and Fe coexisted in the XPS survey spectrum of 250Fe-SA/NPC-800 (Fig. 3(A)), whereas the survey spectrum of NPC excluded the presence of Fe element (Fig. S4). Furthermore, the detailed chemical features of C, N, and Fe were analyzed using the C 1s, N 1s, and Fe 2p core-level spectra of 250Fe-SA/NPC-800, respectively. As illustrated in Fig. 3(B), the high-resolution C 1s spectrum of 250Fe-SA/NPC-800 shows the presence of four types of carbon species, which were assigned to $\text{C}=\text{C}$ (284.6 eV), $\text{C}-\text{O}/\text{C}=\text{N}$ (285.7 eV), $\text{C}=\text{O}/\text{C}-\text{N}$ (288.0 eV), and $\text{O}=\text{C}-\text{O}$ (290.2 eV). The high-resolution N 1s spectrum of 250Fe-SA/NPC-800 could be deconvoluted into five peaks at 398.3, 399.4, 400.4, 401.3, and 403.3 eV, corresponding to five types of nitrogen species, namely pyridinic N, Fe-N, pyrrolic N, graphitic N, and oxidized N, respectively (Fig. 3(C)) [58–61]. In particular, the peak at 399.4 eV indicates that a fraction of the N atoms could bond with iron atoms and preserve them from forming metal bonds. It is worth noting that the percentage of FeN_x calculated from fitting the curves increased from 0 for NPC to 9.2% for 175Fe-SA/NPC-800 and then to 12.6% for 250Fe-SA/NPC-800, along with the increase in Fe precursor loading (Table S3), indicating that Fe atoms were substantially coordinated with N instead of aggregating into nanoparticles or clusters [46]. As for the Fe 2p spectrum, the two peaks at 710.1 and 723.3 eV, corresponding to the Fe 2p_{1/2} and Fe 2p_{3/2} levels, respectively, revealed the presence of Fe(II), while the peak centered at 714.5 eV confirmed the presence of Fe(III). In addition, no peaks associated with Fe(0) were observed [21]. On the basis of the XPS results, the dominant Fe species in 250Fe-SA/NPC-800 were Fe-N_x rather than Fe(0).

To examine in detail the valence states and local coordination structures of the Fe species over the whole 250Fe-SA/NPC-800 catalyst, we performed X-ray absorption fine structure spectroscopy (XAFS) measurements. The X-ray absorption near-edge structure (XANES) Fe K-edge profiles of 250Fe-SA/NPC-800 and of Fe foil, Fe₂O₃, and Fe₃O₄ reference materials are shown in Fig. 4(A). The pre-edge position of 250Fe-SA/NPC-800 was close to that of Fe₃O₄, but with a slightly negative shift, revealing that the oxidation state of Fe in the 250Fe-SA/NPC-800 was a mixture of Fe(II) and Fe(III), and the proportion of Fe(II) was slightly higher than that of Fe₃O₄. Fig. S6 displays the k^2 -weighted Fourier-transformed extended XAFS (EXAFS) curves. The 250Fe-SA/NPC-800 sample showed a strong peak at ~ 1.8 Å corresponding to Fe–N bonds, while no Fe–Fe scattering path at 2.5 Å or obvious Fe–O–Fe scattering path at 3.0 and 3.5 Å could be seen for the Fe foil and Fe₃O₄/Fe₂O₃ references [19,20], respectively, indicating that the Fe atoms were anchored on the NPC in the form of isolated iron ions, with atomic-level dispersion. The EXAFS results were fitted to quantitatively analyze the coordination structure of Fe atoms. The fitting curve (Fig. 4(B)) and data (Table S4) show

Fig. 3. XPS spectra of 250Fe-SA/NPC-800. (A) XPS survey spectrum; (B) High-resolution C 1s spectrum; (C) High-resolution N 1s spectrum; (D) High-resolution Fe 2p spectrum.

Fig. 4. XAFS profiles of 250Fe-SA/NPC-800 catalyst. (A) Fe *K*-edge XANES profiles of 250Fe-SA/NPC-800 catalyst and reference samples; (B) Corresponding EXAFS fitting curves in *R*-space, with the inset showing a schematic model.

that each Fe atom was coordinated to approximately four other atoms, corresponding to an Fe-N₄ structure (inset of Fig. 4(B)) [21]. Therefore, Fe-N₄ is the catalytic active site of 250Fe-SA/NPC-800 for the ORR.

Because the Fe-SA electrocatalysts have great potential for ORR applications, we carried out linear scan sweep voltammetry (LSV) tests with a rotating disk electrode (RDE) to evaluate the electrocatalytic properties of the as-prepared samples and

the 40% Pt/C control in 0.10 M KOH aqueous electrolyte. Based on the LSV curves and the corresponding onset and half-wave potentials (*E*_{onset} and *E*_{1/2}, respectively) displayed in Figs. 5(A) and 5(B), the NPC sample showed poor ORR activity.

Upon increasing the Fe loading, the ORR performances of the Fe-SA catalysts improved gradually. Among the Fe-based catalysts, 250Fe-SA/NPC-800 exhibited the best ORR properties, with the most positive *E*_{1/2} value (0.85 V). At the same time, the

Fig. 5. ORR performance. (A) RDE polarization curves of the samples; (B) Onset and half-wave potentials of the samples (a = NPC, b = 100Fe-SA/NPC-800, c = 175Fe-SA/NPC-800, d = 250Fe-SA/NPC-800, e = 375Fe-NP/NPC-800); (C) LSV polarization curves of 250Fe-SA/NPC-800 with different rotation speeds (400–2025 rpm); (D) K-L plots of 250Fe-SA/NPC-800.

$E_{1/2}$ values of the Fe-SA based catalysts increased with the Fe loading. Because Fe-N₄ is the main active site, higher Fe-N₄ amounts result in higher ORR performances. It should be noted that the ORR activity of Fe-N-C SACs depends on not only the number of Fe-N₄ active sites, but also the N-containing moieties, the electronic properties of the carbon basal plane, and the bulk graphene defects [62]. The ORR performance of 250Fe-SA/NPC-800 was not as good as that of 40 wt% Pt/C and other reported Fe-SA catalysts (Table S5). This is mainly due to the lowest Brunauer-Emmett-Teller (BET) surface area of 250Fe-SA/NPC-800 compared with that of the other Fe SACs, in which the Fe-N₄ sites may be buried in the dense carbon substrates and thus unable to contribute to the ORR process. The electrochemical performance of 375Fe-NP/NPC-800 showed an evident degradation, which could be ascribed to the formation of Fe-based nanoparticles (Fig. S2). Although the loading percentage of Fe species increased, the utilization rate of Fe atoms decreased. To better understand this catalytic effect, we measured the LSV curves of 250Fe-SA/NPC-800 at various rotation speed (400–2025 rpm) and obtained the Koutecky-Levich (K-L) plots at different applied potentials (0.4–0.7 V) (Figs. 5(C) and 5(D)). In the mixed kinetics potential region, the electron transfer number calculated from the K-L equation was approximately 3.6, indicating a mainly four-electron (4e⁻) transfer process; this could be attributed to the fact that the Fe-N₄ sites, serving as active centers, reduce the formation energy barrier of the key intermediate and the free energy change (ΔG) during the 4e⁻ ORR process [11,19]. Moreover, 250Fe-SA/NPC-800 showed a higher stability than 40 wt% Pt/C (Fig. S7). After continuous operation for 6 h, more than 87% of the initial current density was retained on 250Fe-SA/NPC-800, whereas Pt/C showed an obvious deterioration, with a retention of only 49%.

4. Conclusions

In summary, the carbon-assisted pyrolysis of metal complexes has been shown to be an efficient method for the facile synthesis of high-loading Fe-based single-atom catalysts (7.5 wt%). Carbon materials with high surface area were employed as support to improve the overall dispersion of Fe-containing complexes. The coordination between Fe ions and small organic molecules with nitrogen groups could effectively prevent agglomeration of Fe atoms, and thus further increase the Fe content after pyrolysis by a significant extent. In addition, ferric nitrate catalyzed organic ligand to N-doped carbon as substrates. Various characterization analyses showed that single Fe atoms were isolated and anchored on the N-doped carbon supports, forming Fe-N₄ structures. The ORR activity of the Fe-SA catalysts gradually increased with increasing Fe-N₄ loading. The 250Fe-SA/NPC-800 sample exhibited the best performance, with an onset potential of 0.97 V and a half-wave potential of 0.85 V. This work provides a simple approach for the large-scale synthesis of high-loading single-atom catalysts; the performance of the SACs could be further improved by optimizing their surface area and structural properties.

References

- [1] B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, *Nat. Chem.*, **2011**, 3, 634–641.
- [2] H. Fei, J. Dong, M. J. Arellano-Jimenez, G. Ye, N. Dong Kim, E. L. Samuel, Z. Peng, Z. Zhu, F. Qin, J. Bao, M. J. Yacaman, P. M. Ajayan, D. Chen, J. M. Tour, *Nat. Commun.*, **2015**, 6, 8668.
- [3] N. Cheng, S. Stambula, D. Wang, M. N. Banis, J. Liu, A. Riese, B. Xiao, R. Li, T. K. Sham, L. M. Liu, G. A. Botton, X. Sun, *Nat. Commun.*, **2016**, 7, 13638.
- [4] X. Li, W. Bi, L. Zhang, S. Tao, W. Chu, Q. Zhang, Y. Luo, C. Wu, Y. Xie, *Adv. Mater.*, **2016**, 28, 2427–2431.
- [5] Y. Chen, Z. Huang, Z. Ma, J. Chena, X. Tang, *Catal. Sci. Technol.*, **2017**, 7, 4250–4258.
- [6] J. J. Kim, H. E. Kim, H. Lee, *ChemSusChem*, **2018**, 11, 104–113.
- [7] S. Ding, M. J. Hulse, J. P. rez-Ramirez, N. Yan, *Joule*, **2019**, 3,

Graphical Abstract

Chin. J. Catal., 2021, 42: 753–761 doi: 10.1016/S1872-2067(20)63689-0

Fabricating high-loading Fe-N₄ single-atom catalysts for oxygen reduction reaction by carbon-assisted pyrolysis of metal complexes

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A high-loading Fe-N₄ single-atom catalyst with 7.5 wt% Fe loading was prepared by carbon-assisted pyrolysis of Fe complexes. The optimized 250Fe-SA/NPC-800 catalyst exhibited onset and half-wave ORR potentials of 0.97 and 0.85 V, respectively.

- 2897–2929.
- [8] C. Zhu, S. Fu, Q. Shi, D. Du, Y. Lin, *Angew. Chem. Int. Ed.*, **2017**, 56, 13944–13960.
 - [9] X. Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, *Acc. Chem. Res.*, **2013**, 48, 1740–1748.
 - [10] F. Pan, H. Zhang, K. Liu, D. Cullen, K. More, M. Wang, Z. Feng, G. Wang, G. Wu, Y. Li, *ACS Catal.*, **2018**, 8, 3116–3122.
 - [11] Y. Pan, S. Liu, K. Sun, X. Chen, B. Wang, K. Wu, X. Cao, W. C. Cheong, R. Shen, A. Han, Z. Chen, L. Zheng, J. Luo, Y. Lin, Y. Liu, D. Wang, Q. Peng, Q. Zhang, C. Chen, Y. Li, *Angew. Chem. Int. Ed.*, **2018**, 57, 8614–8618.
 - [12] Z. Chen, Q. Zhang, W. Chen, J. Dong, H. Yao, X. Zhang, X. Tong, D. Wang, Q. Peng, C. Chen, W. He, Y. Li, *Adv. Mater.*, **2018**, 30, 1704720.
 - [13] Q. Qin, T. Heil, M. Antonietti, M. Oschatz, *Small Methods*, **2018**, 2, 1800202.
 - [14] Z. Wang, L. Gu, L. Song, H. Wang, R. Yu, *Mater. Chem. Front.*, **2018**, 2, 1024–1030.
 - [15] C. Zhu, S. Fu, J. Song, Q. Shi, D. Su, M. H. Engelhard, X. Li, D. Xiao, D. Li, L. Estevez, D. Du, Y. Lin, *Small*, **2017**, 13, 1603407.
 - [16] S. Fu, C. Zhu, D. Su, J. Song, S. Yao, S. Feng, M. H. Engelhard, D. Du, Y. Lin, *Small*, **2018**, 14, 1703118.
 - [17] R. Jiang, L. Li, T. Sheng, G. Hu, Y. Chen, L. Wang, *J. Am. Chem. Soc.*, **2018**, 140, 11594–11598.
 - [18] Q. Li, W. Chen, H. Xiao, Y. Gong, Z. Li, L. Zheng, X. Zheng, W. Yan, W. C. Cheong, R. Shen, N. Fu, L. Gu, Z. Zhuang, C. Chen, D. Wang, Q. Peng, J. Li, Y. Li, *Adv. Mater.*, **2018**, 30, 1800588.
 - [19] Z. Miao, X. Wang, M.-C. Tsai, Q. Jin, J. Liang, F. Ma, T. Wang, S. Zheng, B.-J. Hwang, Y. Huang, S. Guo, Q. Li, *Adv. Energy Mater.*, **2018**, 8, 1801226.
 - [20] Z. Yang, Y. Wang, M. Zhu, Z. Li, W. Chen, W. Wei, T. Yuan, Y. Qu, Q. Xu, C. Zhao, X. Wang, P. Li, Y. Li, Y. Wu, Y. Li, *ACS Catal.*, **2019**, 9, 2158–2163.
 - [21] L. Zhao, Y. Zhang, L. B. Huang, X. Z. Liu, Q. H. Zhang, C. He, Z. Y. Wu, L. J. Zhang, J. Wu, W. Yang, L. Gu, J. S. Hu, L. J. Wan, *Nat. Commun.*, **2019**, 10, 1278.
 - [22] R. Zhao, Z. Liang, S. Gao, C. Yang, B. Zhu, J. Zhao, C. Qu, R. Zou, Q. Xu, *Angew. Chem. Int. Ed.*, **2019**, 58, 1975–1979.
 - [23] Y. Pan, R. Lin, Y. Chen, S. Liu, W. Zhu, X. Cao, W. Chen, K. Wu, W. C. Cheong, Y. Wang, L. Zheng, J. Luo, Y. Lin, Y. Liu, C. Liu, J. Li, Q. Lu, X. Chen, D. Wang, Q. Peng, C. Chen, Y. Li, *J. Am. Chem. Soc.*, **2018**, 140, 4218–4221.
 - [24] Y. Zhu, W. Sun, W. Chen, T. Cao, Y. Xiong, J. Luo, J. Dong, L. Zheng, J. Zhang, X. Wang, C. Chen, Q. Peng, D. Wang, Y. Li, *Adv. Funct. Mater.*, **2018**, 28, 1802167.
 - [25] F. Li, G.-F. Han, H.-J. Noh, S.-J. Kim, Y. Lu, H. Y. Jeong, Z. Fu, J.-B. Baek, *Energy Environ. Sci.*, **2018**, 11, 2263–2269.
 - [26] R. Trofimovaite, C. M. A. Parlett, S. Kumar, L. Frattini, M. A. Isaacs, K. Wilson, L. Olivi, B. Coulson, J. Debgupta, R. E. Douthwaite, A. F. Lee, *Appl. Catal. B*, **2018**, 232, 501–511.
 - [27] D. Karapinar, N. T. Huan, N. R. Sahraie, J. Li, D. Wakerley, N. Touati, S. Zanna, D. Taverna, L. H. G. Tizei, A. Zitolo, F. Jaouen, V. Mougel, M. Fontecave, *Angew. Chem. Int. Ed.*, **2019**, 58, 15098–15103.
 - [28] F. Huang, Y. Deng, Y. Chen, X. Cai, M. Peng, Z. Jia, J. Xie, D. Xiao, X. Wen, N. Wang, Z. Jiang, H. Liu, D. Ma, *Nat. Commun.*, **2019**, 10, 4431.
 - [29] P. Song, M. Luo, X. Liu, W. Xing, W. Xu, Z. Jiang, L. Gu, *Adv. Funct. Mater.*, **2017**, 27, 1700802.
 - [30] Q. Yang, C. C. Yang, C. H. Lin, H. L. Jiang, *Angew. Chem. Int. Ed.*, **2019**, 58, 3511–3515.
 - [31] X. Cui, X. Dai, A.-E. Surkus, K. Junge, C. Kreyenschulte, G. Agostini, N. Rockstroh, M. Beller, *Chin. J. Catal.*, **2019**, 40, 1679–1685.
 - [32] D. A. Bulushev, M. Zacharska, A. S. Lisitsyn, O. Y. Podyacheva, F. S. Hage, Q. M. Ramasse, U. Bangert, L. G. Bulusheva, *ACS Catal.*, **2016**, 6, 3442–3451.
 - [33] S. Ye, F. Luo, Q. Zhang, P. Zhang, T. Xu, Q. Wang, D. He, L. Guo, Y. Zhang, C. He, X. Ouyang, M. Gu, J. Liu, X. Sun, *Energy Environ. Sci.*, **2019**, 12, 1000–1007.
 - [34] R. Lang, W. Xi, J. C. Liu, Y. T. Cui, T. Li, A. F. Lee, F. Chen, Y. Chen, L. Li, J. Lin, S. Miao, X. Liu, A. Q. Wang, X. Wang, J. Luo, B. Qiao, J. Li, T. Zhang, *Nat. Commun.*, **2019**, 10, 234.
 - [35] X. Sun, M. Liu, Y. Huang, B. Li, Z. Zhao, *Chin. J. Catal.*, **2019**, 40, 819–825.
 - [36] F. Huang, Y. Deng, Y. Chen, X. Cai, M. Peng, Z. Jia, P. Ren, D. Xiao, X. Wen, N. Wang, H. Liu, D. Ma, *J. Am. Chem. Soc.*, **2018**, 140, 13142–13146.
 - [37] Y. Yan, B. Ye, M. Chen, L. Lu, J. Yu, Y. Zhou, Y. Wang, J. Liu, L. Xiao, S. Zou, J. Fan, *Chin. J. Catal.*, **2020**, 41, 1240–1247.
 - [38] B. Han, R. Lang, H. Tang, J. Xu, X.-K. Gu, B. Qiao, J. Liu, *Chin. J. Catal.*, **2019**, 40, 1847–1853.
 - [39] Z. Geng, Y. Liu, X. Kong, P. Li, K. Li, Z. Liu, J. Du, M. Shu, R. Si, J. Zeng, *Adv. Mater.*, **2018**, e1803498.
 - [40] A. Aitbekova, C. J. Wrasman, A. R. Riscoe, L. Y. Kunz, M. Cargnello, *Chin. J. Catal.*, **2020**, 41, 998–1005.
 - [41] H. T. Chung, D. A. Cullen, D. Higgins, B. T. Sneed, E. F. Holby, K. L. More, P. Zelenay, *Science*, **2017**, 357, 479–484.
 - [42] U. Tylus, Q. Jia, K. Strickland, N. Ramaswamy, A. Serov, P. Atanassov, S. Mukerjee, *J. Phys. Chem. C*, **2014**, 118, 8999–9008.
 - [43] A. Serov, K. Artyushkova, P. Atanassov, *Adv. Energy Mater.*, **2014**, 4, 1301735.
 - [44] X. Wan, X. Liu, Y. Li, R. Yu, L. Zheng, W. Yan, H. Wang, M. Xu, J. Shui, *Nat. Catal.*, **2019**, 2, 259–268.
 - [45] J. Wang, G. Han, L. Wang, L. Du, G. Chen, Y. Gao, Y. Ma, C. Du, X. Cheng, P. Zuo, G. Yin, *Small*, **2018**, 14, 1704282.
 - [46] M. Xiao, J. Zhu, L. Ma, Z. Jin, J. Ge, X. Deng, Y. Hou, Q. He, J. Li, Q. Jia, S. Mukerjee, R. Yang, Z. Jiang, D. Su, C. Liu, W. Xing, *ACS Catal.*, **2018**, 8, 2824–2832.
 - [47] Y. Deng, B. Chi, J. Li, G. Wang, L. Zheng, X. Shi, Z. Cui, L. Du, S. Liao, K. Zang, J. Luo, Y. Hu, X. Sun, *Adv. Energy Mater.*, **2019**, 9, 1802856.
 - [48] L. Yang, D. Cheng, H. Xu, X. Zeng, X. Wan, J. Shui, Z. Xiang, D. Cao, *Proc. Natl. Acad. Sci. USA*, **2018**, 115, 6626–6631.
 - [49] D. Lyu, Y. B. Mollamahale, S. Huang, P. Zhu, X. Zhang, Y. Du, S. Wang, M. Qing, Z. Q. Tian, P. K. Shen, *J. Catal.*, **2018**, 368, 279–290.
 - [50] J.-D. Yi, R. Xu, Q. Wu, T. Zhang, K.-T. Zang, J. Luo, Y.-L. Liang, Y.-B. Huang, R. Cao, *ACS Energy Lett.*, **2018**, 3, 883–889.
 - [51] Y. Cheng, S. He, S. Lu, J. P. Veder, B. Johannessen, L. Thomsen, M. Saunders, T. Becker, R. De Marco, Q. Li, S. Z. Yang, S. P. Jiang, *Adv. Sci.*, **2019**, 6, 1802066.
 - [52] M. Sevilla, A. S. M. Al-Jumaily, A. B. Fuertes, R. Mokaya, *ACS Appl. Mater. Interfaces*, **2018**, 10, 1623–1633.
 - [53] E. Bill, E. Bothe, P. Chaudhuri, K. Chlopek, D. Herebian, S. Kokatam, K. Ray, T. Weyhermuller, F. Neese, K. Wieghardt, *Chem. Eur. J.*, **2004**, 11, 204–224.
 - [54] Z. Wu, S. Xu, Q. Yan, Z. Chen, Y. Ding, C. Li, H. Liang, S. Yu, *Sci. Adv.*, **2018**, 4, eaat0788.
 - [55] L. Osmieri, R. Escudero-Cid, A. Videla, P. Ocón, P. Specchia, *Appl. Catal. B*, **2017**, 201, 253–265.
 - [56] Q. Yang, Y. Jia, F. Wei, L. Zhuang, D. Yang, J. Liu, X. Wang, S. Lin, P. Yuan, X. Yao, *Angew. Chem. Int. Ed.*, **2020**, 59, 6122–6127.
 - [57] H. Zhang, J. Wang, Z. Zhao, H. Zhao, M. Cheng, A. Li, C. Wang, J. Wang, *Green Chem.*, **2018**, 20, 3521–3529.
 - [58] H. Xue, T. He, J. M. Chabu, J. Liu, H. Wu, J. Zheng, M. Tan, J. Ma, R.

- Shen, L. Deng, Y. Zhang, *Adv. Mater. Interfaces*, **2018**, 5, 1701345.
- [59] D. Xia, X. Yang, L. Xie, Y. Wei, W. Jiang, M. Dou, X. Li, J. Li, L. Gan, F. Kang, *Adv. Funct. Mater.*, **2019**, 1906174.
- [60] W. Ren, X. Tan, W. Yang, C. Jia, S. Xu, K. Wang, S. C. Smith, C. Zhao, *Angew. Chem. Int. Ed.*, **2019**, 58, 6972–6976.
- [61] Z. Zhang, J. Sun, F. Wang, L. Dai, *Angew. Chem. Int. Ed.*, **2018**, 57, 9038–9043.
- [62] T. Asset, P. Atanassov, *Joule*, **2020**, 4, 33–44.

碳辅助金属配合物热解法制备高含量Fe-N₄单原子催化剂用于氧还原反应

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摘要: 单原子催化剂凭借其超高的原子利用率及在某些反应中表现出的出色催化效果, 被认为是最有前途的电催化剂之一, 引起了研究人员的极大热情和兴趣。制备高金属含量的单原子催化剂是基础研究和实际应用的前提和关键。然而, 由于原子表面自由能随着尺寸的减小而急剧增加, 在制备和催化过程中, 单原子催化剂的金属原子很容易聚集成团簇甚至颗粒, 因此如何制备高负载量的单原子催化剂仍然是一个不小的挑战。在众多单原子催化剂中, 非贵金属中铁基单原子被认为是燃料电池中的Pt催化剂的有效替代品。在燃料电池的核心反应—电催化氧还原反应中, Fe-N₄被证明是铁单原子催化剂中的主要活性中心。因此, 为了获得更好的氧还原性能, 提高铁单原子催化剂中Fe-N₄的含量就显得非常关键。前期已报道了一些关于制备高Fe含量的铁单原子催化剂材料的策略, 例如空间限域策略和配位合成策略。其中吡啶和葡萄糖作为配位剂, 双氰胺和三聚氰胺可热解成氮掺杂碳材料以捕获金属原子, 形成M-N₄。同时, 具有高比表面积的富氧碳载体可以通过掺杂氮来作为固定金属原子的位点。

我们开发了一种简单直接的方法, 通过碳辅助金属配合物热解法制备高金属含量的Fe-N₄单原子催化剂, 即在最佳碳化温度800 °C、三聚氰胺存在下对氮掺杂多孔碳辅助分散铁邻苯二胺配合物进行热解。在该方法中, 氮掺杂多孔碳是一种具有丰富氮缺陷, 高表面积(1267 m²·g⁻¹)和良好分散性的多孔生物质碳材料。邻苯二胺作为含两个氨基的二齿配体, 可以很容易地与过渡金属配位, 形成稳定的平面四配位络合物。此外, 由于在高温条件下过渡金属的催化作用, 邻苯二胺也被用作氮掺杂碳的前体。因此, 氮掺杂多孔碳和邻苯二胺是合成高金属含量铁单原子催化剂的关键前驱体。通过X射线光电谱, 大角度环形暗场扫描透射电子显微镜和X射线吸收精细结构光谱表征, 发现所制备的铁单原子催化剂中铁原子以单个原子的形式锚固在碳载体上, 并与碳基质的四个掺杂氮原子配位, 得到Fe-N₄的构型。通过调节Fe前驱体量, 铁单原子催化剂中Fe的最高负载量达到7.5 wt%, 在目前已经报道的铁单原子催化剂中排第四。

电催化氧还原测试表明, 在0.10 M KOH溶液中, 随着铁含量的增加, 铁单原子催化剂的氧还原性能逐渐提高。其中250Fe-SA/NPC-800样品表现出最高起始电位0.97 V和最正的半波电位0.85 V, 可与市售的40% Pt/C催化剂相媲美。和已报道的铁单原子催化剂相比, 由于我们制得的催化剂的比表面积较低, 只有247 m²·g⁻¹, 所以制约了催化剂的性能。在混合动力势域中, 根据Koutecky-Levich方程计算得出的电子转移数约为3.6, 表明250Fe-SA/NPC-800主要催化四电子转移过程, 这可以归因于以Fe-N₄活性中心降低了四电子过程中关键中间体的形成能垒及过程的自由能变化。此外, 250Fe-SA/NPC-800展现了较高的电化学稳定性。连续工作6 h后, 250Fe-SA/NPC-800保留了超过87%的电流密度, 而Pt/C表现出明显的衰减, 仅保留了49%。

关键词: Fe-N₄单原子催化剂; 氧还原反应; 高含量; 配位效应; 四电子转移过程

收稿日期: 2020-04-19. 接受日期: 2020-06-11. 上网日期: 2020-09-22.

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基金来源: 广东省自然科学基金(2018A0303130101).

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