SPECIAL TOPIC: Single-atom Catalysts

Boosting the activity of Fe–N_x moieties in Fe–N–C electrocatalysts via phosphorus doping for oxygen reduction reaction

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ABSTRACT The Fe–N–C material is a promising non-noble-metal electrocatalyst for oxygen reduction reaction (ORR). Further improvement on the ORR activity is highly desired in order to replace Pt/C in acidic media. Herein, we developed a new-type of single-atom Fe–N–C electrocatalyst, in which Fe–N_x active sites were modified by P atoms. The half-wave potential of the optimized material reached 0.858 V, which is 23 mV higher than that of the pristine one in a 0.1 mol L^{−1} HClO₄ solution. Density functional theory (DFT) calculations revealed that P-doping can reduce the thermodynamic overpotential of the rate determining step and consequently improve the ORR activity.

Keywords: P-doping, single-atom catalysts, oxygen reduction

INTRODUCTION

As one of the most promising clean and renewable energy devices, proton exchange membrane fuel cells (PEMFCs) recently have attracted considerable attention due to their zero emissions [1–3]. The sluggish reaction kinetics of the cathodic oxygen reduction reaction (ORR) requires loading of highly costly Pt-based materials [4,5]. Recently, extensive studies have been focused on developing noble-metal-free electrocatalysts to reduce the material cost [6–9]. Compared with other noble-metal-free electrocatalysts, Fe–N–C materials have drawn the most atten-

tion due to their high activity in acidic media [10–13]. It is generally acknowledged that single Fe atoms coordinated by N (Fe–N_x moieties) are the active sites for the ORR in Fe–N–C [14–17]. To achieve robust and efficient Fe–N_x moieties in Fe–N–C catalysts, a high-temperature heat-treatment (higher than 700°C) is usually employed, during which Fe atoms easily agglomerate into nanosized counterparts [18–20]. Such Fe-containing nanoparticles are not so active for ORR in acidic media.

To solve this issue, extensive work has been devoted to improving Fe–N–C materials with atomically dispersed Fe atoms (denoted as single-atom Fe catalysts), such as silica-protective-layer-assisted technique, atomic isolation method, secondary-atom-assisted synthesis, and confine approach [21–26]. Recently, S doping into Fe–N–C materials has been demonstrated as an effective strategy to elevate ORR activity in acidic media [27,28]. However, S atoms can only be doped at the edge of graphene or defects [29], which may limit the number of S-modified Fe–N_x moieties. Different from S, P can be easily doped into carbon matrix by replacing an arbitrary carbon [30,31]. Furthermore, the synergistic effect of P doping in N-doped carbon has been demonstrated [32–34]. These facts motivate us to explore the effect of P doping into single-atom Fe catalysts.

Herein, we engineered a P-modified Fe–N-doped car-

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bon nanowire (P-FeNCNW), involving a self-assembly synthesis of phytic acid-modified polypyrrole nanowire, Fe^{3+} and Na^+ adsorption, and subsequent simple pyrolysis. Aberration-corrected transmission electron microscopy (TEM) and extended X-ray absorption fine structure (EXAFS) results confirmed the atomic distribution of Fe in P-FeNCNW. Both control experiments and density functional theory (DFT) calculations demonstrated that additional P doping can boost the ORR activity of single-atom Fe–N–C materials.

RESULTS

Fig. S1 shows the preparation scheme of P-FeNCNW. In a typical synthesis, ammonium peroxydisulfate was added into HCl solution containing cetyltrimethyl ammonium bromide to create a white precipitate. Then pyrrole and phytic acid were added into the above mixture. After continuous stirring for 1 day to allow for polymerization, phytic acid-modified polypyrrole nanowires (Fig. S2) were collected by vacuum filtration and washed with water and ethanol. Subsequently, the wet product was then dispersed in a mixture of sodium chloride and iron nitrate for adsorbing Na^+ and Fe^{3+} cations. Finally, the phytic acid-modified polypyrrole nanowires with metal ions were suffered from pyrolysis, acid leaching, and secondary heat-treatment to obtain the P-FeNCNW sample. For comparison, polypyrrole nanowires were synthesized in the absence of phytic acid. As shown in Fig. S3, there is no observable polymer structure change

after the introduction of phytic acid, which excludes the structure variation effect for studying the P-doping effect. FeNCNW (Fig. S4) was obtained by performing the same route of Fe^{3+} and Na^+ adsorption and pyrolysis.

The morphology and structure of P-FeNCNW were characterized by scanning electron microscopy (SEM) and TEM. P-FeNCNW inherits the structure of the raw material, showing a one-dimensional nanowire structure (Fig. 1a, b). High-resolution TEM image (Fig. 1c) shows that P-FeNCNW holds remarkably distorted graphite layers, suggesting its high crystallinity and good electrical conductivity. Meanwhile, such distorted structure means abundant defects and heteroatom-doped moieties, which plays a significant role in facilitating ORR electrocatalysis. Fig. 1d shows a typical high-resolution TEM image of the edge of a P-FeNCNW. There are abundant single-layer and few-layer graphene domains, which can host large numbers of heteroatom-doped moieties [35], such as N and/or P doping, $\text{Fe}-\text{N}_x$, and P modified $\text{Fe}-\text{N}_x$. Furthermore, no nanosized Fe-species was observed, which suggests that Fe can be in a form of isolated atoms in P-FeNCNW.

To reveal the specific surface area and pore structure, N_2 adsorption/desorption measurements were performed. Compared with FeNCNW, P-FeNCNW shows a stronger adsorption at the low-pressure region ($P/P_0=0-0.1$) (Fig. 1e), which demonstrates that P-FeNCNW holds more micropores. The pore distribution curves are shown in Fig. S5 with P-FeNCNW holding a larger micropore

Figure 1 (a) SEM and (b–d) TEM images of P-FeNCNW. (e) N_2 adsorption/desorption isotherms and (f) XRD patterns of P-FeNCNW and FeNCNW.

volume than that of FeNCNW. The Brunauer-Emmett-Teller (BET) surface area of P-FeNCNW is $566 \text{ m}^2 \text{ g}^{-1}$, larger than that of FeNCNW ($445 \text{ m}^2 \text{ g}^{-1}$). These results reveal that the secondary P doping is beneficial to creating micropores and increasing BET surface area. X-ray diffraction (XRD) patterns in Fig. 1f show that both P-FeNCNW and FeNCNW have two characteristic peaks at 25.7° and 43.7° of graphite. No XRD pattern from iron species was detected.

To directly confirm the Fe configuration in P-FeNCNW, aberration-corrected TEM imaging was employed. Fig. 2a shows a typical high-angle annular dark-field scanning TEM (HAADF-STEM) image of P-FeNCNW. Large numbers of bright dots resulting from isolated Fe atoms were marked by red cycles while some Fe species clusters marked by blue cycles were also observed. STEM imaging coupled with energy-dispersive X-ray spectroscopy (EDS) was performed to investigate the chemical components and element distribution in P-FeNCNW and the results are shown in Fig. 2b. C, N, O, P, and Fe elements are uniformly distributed in carbon nanowires. The detected O element may originate from adsorbed oxygen on P-FeNCNW while N, P and Fe should be successfully doped into carbon matrix. To quantitatively evaluate the chemical composition and doping configurations, X-ray photoelectron spectroscopy (XPS) was carried out. C (88.6 at%), N (6.5 at%), O (4.4 at%), P (0.2 at%), and Fe (0.3 at%) elements were

detected in P-FeNCNW (Fig. S6a), in agreement with EDS result and further confirming N, P and Fe were successfully doped into carbon matrix. Inductively coupled plasma mass spectrometry measurement shows the Fe content is 1.54 wt%. Although additional P doping has almost no effect on the contents of N and Fe (Fig. S6), the N configurations in P-FeNCNW and FeNCNW are different (Fig. 2c). Clearly, the percentage of pyridinic N in P-FeNCNW (39.2%) is higher than that in FeNCNW (32.8%). Our result is consistent with previous reports that P doping could increase the pyridinic N in N-doped carbon and greatly boost the ORR activity [36]. Furthermore, EXAFS measurements were performed to evaluate the Fe status at the atomic level. Fig. 2d shows Fourier-transform EXAFS spectrum of P-FeNCNW. There is only a single peak at $\sim 1.4 \text{ \AA}$ originating from the Fe-N bond while the peak at $\sim 2.1 \text{ \AA}$ from Fe-Fe bond is absent. This result further confirms that Fe exists in P-FeNCNW as an atomically dispersed Fe-N_x moiety and is in good agreement with the TEM results. X-ray absorption near-edge structure (XANES) spectrum of Fe in P-FeNCNW (Fig. 2e) shows its absorption edge located between standard FeO and Fe₂O₃, suggesting that the Fe oxidation state in atomic Fe-N_x moieties coexists in 2+ and 3+, which is consistent with previous reports [37,38].

The ORR activity was evaluated in an O₂-saturated 0.1 mol L⁻¹ HClO₄ by using rotating ring-disk electrode (RRDE) technique. Fig. 3a shows the ORR polarization

Figure 2 (a) Typical HAADF-STEM image of P-FeNCNW. (b) STEM image and corresponding EDS element mapping of P-FeNCNW. (c) XPS N 1s spectra of FeNCNW and P-FeNCNW. (d) Fourier-transform EXAFS spectra of P-FeNCNW and Fe foil. (e) Fe K-edge X-ray absorption near-edge structure (XANES) spectra of P-FeNCNW and reference samples.

Figure 3 (a) ORR polarization curves of P-NCNW, FeNCNW, P-FeNCNW and Pt/C. (b) Peroxide yields and electron transfer numbers of FeNCNW and P-FeNCNW. (c) Tafel plots of FeNCNW and P-FeNCNW. (d) ORR polarization curves of P-FeNCNW before and after 5000 potential cycles. All electrochemical measurements were performed in oxygen-saturated 0.1 mol L⁻¹ HClO₄ at 1600 r min⁻¹ with a scan rate of 5 mV s⁻¹.

curves of FeNCNW, P-FeNCNW, and Pt/C (28.2 wt%, TKK). FeNCNW exhibits a good ORR activity with a half-wave potential of 0.835 V, which is at the high end of similar Fe–N–C electrocatalysts with the same loading of 0.2 mg cm⁻² in Refs. [39,40] and better than that of metal-free P–N co-doped carbon nanowire (P–NCNW) catalyst. Interestingly, P-doping can increase the half-wave potential (0.858 V) by 23 mV. Nevertheless, the ORR activity of P-FeNCNW is still poorer than that of Pt/C (0.889 V). The H₂O₂ yield and electron transfer number were calculated on the basis of recorded disk and ring currents. As shown in Fig. 3b, the H₂O₂ yield of P-FeNCNW reached the maximum of 1.7% at ~0.75 V and then decreased to less than 1.0% when the potential was lower than 0.52 V. On the contrast, the highest H₂O₂ yield of FeNCNW was as high as 5.2%. The average electron-transfer-number of P-FeNCNW was 3.98 at all potentials, which is superior to that of FeNCNW (3.94). This result reveals that P-FeNCNW follows a four-electron-transfer pathway and has a much higher ORR efficiency than conventional FeNCNW. The four-electron transfer reaction pathway was also confirmed by the Koutecky-Levich analysis (Fig. S7).

After mass transport correction, the kinetic current densities of P-FeNCNW and FeNCNW were derived and compared in Fig. 3c. The Tafel slope of P-FeNCNW is 68 mV decade⁻¹, slightly smaller than that of FeNCNW (72 mV decade⁻¹). More importantly, P-FeNCNW shows a large kinetic current density of 16.2 mA cm⁻² at 0.8 V, which is 1.8 times that of FeNCNW (9.0 mA cm⁻²). In addition to the catalytic activity, the stability assessment was carried out by cycling the catalyst between 0.6 and 1.0 V at 50 mV s⁻¹. As shown in Fig. 3d, after 5000 potential cycles, the half-wave potential of P-FeNCNW only dropped 18 mV, which is competitive with most of Fe–N–C electrocatalysts [41–43]. We compared P-FeNCNW with commonly reported Fe/Co–N–C catalysts (Table S1). Clearly, P-FeNCNW represents one of the best Fe/Co–N–C catalysts.

DISCUSSION

Based on above results, P doping in single-atom Fe–N–C catalyst can boost its ORR activity. However, if excessive P precursors were added during the synthesis, nanosized Fe₂P species could be formed (Figs S8 and S9), resulting in a low ORR activity (Fig. S10). Interestingly, the content

Figure 4 (a) Computational models and (b) free energy diagrams of the ORR process on Fe-N₄ site for FeN₄C, FeN₄CP1, and FeN₄CP3 models at U=0 and 0.8 V, pH 1, and T=298 K.

of pyridinic N decreased with the formation of Fe₂P species (Fig. S11). We suspect that the concentration of Fe-N_x moieties also decreased with the Fe₂P formation, resulting in a lower density of active sites.

Finally, DFT calculations were performed to understand the mechanism of activity improvement by P-doping in Fe-N-C electrocatalysts. The computational details are presented in the Supporting Information online. The Fe-N₄ configuration was embedded in the graphene sheet to represent the Fe-N-C catalysts (FeN₄C structure, Fig. S12). The first and second neighbor carbon sites around the Fe-N₄ square-planar were substituted by P atoms to model the P-doping. Consequently, five possible models were constructed and the optimized geometry structures are shown in Fig. S13. Among these models, the FeN₄CP1 and FeN₄CP3 (Fig. 4a) are thermodynamically stable according to their lower formation energies. The free energy diagrams of the ORR process on Fe-N₄ site for FeN₄C, FeN₄CP1 and FeN₄CP3 models are shown in Fig. 4b. It can be observed that, at the applied potential of U=0 V, all the reaction steps are downhill in free energy, implying the facile reactions on these three catalysts. However, the thermodynamic limiting potentials for FeN₄C, FeN₄CP3 and FeN₄CP1 are 0.46, 0.47 and 0.48 V, respectively, indicating the theoretical overpotentials of 0.77, 0.76 and 0.75 V for FeN₄C, FeN₄CP3 and FeN₄CP1. Besides, at U=0.80 V, the first and third reaction steps are exothermic, while the second, fourth and fifth steps are endothermic for ORR process on these three models. The rate-determining step (RDS) is the reduction of OH* to H₂O with the thermodynamic overpotential of 0.32, 0.33 and 0.34 eV for FeN₄CP1, FeN₄CP3 and FeN₄C, respectively. The ORR processes on both FeN₄CP1 and FeN₄CP3 models have lower theoretical overpotential and thermodynamic overpotential

compared with that of the FeN₄C, suggesting that P-doping Fe-N-C catalyst is energetically more favorable for the ORR process, which is in good agreement with our experimental observations.

CONCLUSIONS

In conclusion, P-doped single-atom Fe-N-C catalysts were synthesized by employing a self-assembly strategy of phytic acid-modified polypyrrole nanowire, followed by Fe³⁺ and Na⁺ adsorption and subsequent simple pyrolysis. Optimized P doping can boost the activity of single-atom Fe-N-C catalyst by two times in acidic media. DFT calculations demonstrated that P doping around Fe-N₄ moiety modulated the electron structure, thus, decreased the energy barrier in the rate determining step and boosted the ORR activity. This work proposed a new strategy to achieve more active Fe-N-C catalysts by modulating the coordinated environment of single-atom active sites.

Received 31 August 2019; accepted 10 October 2019;
published online 15 November 2019

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Acknowledgements This work was supported by the National Key R&D Program of China (2017YFB0102900), the Research Grant Council (N_HKUST610/17) of Hong Kong Special Administrative Region. It used resources of the Advanced Photon Source, Office of Science user facilities, supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-AC02-06CH11357). Lin Y would like to acknowledge the WSU start-up fund. Li T is thankful for the NIU start-up fund.

Author contributions Li JC, Shao M, and Lin Y designed the experiments; Li JC, Zhong H, Xu M, Li T, Wang L, Shi Q, Feng S, Lyu Z, Liu D, Du D, Beckman SP, and Pan X performed the experiments and data analysis; Li JC, Shao M, and Lin Y wrote the manuscript. All authors contributed to the general discussion, reviewed and revised the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental detail and supporting data are available in the online version of the paper.

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P掺杂提高Fe-N-C催化剂中Fe-N_x活性基团的氧还原催化活性

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摘要 Fe-N-C材料是一类有前景的非贵金属氧还原催化剂。为了在酸性介质中取代Pt/C催化剂, 需要大幅度地改善其氧还原催化活性。本文提出一种通过P原子掺杂的方法来调节单原子Fe-N-C材料中Fe-N_x活性位点的活性。优化得到的材料在0.1 mol L⁻¹ HClO₄溶液中表现出优异的氧还原性能, 其半波电位为0.858 V(比没有P掺杂的Fe-N-C材料高23 mV)。密度泛函理论计算表明, P掺杂能降低限制步骤的热力学过电位, 从而提高其氧还原催化活性。