Fe$_2$O$_3$ Embedded Nitrogen-doped Biomass Carbon as Electro catalyst for the Oxygen Reduction Reaction

Yanling Wu$^{1*}$, Huiji Jiao$^1$, Mingqian Hou$^1$, Peng Zhang$^1$

$^1$School of transportation and civil engineering, Shandong Jiaotong University, Jinan, China

$^*$$^*$wuianling621@163.com

Abstract—Catalyst for ORR is important in the field of energy conversion. Previous research has shown that nanoparticle-embedded into N-doped carbon materials are a good ORR candidates. Here, Fe$_2$O$_3$/N-doped biomass carbon (named Fe$_2$O$_3$/N-bio-C) ORR catalyst via a pyrolysis process of mixture from the Heme precursor and biomass material (named poplar flowers). The as-synthesized electrocatalyst of Fe$_2$O$_3$/N-bio-C exhibits good electroactivity due to the formation of Fe$_2$O$_3$ nanoparticle active sites and abundant N-containing groups. The work points the way to synthesize the low-cost Fe-based N-doped biomass carbon ORR catalysts.

1. Introduction

Recently, carbon-borne platinum nanoparticles (Pt/C) are mainly used as cathocathode ORR catalyst. The scarcity and high adult nature of Pt resources and the slow ORR kinetic process seriously hinder further development of energy devices [1]. Currently, biomass derivatives are receiving increasing attention as outstanding carbon conductive carriers for ORR catalysts. Especially compared with the traditional fossil fuel activated carbon and carbon black, biochar has unique natural porous structure, large specific surface area, easy processing, etc. More importantly, some biomass materials themselves are self-doped with some miscellaneous atoms (such as nitrogen, phosphorus, sulfur and oxygen.), with more rich surface functional groups (such as carbon-nitrogen/phosphorus/oxygen, metal-carbon/nitrogen, etc.) and unique shape nanostructures (such as two-dimensional, three-dimensional morphological structure, etc.), thus having good catalytic activity [2]. In recent years, Fe$_2$O$_3$ has received widespread attention for its low-cost and composition adjustability. However, its large-scale applications are limited by its poor intrinsic conductivity. How to improve ORR activity has become a hot research direction [3]. Effective combination of metal oxides and carbon material can improve the dispersion of metal oxides, thus improving the conductivity of the overall material. However, how simple, low-cost and reasonable to design of such ORR catalysts still has certain challenges.

In view of this, using biomass poplar flower as a carbon carrier, heme is loaded into biomass poplar flower material through physical adsorption, calcined at 900 °C, and successfully with catalytically active Fe$_2$O$_3$ nanoparticles were loaded onto nitrogen-doped carbon carriers, obtaining a low-cost composite ORR catalyst material (Fe$_2$O$_3$/N-bio-C). And the internal composition, external morphology, graphitization degree and pore structure of bio-C and Fe$_2$O$_3$/N-bio-C catalyst were analyzed by PXRD, SEM, Raman, BET, and XPS characterization methods.
2. The Experiment Section

2.1. Experimental reagents
In the experiment, Heme was bought from Aladdin Reagent Co., Ltd. The methanol was analytically pure.

2.2. Preparation of the materials
Poplar flowers (1.0 g) and heme (0.1 g) were added to methanol (20 mL) and stirred continuously for a day. The mixture was dried, and then ground evenly after cooling. The above-described mixture was then carbonized for 3 h at 800 °C in an inert atmosphere. The final target sample is obtained (named Fe₂O₃/N-bio-C). For comparison, biomass porous graphite carbon material (recorded as bio-C) [4] were done under the same conditions.

2.3. Characterization of the material structure
The phase structure was tested by a X-ray powder diffractor. The sample morphology was characterized by scanning electron microscope (ZIESS, Sigma 500, JSM-6510L). The defect and graphitization of the material were determined by laser microscope Raman spectrometer (Raman, Nanophoton RAMANtouch) and the laser wave source was 532 nm. The porosity of the sample was tested by a specific surface area analyzer (MicroActive for ASAP 2460). The XPS measurement was tested on a Kratos instrument using single-chromatic aluminum K radiation.

2.4. Electrochemical performance test
Electrochemical performance test was performed using CHI 660E electrochemical workstation (Shanghai, China) and spinning disk electrodes (USA, Pine). The preparation process is as follows: the catalyst powder, ethanol and 5 wt% Nafion solution were mixed and ultrasound. Then, the catalyst ink (10 µL, 0.30 mg cm⁻²) was placed on the glass carbon electrode. All tests were performed in a 0.1M KOH electrolyte with a circulating voltamian curve (CV). The scan range was 0~0.8 V. The scan range of linear scan curve (LSV) was 0.2~0.8 V with an RDE speed of 400~2500 rpm.

3. Results and Discussion

3.1. XRD analysis
The crystal structure of the prepared bio-C and Fe₂O₃/N-bio-C were analyzed using PXRD, respectively (Fig. 1). The bio-C and Fe₂O₃/N-bio-C samples both have a wide (002) diffraction peak at ~26° and an obvious (101) diffraction peak at ~44°, indicating that the graphite structure was more disordered, but is dominated by sp² hybridization. Meanwhile, other diffraction peaks also appear in Fe₂O₃/N-bio-C catalyst, and the remaining diffraction peaks can be well matched with Fe₂O₃ (JCPDS No.39-1346) [5].
3.2. **SEM analysis**

The morphology of bio-C and Fe$_2$O$_3$/N-bio-C catalysts prepared was characterized by SEM (Fig. 2). First, the SEM image shows the groove sheet layer structure of the bio-C (Fig. 2a). After the composite material, it is seen that the groove sheet layer structure is loaded with some nanoparticles, as shown in Fig. 2b. We further explored the elemental composition of Fe$_2$O$_3$/N-bio-C catalyst through EDS, and found that the material contained Fe, C, N, O et al., as shown in Fig. 3. In addition, the element distribution map (Fig. 4) further indicates that the Fe, C, N, O is evenly distributed at Fe$_2$O$_3$/N-bio-C sample.

![Fig. 1 The PXRD pattern of the Fe$_2$O$_3$/N-bio-C catalyst](image1.png)

![Fig. 2 The SEM diagrams of (a) bio-C and (b) Fe$_2$O$_3$/N-bio-C catalysts](image2.png)

![Fig. 3 The EDS diagram of the Fe$_2$O$_3$/N-bio-C catalyst](image3.png)
3.3. Raman analysis
Raman (Raman) spectra can be used to characterize structural defects and degree of disorder in carbon. Fig. 5 shows Raman spectrograph of bio-C and Fe₂O₃/N-bio-C catalyst. As can be seen from the Figure, two peaks were seen at 1330 cm⁻¹ and 1590 cm⁻¹ respectively, caused by the sp³ defect site (D band) of the graphite layer and the E₂g vibration mode (G band) of the sp² bond pair. Among them, the ratio of the strength of D peak to the strength of G peak, I_D/I_G, can be used to represent the degree of structural defect of the catalyst material. The larger the value, the more obvious the structural defects [6]. The I_D/I_G values of bio-C and Fe₂O₃/N-bio-C catalysts are 1.065 and 1.042, respectively, and a weak 2D peak appears in Fe₂O₃/N-bio-C catalyst, indicating that the graphitization degree of Fe₂O₃/N-bio-C catalyst is improved after the composite. This will facilitate charge transfer [7].

3.4. Analysis of the specific surface area
For further studies of bio-C and Fe₂O₃/N-bio-C pore structure of catalyst using N₂ (Fig. 6 and Table 1). The absorbent-desorption curves and aperture distribution curves of bio-C and Fe₂O₃/N-bio-C are shown, respectively. Fe₂O₃/N-bio-C catalyst presents a typical IV type characteristic with apparent
hysteresis gyrus, showing the existence of mesoporous structures (Fig. 6a) [8]. The specific surface areas of bio-C and Fe$_2$O$_3$/N-bio-C are 201.43 m$^2$/g and 7.91 m$^2$/g, respectively. The experimental data show that the specific surface area of the composite material decreases sharply, which is caused by the deposition of Fe$_2$O$_3$ nanoparticles on the surface of the biological carbon material, but the channel structure of the biomass is not blocked [9]. As seen in Fig. 6b, the pore size of Fe$_2$O$_3$/N-bio-C is mainly distributed ~3.64 nm, which further proves that it is a mesoporous material.

![Figure 6](image_url)

**Table 1** The physical parameters of bio-C and Fe$_2$O$_3$/N-bio-C catalysts

| Sample         | Surface area (m$^2$/g$^{-1}$) | Average aperture (nm) | Pore volume (cm$^3$/g$^{-1}$) |
|----------------|-------------------------------|------------------------|-------------------------------|
| bio-C          | 201.43                        | 1.74                   | 0.087                         |
| Fe$_2$O$_3$/N-bio-C | 7.91                          | 3.64                   | 0.010                         |

3.5. **XPS analysis**

Specifically, C 1s was divided into three peaks (C=C, C-C, and C-N/C=O) (Fig. 7a). The results show that the Fe$_2$O$_3$/N-bio-C sample mainly exists in the form of graphite [10]. The C-N/C=O peak at 286.8 eV shows that N and O are co-doped into graphite carbon. The N 1s spectrum of Fe$_2$O$_3$/N-bio-C has four peaks (pyridine N, pyrrol C, graphite N and pyridine N), (Fig. 7b). Among the four forms of N element, pyridine N, pyrrol C, graphite N with high electrical activity are dominant. The Fe 2p spectrum of Fe$_2$O$_3$/N-bio-C can be divided into Fe$^{3+}$ 2p$^{3/2}$ (711.0 eV), Fe$_2$O$_3$ 2p$^{3/2}$ (717.1 eV), Fe$^{3+}$ 2p$_{1/2}$ (724.9 eV), and Fe$_2$O$_3$ 2p$_{1/2}$ (732.3 eV), respectively [18], (Fig. 7c). In addition, Fe$_2$O$_3$/N-bio-C analyzed XPS spectra of O 1s region, labeled as O1, O2 and O3 respectively (Fig. 7d), belonging to metal-oxygen bond (530.2 eV), hypoxic coordination at the defect site (531.7 eV), and adsorption of water (533.4 eV), respectively [11-13].
Fig. 7 The XPS curves of the (a) C 1s, (b) N 1s, (c) Fe 2p, and (d) O 1s for Fe$_2$O$_3$/N-bio-C

3.6. ORR catalytic properties

First, the ORR performance of bio-C and Fe$_2$O$_3$/N-bio-C catalysts was measured by CV under saturated O$_2$ and N$_2$, respectively, as shown in Fig. 8a. Compared with bio-C, the peak potential of Fe$_2$O$_3$/N-bio-C catalyst shifted to the corrected value, indicating that the catalytic activity of ORR was successfully improved after further composite. The ORR activity of bio-C and Fe$_2$O$_3$/N-bio-C catalysts was further investigated by LSV, as shown in Fig. 8b. By contrast, the ORR performance of Fe$_2$O$_3$/N-bio-C is the best. The order of ORR activity was bio-C ($E_{onset}$= 0.81 V, $E_{1/2}$= 0.63 V, $J_L$= −3.30 mA·cm$^{-2}$) < Fe$_2$O$_3$/N-bio-C ($E_{onset}$= 0.90 V, $E_{1/2}$= 0.79 V, $J_L$= −4.88 mA·cm$^{-2}$). Although the specific surface area measured by Fe$_2$O$_3$/N-bio-C catalyst is lower than bio-C material. Furthermore, the LSV curves at different speeds were collected (Fig. 8c). According to the data in Fig. 8c, the K-L curves of Fe$_2$O$_3$/N-bio-C catalyst at different voltages can be drawn. All K-L curves show a linear relationship within the potential range of 0.4V ~ 0.6V (vs.RHE), indicating the kinetics of ORR first-order reaction on the catalyst (Fig. 8d). The calculated electron transfer number of Fe$_2$O$_3$/N-bio-C is 2.95, which means that the Fe$_2$O$_3$/N-bio-C catalyst may tend to the two - and four-electron hybrid path of ORR.
Fig. 8 (a) CV curves of bio-C and Fe$_2$O$_3$/N-bio-C (O$_2$-saturated, solid lines; N$_2$-saturated, dotted lines); (b) LSV curves of the as-synthesized carbon materials and Pt/C (20 wt%) catalyst; (c) LSV curves of Fe$_2$O$_3$/N-bio-C at different rotational speeds; (d) K-L plots of Fe$_2$O$_3$/N-bio-C.

4. Conclusion
In this paper, a low-cost Fe$_2$O$_3$/N-bio-C catalyst for oxygen reduction was prepared by mixing biomass poplar flowers with heme containing ferrous iron using a simple physical adsorption method. Compared to the bio-C, the catalyst showed better catalytic activity at 0.1 M KOH ($E_{\text{onset}} = 0.90$ V, $E_{1/2} = 0.79$ V, $J_1 = 90$ mA·cm$^{-2}$). The interaction of Fe$_2$O$_3$ nanoparticles and nitrogenous functional groups in Fe$_2$O$_3$/N-bio-C catalyst enhances the electron transport between the interface of the active component and improves the catalytic activity of ORR. This work offers an simple method for the design of low-price electrocatalysts using sustainable and abundant biomass resources.

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References
[1] Tan, H.B., Tang, J., Kim, et al. (2019) Rational design and construction of nanoporous iron- and nitrogen-doped carbon electrocatalysts for oxygen reduction reaction. J. Mater. Chem. A, 7: 1380-1393.
[2] Du, L., Zhang, G.X., Liu, X.H., et al. (2020) Biomass-derived nonprecious metal catalysts for oxygen reduction reaction: The demand-oriented engineering of active sites and structures, Renew. Energ., 2: 561-581.
[3] Xiao, Z.R., Sheng, G.Q., Hou, F., et al. (2019) Highly dispersed γ-Fe$_2$O$_3$ embedded in nitrogen doped carbon for efficient oxygen reduction reaction, Catal. Sci. Technol., 9: 4581-4587.
[4] Wu, Y.L., Wang, Y.M., Xiao, Z.X., et al. (2021) Electrocatalytic oxygen reduction by a Co/Co$_3$O$_4$@N-doped carbon composite material derived from the pyrolysis of ZIF-67/poplar flowers, RSC Adv., 11: 2693-2700.
[5] Qu, B., Sun, Y., Liu, L.L., et al. (2017) Ultrasmall Fe$_2$O$_3$ nanoparticles/MoS$_2$ nanosheets...
composite as high-performance anode material for lithium ion batteries, Sci. Rep., 7: 42772.

[6] Zhou, W.J., Xiong, T.L., Shi, C.H., et al. (2016) Bioreduction of precious metals by microorganism: Efficient Gold@N-doped carbon electrocatalysts for the hydrogen evolution reaction. Angew. Chem., 55: 8416-8420.

[7] Hou, J.H., Cao, C.B., Idrees, F., et al. (2015) Hierarchical porous nitrogen-doped carbon nanosheets derived from silk for ultrahigh-capacity battery anodes and supercapacitors, ACS Nano., 9: 2556-2564.

[8] Miao, Z.P., Wang, X.M., Zhao, Z.L., et al. (2021) Rational design and improving the stability of non-noble-metal M-N-C catalysts for proton-exchange-membrane fuel cells through M – N bond length and coordination regulation. J. Mater. Chem. A, 33: 2006613-2006622.

[9] Zhong, X.W., Yi, W.D., Qu, Y.J., et al. (2020) Co single-atom anchored on Co₃O₄ and nitrogen-doped active carbon toward bifunctional catalyst for zinc-air batteries, Appl. Catal. B-Environ., 260: 118188.

[10] Ai, K.L., Liu, Y.L., Ruan, C.P., et al. (2013) Sp² C-dominant N-doped carbon submicrometer spheres with a tunable size: A versatile platform for highly efficient oxygen-reduction catalysts, Adv. Mater., 25: 998-1003.

[11] Yan, W., Wu, Y.L., Chen, Y.L., et al. (2020) Facile preparation of N-doped corncob-derived carbon nanofiber efficiently encapsulating Fe₂O₃ nanocrystals towards high ORR electrocatalytic activity, J. Energy Chem., 44: 121-130.

[12] Yuan, C.Z., Li, J.Y., Hou, L.R., et al. (2012) Ultrathin mesoporous NiCo₂O₄ nanosheets supported on Ni foam as advanced electrodes for supercapacitors, Adv. Funct. Mater., 22: 4592-4597.

[13] Choudhury, T., Saied, S.O., Sullivan, J.L., et al. (1989) Reduction of oxides of iron, cobalt, titanium and niobium by low-energy ion bombardment, J. Phys. D, 22: 1185-1195.