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1 Boosting the primary Zn-air battery oxygen reduction performance A02741C

2 with mesopore-dominated semi-tubular doped-carbon nanostructures

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Abstract: The low surface density of catalytic sites and undeveloped porosity become a 15 bottleneck for boosting the oxygen reduction reaction (ORR) activity of carbon catalysts. 16 Herein, we propose a novel strategy for synthesis of porous semi-tubular iron-nitrogen-doped-17 carbon nanostructures via two-step calcination of ferriporphyrin-based biomaterial by means of 18 a natural tubulose nanoclay as a morphology-controlled template, followed by post Zn-19 20 activating and acid-leaching processes. The formation of mesopore-dominated semi-tubular 21 carbons is beneficial for accelerating the ORR catalysis rate and improving the catalytic activity owing to the increased mass transport capacity of reactants to nitrogen-rich catalytic sites 22 existing in the pores. The resultant doped-carbon catalyst not only displays excellent 23 electrocatalytic behavior with an ORR onset potential (~ 1.01 V) and a half-wave potential 24

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(~0.85 V), but also exhibits a maximum power density of ~191 mW cm⁻² comparable to the procession devices. It is probably due to the production of mesopore-dominated semi-tubular
structures, more active-nitrogen species and dense surface active-sites. This work can pave a
new way for original design of low-cost and high-performance doped-carbon catalysts by using
natural biomaterials for the wide application of electrochemical energy devices.

Keywords: Primary Zn-air battery; Semi-tubular carbon; Mesopore-dominated; ORR
 electrocatalysis; Hemin biomaterial

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10 1. Introduction

The challenges of energy shortage and climate change have dramatically increased, resulting in 11 an urgent requirement to pursue green energy devices. Clean metal-air batteries (MABs) with 12 13 advantages of high specific-energy, low cost and stable-performance gradually became one of the ideal and significant alternative energy devices in recent years.¹⁻⁴ The rate and pathway 14 diversity of oxygen reduction reaction (ORR) at the cathode determines the general 15 performance of MABs.⁵ Therefore, the search for high-performance electrocatalyst to 16 accelerate the ORR performance is the key solution to solve those problems. Precious-metal Pt-17 based catalysts, as we all know, were largely used as cathodic catalysts because of their 18 19 excellent ORR activity. However, it's inadequate supply and high prices brought out the bottleneck of the large-scale application of MABs. Thus, increasing great efforts have been 20 undertaken to develop non-precious metal catalysts (NPMCs) with characteristics of high 21 activity and rich sources, especially doped-carbon catalysts.⁶⁻¹⁰ And a large number of 22 researches have widely used renewable biomaterials as precursors of carbon catalysts instead 23 of chemical compounds or complexes ¹¹⁻¹⁴, e.g., shrimp-shell¹⁵, enoki mushroom¹⁶, nori¹⁷, wine 24 mash¹⁸, coprinus comatus¹⁹, pig blood²⁰, fish biowastes²¹ were previously reported to 25

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synthesize the doped-carbon catalysts for the ORR²². Besides, two-step carbonization of the Online 1 hemoglobin as a renewable, abundant and cheap biomaterial, firstly proposed by Maruyama et 2 al., served as a novel avenue to boost the ORR catalytic property of doped carbon catalysts ²³. 3 Our group also developed blood protein with abundant protein/amino acids as the nitrogen 4 source of doped-carbon catalysts with good ORR activity and outstanding long-term stability 5 in terms of a similar strategy.²⁰ However, the low surface density of catalytic sites and 6 undeveloped porosity on the majority of doped-carbon catalysts with complicated compositions 7 and structures might be the main reasons for lower catalytic activity compared with the Pt-based 8 9 catalysts.

Hemin (iron (III) protoporphyrin (IX) chloride, molecular formula C₃₄H₃₂ClFeN₄O₄) as a 10 pivotal component of hemoglobin and a sort of natural transition-metal-based macrocyclic 11 compounds is considered as one of promising iron/nitrogen-containing precursors for designer 12 doped-carbon electrocatalysts because of its self-ability to support transition metal, nitrogen, 13 and carbon sources ²⁴⁻²⁶. To better enhance the ORR activity of doped-carbon catalysts, not only 14 the chemical components need to be designed, but also its intrinsic structure needs to be 15 regulated ²⁷⁻²⁸ As previously mentioned, the design of hollow or tubular porous structures using 16 a template-assisted strategy can effectively enhance the surface active-site density and promote 17 the pore development to boost the ORR activity of carbon catalysts. ²⁹⁻³³ Halloysite nanoclay 18 (HN) with a natural nanotube structure is composed of two layers in terms of the inner layer of 19 Al-OH groups and the outer layer of Si-O-Si groups), respectively.³⁴ The excellent dispersibility 20 and strong surface adsorbability of nanoclay as an accessible and environmentally-friendly 21 template in water solution can help the contact ability and homogeneity of hemin in ammonia 22 23 solution ³⁵.

Hence, we report the synthesis of iron-nitrogen-doped carbon nanomaterials (Hemin@HN-800Zn) made by two-step annealing hemin by means of HN as a template and ZnCl₂ as a post

pore-former under nitrogen atmosphere. The role of ZnCl₂ may largely facilitate to contract View Article Online 1 further dehydroxylation and dehydration, and its vaporization at high-temperature to better 2 3 produce the porous structure. To the best of our knowledge, it is firstly reported that the utilization of nanoclay template can induce the formation of semi-tubular nanostructure 4 dominated by mesoporous characteristics to facilitate the rapid transportation of the electrolyte, 5 reactants and products to accelerate the rate of oxygen reduction catalysis. The catalytic tests 6 7 indicate that Hemin@HN-800Zn exhibited comparable catalytic activity and long-term stability, as well as similar ORR catalysis mechanism, compared to the top-ranking Pt catalyst. In 8 9 addition, the test of home-made Zn-air battery also suggests that the power density of Hemin@HN-800Zn catalyst is can be up to ~191 mW cm⁻², which approaches that of the Pt 10 catalyst but is higher than that of previously reported carbon-based or other non-Pt catalysts. 11 Such excellent ORR performance may be partially attributed to full exposure of more accessible 12 catalytic sites as well as a large concentration of nitrogen doping into high-porosity semi-13 tubular carbon nanostructure. This study can provide a new idea and route for the original 14 design of various precious doped-carbon materials for a wide range of reactions in 15 electrochemical energy conversion devices. 16

17 2. Experimental

18 2.1 Synthesis of doped-carbon nanostructures

First, 20 mg of nanoclay and 4 mg of hemin, provided by Aladdin Chemical Co.Ltd., were uniformly dispersed in 30 ml ammonia (50 wt.%) and vigorously stirred for 10 h at 25°C so that hemin can be evenly and absolutely absorbed on the nanoclay surface. Subsequently, the gained Hemin@HN precursor was freeze-dried for 12 h. After that, the precursor was annealed at 800 °C for 2 h under N₂ protection to yield initial ORR catalysts (Hemin@HN-800). The heating rate was kept at 10 °C min⁻¹. After doing this, post Zn-activating process was further performed, as follows: 4 mg of ZnCl₂ was added into the initial Hemin@HN-800 catalyst,

grounded up for 30 min and further annealed at corresponding temperatures for 1_{Dh} und $\frac{View Article Online Online$ 1 protection. For comparison, we synthesize Hemin@HN-700 and Hemin@HN-900 catalysts at 2 3 different temperatures under similar conditions. The diagrammatic synthesis of mesoporous dominated-carbon semi-tubular nanostructures is indicated in Fig. 1. At last, all prepared 4 Hemin@HN-800Zn, 5 catalysts (e.g., Hemin@HN-700Zn, Hemin@HN-900Zn) was successively immersed in 0.2 mol l⁻¹ HF, 0.1 mol l⁻¹ HCl and deionized water for three times 6 7 (15 min every time) to drastically remove the residues of nanoclay, ZnCl₂ and other metal 8 oxides.

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Fig. 1

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11 2.2 Characterization

High-resolution scanning and transmission electron microscopy images were gained on Hitachi UHR S4800 and FEI Tecnai-G2 F30 instruments, separately. X-ray photoelectron spectroscopy (XPS) data were collected on a Kratos XSAM800 spectrometer. Nitrogen adsorption/desorption isotherms were tested on a Micromeritics ASAP 2010 analyzer at 77 K. X-ray diffraction (XRD) data were obtained on a Shimadzu XRD-6000 X-ray diffractometer (Cu Ka₁ radiation, λ =1.54178 Å) at a scan rate of 4° min⁻¹. Horiba HR800 Raman system was used to measure the Raman spectroscopy with an excitation wavelength of 532 nm.

19 2.3 ORR Electrochemical tests

All electrochemical data were collected on a CHI760E Bipotentiostat (Shanghai Chenhua Instruments Co.Ltd., China) with a three-electrode system, which is composed of a rotation ring (Pt)-disk (glassy carbon, Φ =5 mm) working electrode (RRDE, American Pine Instrument Co.Ltd.), a saturated calomel reference electrode (SCE) and a graphite-rod counter electrode (1 cm²). The preparation of the catalyst-coated RRDE refers to the previous reports [18,23]. Generally, 10 µl of 10 mg ml⁻¹ catalyst dispersion was dropped onto RRDE and naturally dried.

The mass-loading of the catalyst was limited to be about 510 μ g cm⁻². All electrode potentials cle online versus the SCE in alkaline electrolytes were converted into the potentials versus the reversible hydrogen electrode (RHE) on the basis of the Nernst equation. The scanning rate is 5 mV s⁻¹ and the electrolyte is 0.1 mol l⁻¹ KOH solution in all voltammetry tests. The transferred electron number (n) and H₂O₂ yield (H₂O₂%) during the ORR were estimated using the following **Eqs.** (1) and (2), respectively. The calculated equations are as follows:

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$$\% HO_2^- = 100 \times \frac{2I_r / N}{I_d + (I_r / N)}$$
 (1)

$$8 \qquad n = 4 \times \frac{I_d}{I_d + I_r / N} \tag{2}$$

9 where I_d is the Faradaic disk-current, I_r is the Faradaic ring-current, and N is the collection 10 efficiency of ring electrode (0.38). The Pt-ring potential was set at 1.5 V (vs. RHE) as reported 11 elsewhere.

12 **3. Results and Discussions**

13 3.1 Electrocatalyst Characterization

The SEM image was used to observe the surface features of Hemin@HN-800Zn (Fig. 2a). It 14 can be clearly revealed that Hemin@HN-800Zn is composed of semi-tubular nanostructures 15 with abundant mesoporous textures. The formation of the structure may be owing to a 16 reasonable fact that the nanoclay was fully covered with hemin molecules during freeze-drying 17 18 and calcination processes, and the following acid-leaching behavior can effectively remove the nanoclay residues to produce the hollow-structured semi-tubular morphology. The structure of 19 semi-tubular can help to facilitate the full exposure and utilization of a large number of nitrogen-20 21 rich active sites on the doped-carbon catalyst surface. A large amount of mesopores on the semitubular carbon surface can be also seen in corresponding TEM images (Fig. 2b and 2c). As 22 displayed in Fig. 2d and 2e, Hemin@HN-800Zn also suggests a disordered carbon structure 23

with an interlayer spacing of ~0.35 nm, slightly higher than that of graphite layers, which $\frac{View Article Online}{MAU}$ 1 be mainly induced by the doping of high nitrogen content (6.53 at.%). X-ray diffraction pattern 2 3 of Hemin@HN-800Zn (Fig. 1S) further shows the amorphous graphite structure without other crystallization phases, which is supported by high-resolution TEM and HAADF-TEM images 4 (Fig. 2f). Element mapping of Hemin@HN-800Zn displays the uniform distribution of four 5 main elements (C, N, O and Fe) on its surface, as shown in Fig. 2g. To our amusement, the size 6 7 of the bright dots implies that Fe elements are in the existence of a single-atom state presumably.³⁶ The metal Fe content was tested by inductively coupled plasma atomic emission 8 spectrometer (Agilent ICPOES730), which is only 2.8127 mg g⁻¹ in the Hemin@HN-800Zn 9 catalyst. 10

The BET specific surface area and pore characteristics of Hemin@HN-800Zn are of great 11 significance in connection with its ORR catalytic behavior, which was measured by N₂ 12 adsorption-desorption isotherms. The tested results were shown in Fig. 2h. Hemin@HN-800Zn 13 has exhibited a Langmuir IV isotherm with a type H4 hysteresis loop. The hysteresis loop can 14 be evidently found at the relative pressure of 0.45 to 1.0, hinting that the increased porosity of 15 Hemin@HN-800Zn in the range of mesopore. The BJH pore-size distribution (Inset of Fig. 2h) 16 of Hemin@HN-800Zn shows large mesoporous structures with two maximum value (3.7 nm 17 and 20.8 nm) of pore size in Hemin@HN-800Zn, further proving the results of the above-18 mentioned SEM and TEM analyses. The BET surface area is 473.75 m² g⁻¹ and the average 19 20 pore width is ~9.5 nm on Hemin@HN-800Zn. In addition, total pore volume (V_p) of Hemin@HN-800Zn is ~0.66 cm³/g, but its t-Plot micropore volume (V_{micro}) is ~0.13 cm³/g. The 21 resultant V_{micro}/V_p ratio is only 19.7 %, meaning the mesopore dominates in pore distribution. 22 The occurrence of hierarchical micro-/meso-porous textures in Hemin@HN-800Zn can be 23 partially attributed to the post Zn-activating process and the thermal decomposition of ZnCl₂ 24 pore-former during the second-step annealing. Furthermore, the mesopore-dominated texture is 25

beneficial for increasing ORRcatalytic activity, because it provides more nanochannels for activity for a strice online
 transportation of the electrolyte, reactants and products and enhance the contact between
 reactants and active sites to better decrease the oxygen-transportation resistance to the catalytic
 sites of Hemin@HN-800Zn.³⁷

Fig. 2

Raman spectroscopy was also used to study the defect and disordered structures of 8 9 Hemin@HN-800Zn. (Fig. 3a) The Raman spectrum of each sample is composed of two peaks: "D" peak and "G" peak. The D band located at around 1355 cm⁻¹ is associated with the lattice 10 defect of carbon atoms. The G band located at around 1586 cm⁻¹ is due to the E_{2g} mode for in-11 phase stretching vibration of sp²-bonded carbon.³⁸ The peak intensity ratio of the D band to the 12 G band (I_D/I_G) can correctly indicate the degree of structural defects. The I_D/I_G ratio (1.08) of 13 Hemin@HN-800Zn is larger than that of Hemin@HN-700Zn (1.05) and Hemin@HN-900Zn 14 (1.02), demonstrating that the Hemin@HN-800Zn exhibits more defect structures induced by 15 N-doping.³⁹ Furthermore, FT-IR spectrum was tested to investigate the chemical structures of 16 all carbon catalysts (Fig. 3b). All catalysts show that the C-C bond, C-N/C-O bonds, and 17 C=N/C=O bonds are located at 928 cm⁻¹, 1072 cm⁻¹, and 1572 cm⁻¹, respectively.⁴⁰ Interestingly, 18 the peaks at ca. 560 cm⁻¹ and 675 cm⁻¹ can separately correspond to the existence of Fe-O and 19 20 Fe-N structures. The above results also suggest the successful doping of nitrogen into the carbon matrix to produce C-N and Fe-N active structures in Hemin@HN-800Zn. 21

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25 Fig. 4a displays the XPS analysis results of Hemin@HN-700Zn, Hemin@HN-800Zn,

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Fig. 3

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Hemin@HN-900Zn. The appearance of main peaks of nitrogen, carbon and oxygen cation a 1 clearly observed, suggesting the nitrogen atoms are successfully included in the carbon matrix 2 of all carbon catalysts. However, the peak of Fe species is not found probably because ultralow 3 Fe content has gone beyond the XPS detection limit, being proved by the Fe element mapping 4 The C1s region of Hemin@HN-800Zn (Fig. 4b) was first fitted into four peaks with 5 (Fig. 2g). the binding energy of 284.7 eV, 285.4 eV, 286.29 eV and 290.0 eV, which are assigned to C=C, 6 C-C/C-N, C-N and O-C=O, respectively.⁴¹ The percentage of the C=N structure in 7 Hemin@HN-800Zn is ~24.5%, which higher than other carbon catalysts. It further supports the 8 9 successful doping state of nitrogen atoms into the carbon nanostructure. As shown in Fig. 4c, the N1s spectrum of Hemin@HN-800Zn can be deconvoluted into four peaks, corresponding 10 to pyridinic-N, Fe-N, graphitic-N and pyridinic N⁺-O⁻, which are respectively located at 398.4 11 eV, 399.6 eV, 400.78 eV, 401.64 eV.⁴² According to a similar fitting strategy, we analyzed the 12 N1s spectra of other carbon catalysts (Fig. 4d and 4e), as summarized in Table 1S. The 13 graphitic-N dominates all nitrogen species in doped-carbon catalysts. With the rising of the 14 annealing temperature, the percentage of Fe-N has no obvious change, but the total N content 15 in catalysts has been gradually decreased and the percentage of pyridinic-N has been clearly 16 changed. When the temperature is 800 °C, the percentage of pyridinic-N reaches the maximum 17 (19.7%), but as the calcination temperature reaches 900 °C, its percentage reversely decreases 18 until to only 8.1%. And the catalytic activity of Hemin@HN-800Zn was the best, while that of 19 20 Hemin@HN-900Zn is obviously decreased. It suggests that the pyridinic-N species with a planar structure should be active in ORR electrocatalysis. Besides, it is also found that inactive 21 pyridinic N⁺-O⁻ accounts for the lowest proportion in total N content for Hemin@HN-800Zn, 22 implying that Fe-N and graphitic-N may be main components of catalytic sites, but pyridinic-23 N may be directly related to the ORR activity in Hemin@HN-800Zn. The O1s region of 24 Hemin@HN-800Zn was shown in Fig. 4f. The O1s peak at 530.87, 531.81, 532.88 eV could 25

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- Fig. 4
- 6 3.2 ORR electrocatalytic activity

7 For one thing, the ORR electrocatalytic activities of Hemin@HN-800, Hemin@HN-700Zn, Hemin@HN-800Zn and Hemin@HN-900Zn were tested in 0.1 mol 1-1 O2-saturated KOH 8 9 solution by cyclic voltammetry (CV). There is a significant disparity in the ORR activity of these catalysts, as shown in Fig. 5a and Fig. 2S, which is proved by the differences among these 10 CV curves. Under the same test conditions, Hemin@HN-800Zn with the metal-Fe loading of 11 0.28127 µg exhibits the best ORR catalytic activity among the tested samples with the most 12 positive E_p (0.90 V) and the highest I_p (0.92 mA cm⁻²) values. And the ORR activity of 13 Hemin@HN-800 has been improved obviously under the pore-forming effect of ZnCl₂. Non-14 featured CV curve can be also observed in the N₂-saturated KOH solution, qualitatively 15 showing the selectivity of Hemin@HN-800Zn to the ORR electrocatalysis. The corresponding 16 ORR polarization curves of all doped-carbon catalysts were measured by the ring disk electrode 17 (RDE) combined with linear sweep voltammetry (LSV) technique, and the rotation rate was 18 fixed at 1600 rpm (Fig. 5b and Fig. 3S). All catalytic activity data were exhibited in Table 1S. 19 Notably, Hemin@HN-800Zn has exhibited the highest onset potential (E_{ORR} = 1.01 V) and half-20 wave potential ($E_{1/2} = 0.85$ V), which can be comparable to other catalysts reported in the 21 previous references (Table 2S). Besides, the limited current density of Hemin@HN-800Zn at 22 0.3 V is 5.22 mA cm⁻², apparently higher than that of other carbon-based catalysts prepared in 23 this work. These results suggest Hemin@HN-800Zn has superior ORR catalytic properties 24 among the tested samples. 25

Fig. 5

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To deeply study the origin of ORR activity difference on doped-carbon catalysts with post Zn-4 activating process, the electrochemical active surface areas (ECSA) are evaluated by the CV 5 6 method to check the double-layer capacitances (C_{dl}) in a certain non-faradic region (1.05 to 7 1.15 V versus RHE). Fig. 5c, Fig. 4S and Fig. 5S shows CV curves of three carbon catalysts tested at different scan rates (20 to 80 mV s⁻¹). The double-layer capacitance was calculated in 8 9 Fig. 5d. There is a linear relationship between current density and the square root of the scanning rate, presenting a typical diffusion-controlled electrochemical process. Hemin@HN-10 800Zn shows a C_{dl} of 10.78 mF cm⁻², being beyond that of Hemin@HN-700Zn (3.72 mF cm⁻²) 11 and Hemin@HN-900Zn (8.14 mF cm⁻²), demonstrating a correspondingly larger ECSA of 12 Hemin@HN-800Zn with more dense surface catalytic sites to enhance the ORR catalytic 13 14 activity. For this reason, the superior ORR catalytic property of Hemin@HN-800Zn can be ascribed to four aspects: i) The formation of semi-tubular nanostructure can be effective 15 exposure and full utilization of nitrogen-rich catalytic sites; ii) The engendering of mesopore-16 17 dominated characteristics can help to accelerate the transportation of the electrolyte, reactants and products to facilitate the ORR; iii) The higher percentage of active nitrogen species (e.g., 18 pyridinic-N, Fe-N and graphitic-N) can be produced in Hemin@HN-800Zn during calcination 19 process; iv) Hemin@HN-800Zn exhibits a higher surface active-site density, resulting from its 20 larger ECSA, to increase the inherent ORR activity. 21

However, up to now, the function of the real 'catalytically active sites' remains controversial because their contribution to the ORR activity is not well-defined. When the active sites in carbon-doped ORR catalysts were studied, it can be found that active nitrogen species such as pyridinic-N and graphitic-N in catalysts can also activate oxygen molecules and catalyze the

ORR process,⁴⁴ but their contributions to the ORR activity are unclear. Some important Article Online 1 researches pointed out that pyridinic-N and graphitic-N may be related to ORR onset potential 2 and limited current density, respectively.⁴⁵ The selectivity of pyridinic-N to four-electron 3 reaction pathway is better than that of graphitic-N,³⁷ while the former's ORR activity is high 4 but the stability is poor.⁴⁶ In addition, to better clarify the role of excessive metal-Fe atoms in 5 active sites neglected commonly, we have first designed an additional poisoning experiment by 6 7 using 10 mM thiocyanate ion (SCN⁻) as a poisoning electrochemical probe based on the strong binding force of SCN⁻ and Fe³⁺. We separately tested the LSV curves of Hemin@HN-800Zn 8 9 catalyst in O₂-saturated KOH versus O₂-saturated KOH containing 10 mM SCN⁻, as shown in Fig. 6S in supporting information. We found that the half-wave potential for ORR was 10 negatively shifted by about 20 mV and the limited current density was obviously reduced after 11 testing in O₂-saturated 0.1 mol l⁻¹ KOH containing 10 mM SCN⁻. Additionally, the half-wave 12 potential for ORR has also decreased about 60 mV, while the Hemin@HN-800Zn catalyst was 13 leached in 0.5 mol 1⁻¹ H₂SO₄ solution for 24 h to potentially destroy the Fe-N coordinate 14 structures. The decrease on the ORR activity, caused by the acid-leaching effect and the 15 poisoning effect of 10 mM SCN-, has provided a direct evidence for the significance of the 16 Fe-N structure towards the improvement of the ORR catalytic activity. Thus, it probably 17 suggests that Hemin@HN-800Zn may have metal-centered active sites (Fe-N) for the ORR, 18 which was supported by many reported researches.^{47,48} Furthermore, based on the XPS results 19 20 and electrochemical data, there is relatively sufficient reason to judge that the graphitic-N may be one of main components of active sites, but pyridinic-N may be also related to the promotion 21 of ORR activity in Hemin@HN-800Zn. 22

To investigate the ORR mechanism of Hemin@HN-800Zn, a series of polarization curves were
measured at different rotational speeds (600, 800, 1200, 1600, 2000, 2400 rpm) in O₂-saturated
KOH solution, as displayed in Fig. 6a. The overall electron transfer number (n) can be

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is proportional to the RDE rotation rate. The diffusion-limited current density (j_d) on RDE was 2 3 estimated by utilizing the K-L equation.⁴⁹ $1/j_d = 1/j_k + 1/0.62 nFC_O D_O{}^{2/3} \upsilon^{-1/6} \omega^{1/2}$ 4 where j_k , F, C₀, D₀, n and v are the kinetic current density of the ORR, the Faradaic constant 5 (96,485 C mol⁻¹), the O_2 saturation concentration in the aqueous solution (1.2*10⁻⁶ mol cm⁻³), 6 Published on 27 April 2020. Downloaded by Université de Paris on 4/27/2020 3:47:59 AM the O₂ diffusion coefficient in 0.1 mol l⁻¹ KOH electrolyte (1.9*10⁻⁵ m²s⁻¹), the kinetic viscosity 7 8 9

of the solution (0.01 cm²s⁻¹), the electrode rotation rate (rpm), respectively. Fig. 6b shows corresponding K-L plots under different potentials (0.3, 0.4, 0.5, 0.6 and 0.7 V). It can be seen that each line has an excellent linear relationship, and each line is parallel or almost overlapped 10 with each other. These results demonstrate that the calculated electron transfer numbers at 11 different potentials are similar and the concentration of dissolved O2 accords with the first-order 12 13 reaction kinetics. Then the calculated *n* value on Hemin@HN-800Zn was about 3.89. The ORR mechanism and kinetic behavior were further studied by RRDE tests. As indicated in Fig. 6c, 14 Hemin@HN-800Zn has the highest disk current and lowest ring current. The average n value 15 and H_2O_2 yield rates of catalysts can be also calculated in **Fig. 6d**. Hemin@HN-800Zn shows 16 the best performance with an average n of 3.93 and an average H_2O_2 yield of 3.67 in the 17 potential range of 0.2 V to 0.8 V, being superior to other carbon catalysts as well as comparable 18 to those of the Pt catalyst, as displayed in **Table 1S**. For Hemin@HN-800Zn, the average n19 value on RRDE test is almost identical to that on RDE test. The above results indicate that O₂ 20 21 is mainly converted into -OH with a pathway of four-electron reduction during the ORR. Thus, it may be one kind of ideal catalysts for oxygen reduction in alkaline medium. 22

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The long-term stability for ORR electrocatalytic activity of Hemin@HN-800Zn is one of the activity of Hemin@HN-800Zn is one of the activity of Hemin@HN-800Zn is one of the activity of the activity of Hemin@HN-800Zn is one of the activity 1 important concerns because it is of great significance for the practical application of catalyst. 2 3 Therefore, it is necessary to test the catalytic stability of Hemin@HN-800Zn via using an accelerated aging test (AAT), as indicated in Fig. 7. Compared with the initial peak current 4 density (0.92 mA cm⁻²), the current density (j_d) has retained 89.1% (0.82 mA cm⁻²) after CV 5 test for 5000 cycles. The peak potentials (E_P) have reduced from 1.04 V to 0.98 V. The onset 6 7 potentials (E_{ORR}) also have retained 96.0% (0.97 V) of the original onset potentials (1.01 V), but the ORR current density has been almost unchanged. These results synthetically suggest 8 9 that Hemin@HN-800Zn performs well in the long-term stability test.

Fig. 7

13 **3.3 Primary Zinc-Air Battery Test**

To further explore its potential application in practical energy devices, we constructed a primary 14 liquid-flowing Zn-air battery for evaluating the ORR general performance, as shown 15 schematically in Fig. 8a. The battery was a home-made electrochemical cell, in which 16 Hemin@HN-800Zn was loaded on carbon paper (1 cm²) as the cathode and Zn foil with a 17 contact area of 1 cm² was used as the anode. 6 mol l⁻¹ KOH electrolyte was filled into the cell 18 (10 ml volume). The open-circuit voltage of Zn-air battery using the Hemin@HN-800Zn 19 20 catalyst as a cathode is indicated in Fig. 7S. The polarization curves and corresponding power density plots of the battery were shown in **Fig. 8b**, it can be found that the maximum power 21 density was *ca*. 191mW cm⁻² at the current density of 267 mA cm⁻², being slightly lower than 22 23 that of Pt/C catalyst (only ~25 mW cm⁻²). Moreover, Fig. 8c shows the power density comparison between our sample and other previously reported catalysts.⁵⁰⁻⁵⁹ It is interesting 24 that Hemin@HN-800Zn prepared in this work has exhibited the highest power density among 25

these catalysts. To further evaluate the long-term durability of the battery, we carried outerthe online
battery continuous discharge at a current density of 5 mA cm⁻² for 12 h. As indicated in Fig.
8d, the cell voltage using Hemin@HN-800Zn catalyst has been hardly decreased, supporting
the excellent durability of Hemin@HN-800Zn. These outstanding general performances of the
Zn-air battery imply that Hemin@HN-800Zn is a promising candidate in future applications of
air batteries or other electrochemical energy devices.

Fig. 8

10 4. Conclusion

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Herein, we propose a new strategy for facile synthesis of iron-nitrogen-doped porous carbon 11 nanocatalysts (Hemin@HN-800Zn) made by two-step annealing hemin biomaterial on the basis 12 of a template-assisted method under nitrogen atmosphere. The utilization of nanoclay template 13 can induce the formation of semi-tubular doped-carbon nanostructures dominated by mesopore-14 dominated characteristics owing to the post ZnCl₂-activating process. The synthesized catalyst 15 shows excellent ORR performance with an onset potential of 1.01 V and a half-wave potential 16 of 0.85 V and follows a direct four-electron transfer pathway in alkaline electrolyte. Moreover, 17 Hemin@HN-800Zn has exhibited an unexpectedly high-power density of 191mW cm⁻² in 18 primary Zn-air battery, only 25 mW cm⁻² lower than that of the Pt catalyst. After continuous 19 20 discharge of 5 mA cm⁻² for 12 h, the cell voltage has been hardly decreased using the Hemin@HN-800Zn catalyst. The excellent ORR catalytic performance may be attributed to the 21 formation of the semi-tubular nanostructure, the engendering of mesopore-dominated 22 23 characteristics, higher percentage of active nitrogen species, and higher surface active-site density, in which can jointly facilitate the improvement of ORR catalytic activity. This study 24 can provide a new idea and route for the original design of various precious doped-carbon 25

1 materials by using natural biomaterials for a wide range of reactions in electrochemical entry Additional Additiona Additional Additiona Additional Additional Addi

2 conversion devices.

3 Acknowledgements

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1 Figures caption

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Fig. 1. A schematic diagram of mesopore-dominated semi-tubular doped-carbon nanostructures
.

Fig. 2. (a) SEM, (b-e) TEM and (f-g) HAADF-TEM images of Hemin@HN-800Zn. (h)
Nitrogen adsorption-desorption isotherms; Inset is the corresponding BJH pore-size distribution
of Hemin@HN-800Zn.

7 Fig. 3. (a) Raman and (b) FT-IR spectra of Hemin@HN-800Zn.

Fig. 4. (a) Survey and (c-e) N 1s XPS spectra of Hemin@HN-700Zn, Hemin@HN-800Zn, and
Hemin@HN-900Zn. (b) C1s and (f) O1s XPS spectra of Hemin@HN-800Zn.

Fig. 5. (a) CV curves of Hemin@HN-700Zn, Hemin@HN-800Zn, and Hemin@HN-900Zn in
N₂ versus O₂-saturated KOH. (b) LSV curves of Pt/C, Hemin@HN-700Zn, Hemin@HN-800Zn,
and Hemin@HN-900Zn in N₂ versus O₂-saturated KOH. (c) CV curves of Hemin@HN-800Zn
tested at different scan rates. (d) The double-layer capacitance of Hemin@HN-700Zn,
Hemin@HN-800Zn, and Hemin@HN-900Zn.

Fig. 6. (a) ORR polarization curves of Hemin@HN-800Zn at different rotation speeds in O₂saturated KOH. (b) The corresponding K-L plots under different potentials (0.3-0.7 V). (c) Disk and ring currents obtained with LSV on RRDE for Pt-C, Hemin@HN-700Zn, Hemin@HN-800Zn, and Hemin@HN-900Zn in O₂-saturated KOH. (d) The corresponding electron transfer numbers and H₂O₂ yields at the potential range of 0.2-0.8 V derived from (c).

Fig. 7. (a) CV and (b) LSV curves of Hemin@HN-800Zn and Pt-C before and after doing an
accelerated aging test (AAT).

Fig. 8. (a) A schematic diagram of primary Zn-air battery. (b) Polarization and power density curves of primary Zn-air battery with Hemin@HN-800Zn and Pt/C. (c) Comparison of the power density between this work and other results. (d) The ORR chronopotentiometric response for a durability test at a constant current density of 5 mA cm⁻² for 12 h.



Figure 2



2 3

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Figure 5

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Figure 6

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Figure 7

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A table of contents entry

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Mesopore-dominated semi-tubular doped-carbon nanostructures derived from nanocaly templates were designed for boosting the primary Zn-air battery oxygen reduction performance.