Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Nitrogen and Phosphorus Co-Doped Hierarchically Porous Carbons derived from Cattle Bones as Efficient Metal-Free Eletrocatalysts for Oxygen Reduction Reaction

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1. Materials

The dried cattle bone powder was purchased from market in Beijing. Phytic acid (PA), dicyandiamide (DCDA), methanol, ethanol, and KOH were purchased from Sinopharm. Nafion (5 wt. %) and high-purity Ar gas were brought from DuPont and Beijing AP BAIF Gases Industry Co., Ltd, respectively. All chemicals were of analytical grade and applied without further purification. Ultrapure water (Millipore, 18.2 M Ω cm) was used for the material preparation.

2. Characterizations

The morphologies of the electrocatalysts were characterized by the field-emission scanning electron microscopy (FE-SEM, FE-JSM-6701F, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2100, JEM-2010F, JEOL, Japan). Nitrogen adsorption-desorption isotherms were recorded with a Quantachrome AUTOSORB-1 instrument to evaluate the specific surface area and pore size distribution of the electrocatalysts. X-ray diffraction (XRD) patterns were recorded with a X-ray diffractometer (D/max-2500, Rigaku, Japan) with Cu K_a radiation ($\lambda = 1.54056$ Å) as the X-ray source. The X-ray photoelectron spectroscopy (XPS) measurements were performed with the ESCALAB 250 spectrometer (Thermo Fisher). The Raman spectra and Fourier Transform Infrared (FT-IR) spectra were obtained with a LabRAM HR800 confocal microscope (using a laser of 632.8 nm) and a Perkin Elmer spectrum 100 FT-IR spectrometer, respectively.

3. Electrochemical measurement

Rotating ring-disk electrode (RRDE) technique controlled by ALS/DY2323 Bipotentiostat workstation was used to evaluate the electrochemical performance of the electrocatalysts. The standard three-electrode system was employed to test the ORR performance, consisting of a Pt wire as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and electrocatalyst coated glassy carbon electrode (GDE) (surface area : 0.125 cm²) as working electrode. All potentials in this work were calibrated with reference to the reversible hydrogen electrode (RHE). The working electrocatalyst was prepared electrocatalyst was prepared as follows: 5 mg of electrocatalyst was added into 1 mL of ethanol with Nafion solution (10 μ L) and ultrasonically dispersed for 30 min to obtain a homogeneous slurry. Then, 21 μ L of the slurry was uniformly dropped onto a freshly polished GDE with a loading of 0.80 mg_{cat} cm⁻² and dried under ambient condition. For comparison, the commercial Pt/C (20 wt. % of Pt) electrode was also prepared with a loading of 0.40 mg_{cat} cm⁻² (ultrasonically dispersing 5 mg of Pt/C into 1 mL of ethanol with 50 μ L of Nafion).

RDE measurement: The transferred electron number for the ORR was estimated by the Koutecky-Levich (K-L) equation [S1]:

$$j^{-1} = j_k^{-1} + \frac{1}{\left(0.2nFC_{O_2}D_{O_2}^{2/3}v^{-1/6}\omega^{1/2}\right)}$$
(1)

where, j_k is the kinetic current density, j is the measured current density normalized to the geometry surface area of the electrode, n is transferred electron number for the ORR process per oxygen molecule, F is the Faraday constant (96485 C mol⁻¹), D_{0_2} is the diffusion coefficient, v is the kinematic viscosity, C_{0_2} represents the bulk concentration of O₂, and ω is the rotation rate. The following values are referred when calculating the transferred electron number: ${}^{D_{O_2}} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $v = 0.01 \text{ cm}^2 \text{ s}^{-1}$, ${}^{C_{O_2}} = 1.2 \times 10^{-6}$ mol cm⁻³. The constant of 0.2 is adopted as the rotation rate is expressed in rpm. According to the K-L equation, n can be calculated from the slope of j^{-1} plotted against $\omega^{-1/2}$. For the Tafel plot, the j_k was calculated based on the following equation:

$$j_k = \frac{j \times j_d}{j_d - j} \tag{2}$$

where, j_d is the diffusion limiting current density.

RRDE measurement: For the RRDE measurement, the disk electrode was scanned at a rate of 5 mV s⁻¹ and the ring potential was set constant at 1.5 V. The ${}^{\%}HO_{2}^{-}$ and n were determined by the followed equations:

$$%HO_2^{-} = 200 \frac{I_r/N}{I_d + I_r/N}$$

$$n = 4 \frac{I_d}{I_d + I_r/N}$$

(4)

where, I_d is disk current, I_r is ring current, and N is current collection efficiency of the Pt ring (N=0.40).



Fig. S1 (a) CV curves of NHPC and N,P-HPC prepared at different pyrolysis temperature in N₂- (dotted line) and O₂-saturated (solid line) 0.1 M KOH (scan rate: 50 mV s⁻¹). (b) The corresponding RRDE voltammograms of the above samples and the commercial Pt/C in O₂-saturated 0.1 M KOH (scan rate: 5 mV s⁻¹; rotation rate: 1600 rpm).



Fig. S2 (a) CV curves of NHPC, N-HPC, P-HPC and N,P-HPC prepared with different molar ratios of N_{extra}/P of 2:1 (denoted as N,P-HPC-2), 1:1 (N,P-HPC), and 1:2 (N,P-HPC-0.5) in N₂- (dotted line) and O₂ -saturated (solid line) 0.1 M KOH (scan rate: 50 mV s⁻¹). (b) The corresponding RRDE voltammograms of the above samples and the commercial Pt/C in O₂-saturated 0.1 M KOH (scan rate: 5 mV s⁻¹; rotation rate: 1600 rpm). Summary of (c) $E_{1/2}$ and (d) J_k for N-HPC, N,P-HPC-2, N,P-HPC, N,P-HPC-0.5, and P-HPC.



Fig. S3 Representative SEM and TEM images of (a, b) N-HPC, (c, d) N,P-HPC-2, (e, f) N,P-HPC-0.5, and (g, h) P-HPC.



Fig. S4 FT-IR spectra of NHPC, N-HPC, N,P-HPC, and P-HPC.



Fig. S5 LSV curves of (a) NHPC, (b) N-HPC, (c) P-HPC, and (d) the commercial Pt/C in O_2 -saturated 0.1 M KOH (scan rate: 5 mV s⁻¹) at various rotation rates (400-2025 rpm) (Inset shows the corresponding K-L plots).

Samples	S_{BET} (m ² g ⁻¹)	<i>S_{micro}</i> (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	% V _{meso}
NHPC	2165	1278	1.869	60.7
N-HPC	1747	1268	1.256	51.4
N,P-HPC-2	1632	1167	1.164	57.3
N,P-HPC	1516	1076	0.9834	55.1
N,P-HPC-0.5	1479	1005	0.9208	51.6
Р-НРС	1389	968	0.7794	43.2

Table S1. Pore structure characterization of NHPC, N-HPC, N,P-HPC and P-HPC.

 Table S2. Element contents of NHPC, N-HPC, N,P-HPC and P-HPC determined by

 XPS.

Samples	Atomic composition (at. %)						
	С	0	Ν	Р			
NHPC	80.09	17.41	2.50	0			
N-HPC	83.48	12.86	3.66	0			
N,P-HPC-2	79.44	14.43	3.64	2.49			
N,P-HPC	76.00	16.84	3.20	3.96			
N,P-HPC-0.5	77.96	14.84	3.15	4.05			
Р-НРС	77.67	14.79	2.54	4.63			

	Relative content of different N species to total N (%)					
Samples	Pyridinic N	Pyrrolic N	Graphitic N	Oxidized pyridinic N		
NHPC	43.67	26.84	10.68	18.81		
N-HPC	56.13	14.74	11.93	17.20		
N,P-HPC	55.65	17.08	10.24	17.03		
Р-НРС	41.52	27.35	13.89	17.24		

 Table S3. The relative contents of different N species from high-resolution N 1s

 spectra.

Table S4. The relative contents for different P species from high-resolution P 2p spectra.

Samples	Relative content of different P species to total P (%)			
	Р-С	Р-О		
N,P-HPC	66.88	33.12		
P-HPC	57.60	42.40		

Electrocatalyst	Loading (µg cm ⁻²)	<i>E</i> _{1/2} (V)	J _k (mA cm ⁻²) @ 0.8 V	n	Ref.
NPMC-1000	150	0.850	29.25	4.00	[R1]
NP-HPC	204	0.830	13.70	3.89	[R2]
N-Graphene	280	0.828	8.020	3.90	[R3]
P,N Co-Doped Graphene Frameworks	100	0.845	29.80	3.99	[R4]
NPS-CNS	600	0.800	7.905	3.8-4.0	[R5]
N,P-MC	200	0.840	15.25	4.00	[R6]
N-doped carbon nanotube arrays	-	0.840	-	3.90	[R7]
C ₃ N ₄ @mesoporous carbon	280	0.750	1.915	3.80	[R8]
B, N-graphene	280	0.680	0.318	3.81	[R9]
Te, P-doped porous carbon fiber	100	0.790	4.811	4.00	[R10]
N-doped hierarchical porous carbon	290	0.850	37.462	4.0	[R11]
N-doped porous carbon nanosheets	200	0.770	1.846	3.9-4.0	[R12]
N, S-doped carbon nanosheets	200	0.770	1.379	3.98	[R13]
N-doped porous carbon fiber	100	0.820	6.926	4.0 ± 0.09	[R14]
N, P-doped CGHNs	300	0.820	5.223	4.0	[R15]
N-doped graphene	600	0.840	37.333	3.95	[R16]
NHPC	800	0.740	0.589	3.30	This work

Table R5. Summary of ORR performance in alkaline electrolyte (0.1 M KOH) for recently reported metal-free electrocatalysts in the literatures.

N,P-HPC	800	0.853	38.196	4.00	This work
Pt/C	400	0.841	20.11	4.00	This work
P-HPC	800	0.828	11.56	3.95	This work
N-HPC	800	0.805	5.048	3.90	This work

REFERENCES

- [R1] J. Zhang, Z. Zhao, Z. Xia and L. Dai, Nat. Nanotechnol., 2015, 10, 444.
- [R2] Y. Zhu, Y. Liu, Y. Liu, T. Ren, G. Du, T. Chen and Z. Yuan, J. Mater. Chem. A, 2015, 3, 11725.
- [R3] J. Li, Y. Zhang, X. Zhang, J. Han, Y. Wang, L. Gu, Z. Zhang, X. Wang, J. Jian,P. Xu and B. Song, ACS Appl. Mater. Interfaces, 2015, 7, 19626.
- [R4] G. Chai, K. Qiu, M. Qiao, M. M. Titirici, C. Shang and Z. Guo, *Energ. Environ. Sci.*, 2017, **10**, 1186.
- [R5] Y. N. Zhu, C. Y. Cao, W. J. Jiang, S. Yang, J. Hu, W. Song and L. Wan, J. Mater. Chem. A, 2016, 4, 18470.
- [R6] Z. Zhang, J. Sun, M. Dou, J. Ji and F. Wang, ACS Appl. Mater. Inter., 2017, 9, 16236.
- [R7] K. Gong, F. Du, Z. Xia, M. Durstock and L. Dai, Science, 2009, 323, 760.
- [R8] Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith, M. Jaroniec, G. Lu and S. Qiao, J. Am. Chem. Soc., 2011, 133, 20116.
- [R9] Y. Zheng, Y. Jiao, L Ge, M. Jaroniec and S. Qiao, Angew. Chem., 2013, 125, 3192.
- [R10] W. Zhang, Z-Y Wu, H-L Jiang and S-H Yu, J. Am. Chem. Soc, 2014, 136, 14385.
- [R11] M. Graglia, J. Pampel, T. Hantke, T-P Fellinger and D. Esposito, ACS Nano, 2016, 10, 4364.

[R12] H. Yu, L. Shang, T. Bian, R. Shi, G. I. N. Waterhouse, Y. Zhao, C. Zhou, L-Z.Wu, C-H Tung and T. Zhang, *Adv. Mater.*, 2016, 28, 5080.

- [R13] K. Qu, Y. Zheng, S. Dai and S. Qiao, Nano Energy, 2016, 19, 373.
- [R14] Q. Liu, Y. Wang, L. Dai and J. Yao, Adv. Mater., 2016, 28, 3000.
- [R15] J. Yang, H. Sun, H. Liang, H. Ji, L. Song, C. Gao and H. Xu, *Adv. Mater.*, 2016, 28, 4606.
- [R16] H. Yang, J. Miao, S-F Hung, J. Chen, H. Tao, X. Wang, L. Zhang, R Chen, J.
- Gao, H. Chen, L. Dai and B. Liu, Sci. Adv., 2016, 2, e1501122.