Supporting Information

Carbon Dots Hybrid Porous Carbon Nanofibers as Efficient Electrocatalysts for

Oxygen Reduction Reaction

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1. Characterizations

The morphologies and structures of the various types of fabricated fibers were characterized using field emission scanning electron microscopy (FESEM; Zeiss, Sigma 300). TEM and HRTEM analyses were conducted using a JEOL JEM 2100Plus TEM operating at 200 kV to obtain transmission electron microscopy and high-resolution transmission electron microscopy images. X-ray photoelectron spectroscopy spectra were recorded utilizing a Thermo Scientific K-Alpha XPS spectrometer. Raman spectra were obtained using a LabRAM HR800 (HORLBA JY) instrument. Specific surface area and porosity data were acquired via nitrogen adsorption measurements (Kubo-x1000).

2. Figures and tables



Figure S1. SEM images of (a) electrospun nanofibers, (b) oxidized nanofibers, and (c) mesoporous carbon nanofiber membranes



Figure S2. (a) TEM image of the C-dots. (b) The corresponding HRTEM image of the C-dots.



Figure S3. (a)TEM image of the PCNFs-900 without adding C-dots. (b)The corresponding HRTEM image of the PCNFs-900 without adding C-dots.



Figure S4. XPS survey spectra of the (a) PCNFs-900, (b) N,P-PCNFs-800, (c) N,P-PCNFs-900 and (d) N,P-PCNFs-1000.



Figure S5. LSV curves of the Pt/C at different rotation speeds and the K–L plot at different potentials of Pt/C.

Table S1 Relative contents of C, N, P, and O in the C-dots and N, P-PCNFs based on XPS measurements.

Sample –	Relative contents (%)			
	С	Ν	Ο	Р
N, P doped C-dots	54.3	8.6	29.7	7.3
3%-N, P-PCNFs-900	89.6	3.8	5.0	1.6
PCNFs-900	92.3	2.5	5.2	0

Table S2 The atomic ratios of N_x/N_{total} in the N-P/CNFs [pyridinic nitrogen (N1), pyrrolic nitrogen (N2), graphitic nitrogen (N3), oxidized nitrogen (N0)].

	Relative contents (%)			
Sample	Pyridinic N1	Pyrrolic N2	Graphitic N3	Oxidized
				N0
3%-N, P-PCNFs-800	38.1	25.3	26.6	10.0
3%-N, P-PCNFs-900	26.5	21.6	37.5	14.4
3%-N, P-PCNFs-1000	17.6	19.6	43.4	19.3
PCNFs-900	28.3	15.9	35.2	20.6

Sample –	Relative contents (%)		
	P-O (133.9)	P-C (132.5)	
3%-N, P-PCNFs-900	44.2	55.8	

Table S3 The atomic ratios of P-C and P-O in the 3%-N, P-PCNFs-900.

Table S4. The onset potential and half-wave potential of electrocatalysts measured in 0.1 M KOH.

Samula	E _{overpotential} (V vs. RHE)		
Sample	$E_{\text{onset potential}}$	$E_{\rm half-wave potential}$	
PCNFs-900	0.77	0.67	
3%-N-PCNFs-900	0.81	0.68	
1%-N, P-PCNFs-900	0.83	0.71	
2%-N, P-PCNFs-900	0.84	0.70	
3%-N, P-PCNFs-800	0.81	0.69	
3%-N, P-PCNFs-900	0.88	0.72	
3%-N, P-PCNFs-1000	0.80	0.68	
Pt/C (20 wt%)	0.92	0.76	

Table S5.

Sample -	E _{overpotential} (V vs. RHE)		Deference
	$E_{\text{onset potential}}$	E half-wave potential	Kelefence
NPMC-1000	0.94	0.85	1
N, P-GDs/N-3DG	0.84	0.81	2
P-MC-4	0.86	0.80	3
NPCS-900	0.91	0.83	4
Fe©N-C-12	0.87	0.83	5
Co incorporated into	0.85	0.78	6

nitrogen-doped			
carbon nanotubes			
3%-N,P-PCNFs-900	0.88	0.72	

Supplementary References

1. J. T. Zhang, Z. H. Zhao, Z. H. Xia, L. M. Dai, A metal-free bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions, *Nature Nanotechnology*, 2015, 10, 444-452.

2. X. Tong, Mohamed Cherif, G. X. Zhang, X. X. Zhan, J. G. Ma, Ali Almesrati, Francois Vidal, Y. J. Song, Jerome P. Claverie, S. H. Sun, N, P-Codoped Graphene Dots Supported on N-Doped 3D Graphene as Metal-Free Catalysts for Oxygen Reduction, *ACS Applied Materials & Interfaces*, 2021, 13 (26): 30512-30523.

3. H. Zhao, Z. P. Hu, Y. P. Zhu, L. Ge, Z. Y. Yuan, P-doped mesoporous carbons for high-efficiency electrocatalytic oxygen reduction, *Chinese Journal of Catalysis*, 2019, 40, 1366-1374.

4. S. Chen, L. L. Zhao, J. Z. Ma, Y. Q. Wang, L. M. Dai, J. T. Zhang, Edge-Doping Modulation of N, P-Codoped Porous Carbon Spheres for High-Performance Rechargeable Zn-Air Batteries, *Nano Energy*, 2019, 60, 536-544.

5. Y. Ye, H. Li, F. Cai, et al., Two-Dimensional Mesoporous Carbon Doped with Fe–N Active Sites for Efficient Oxygen Reduction, *ACS Catal.*, 2017, 7, 7638–7646.

6. B. Peng, H. Zhang, H. Z. Shao, K. Xu, G. Ni, J. Li, H. Y. Zhua, Costas M. Soukouliscd, Chemical intuition for high thermoelectric performance in monolayer black phosphorus, α -arsenene and aW-antimonene, *J. Mater. Chem. A: Mater. Energy Sustain.*, 2018, 6, 3386–3390.