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

Supporting information

Fluorine and phosphorus atoms cooperated on an N-doped 3D porous carbon network with enhanced ORR performance toward the zinc-air batteries

Experimental section

1.1. Chemicals

Melamine (99%), 3-fluoroaniline (98%), phytic acid (70%), ammonium persulfate (98.5%), hydrochloric acid, aniline.

1.2. Synthesis of C_3N_4

A certain amount of melamine was placed in a porcelain cup, which was heated up to 500℃ and retained 2 hours at 500℃ in a muffle furnace. After the temperature cooling to room temperature, the C_3N_4 sample was obtained.

1.3. Synthesis of catalysts

1.5g of C_3N_4 was dispersed in 80 ml of 0.1mol/L hydrochloric acid solution, followed by the addition of 0.870ml of 3-fluoroaniline and phytic acid. 20ml of 0.1mol/L hydrochloric acid solution with 2g of ammonium persulfate were mixed above solution. The obtained mixtures were stirred at room temperature for 24 hours. After being filtered, washed and dried at 80℃ for 8 hours, the precursor is obtained. Subsequently, precursor was placed in a tube furnace and heated up to 950 ℃ at 5 ℃/min, and maintained at 950 ℃ for 2 hours, then cooled down naturally, the F/P-N-C-950 catalyst was prepared. Similarly, the P-N-C-950 catalyst was prepared by employing aniline to replace 3-fluoroaniline; F-N-C-950 catalyst was fabricated without the addition of phytic acid; N-C-950 catalyst was prepared without the addition of C_3N_4.

1.4. Electrochemical testing

Electrochemical tests were performed in a three-electrode system using a CHI 760E electrochemical workstation. The Hg/HgO electrode was used as the reference electrode in the alkaline electrolyte, the carbon rod was used as the counter electrode,

and the glassy carbon electrode (GC, 0.196 cm^{-2}) was chosen as the working electrode.5 mg of carbon catalyst was dispersed in 1 ml of nafion/isopropanol solution (0.25 wt% Nafion) with sonication. The 10 μL of catalyst ink was dropped on glassy carbon electrode, after drying, the final carbon catalyst loading is around 0.25 $mg \cdot cm^{-2}$. Cyclic voltammetry and linear scanning voltammetry were used to evaluate the catalytic performance in 0.1 M KOH solution. The stability of the catalyst was evaluated by chronoamperometry.

The rotating ring disc electrode (RRDE) testing was employed to investigate hydrogen peroxide yield (% hydrogen peroxide) and electron transfer number (n), and calculated as follows.

$$H_2O_2\ (\%) = 200 I_r\ (N I_d + I_r)^{-1}$$

$$n = 4\ I_d\ (I_d + I_r N^{-1})^{-1}$$

Where I_d and I_r denoted the disk and ring currents and N is the ring collection efficiency.

In the home-made zinc-air battery, hydrophobic carbon paper (catalyst mass loading of 1 $mg \cdot cm^{-2}$), zinc flakes, and 6 M KOH solution were employed as the air cathode, anode, and electrolyte, respectively. The discharge curves of zinc air battery were obtained using the CHI760E workstation at room temperature. Constant current discharge measurements were conducted on a battery testing system (NEWARE).

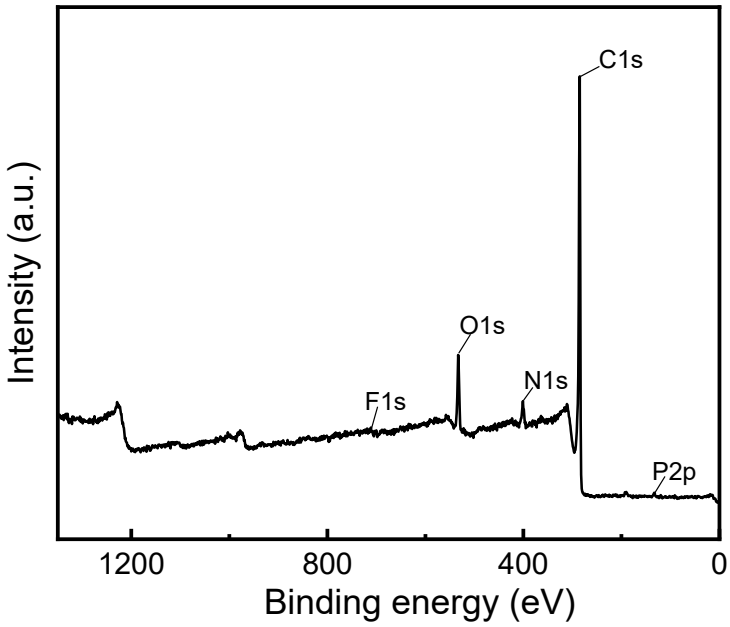

Fig. S1 The XPS full spectrum for F/P-N-C-950 sample

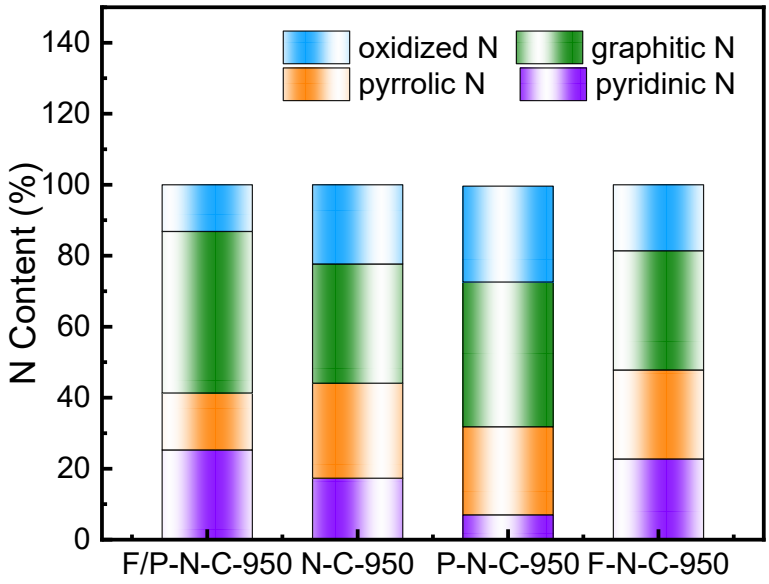

Fig. S2 The content of different N species in the F/P-N-C-950, F-N-C-950, P-N-C-950, N-C-950 obtained from the fitting of XPS spectra.

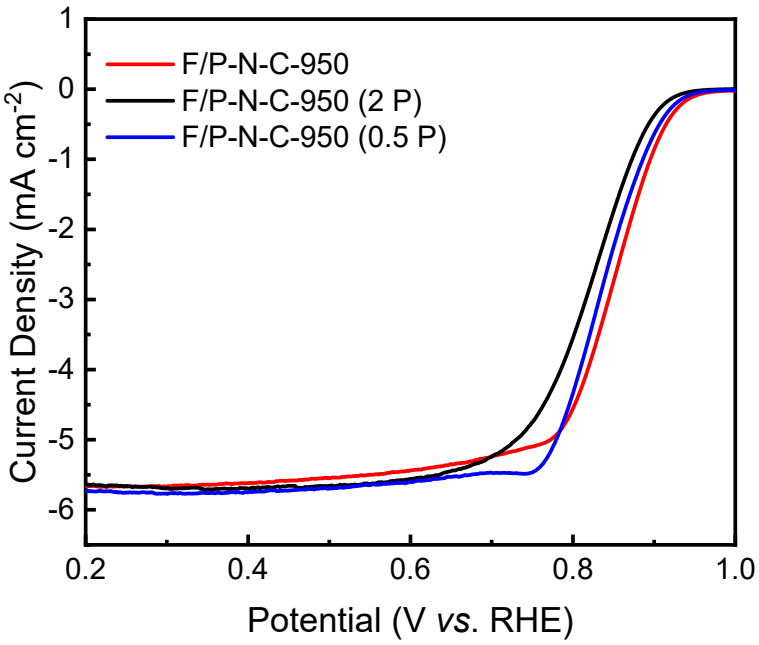

Fig. S3 LSV curves for F/P-N-C-950, F/P-N-C-950 (0.5 P) and F/P-N-C-950 (2 P) in O_2-saturated 0.1 M KOH.

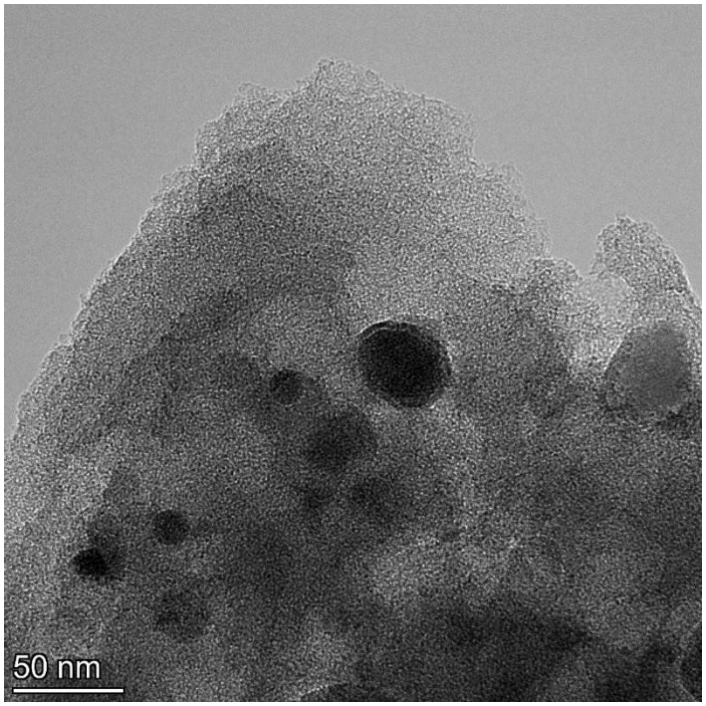

Fig. S4 TEM image of F/P-C-950

Table. S1 The comparison of ORR performance of F/P-N-C-950 and the recently reported carbon catalysts in alkaline solution.

Materials	E_0 (V *vs.* RHE)	$E_{1/2}$ (V *vs.* RHE)	Catalyst loading ($mg \cdot cm^{-2}$)	References
F/P-N-C-950	0.99	0.848	0.25	This work
FN_3SG	0.99	0.803	0.20	[1]
B, N-Carbon	0.98	0.840	0.30	[2]
NFCNAs-18-1000	0.91	0.825	0.10	[3]
N, P, O-Carbon-PA	0.98	0.840	0.20	[4]
NPS-G	0.96	0.857	0.40	[5]
NPCSs	0.91	0.830	0.20	[6]
PANI1-PATH2-CF	——	0.860	——	[7]
N-F-CNFs-950	0.97	0.833	——	[8]
N, F-MCFs-A	0.94	0.810	——	[9]
N, P-GC-1000	1.03	0.850	——	[10]
N, P-SiCDC1	0.90	0.790	——	[11]
FeNC-24	——	0.852	——	[12]
A-FeNC	——	0.850	——	[13]

Table. S2 The comparison of zinc-air battery performance with F/P-N-C-950 and the recently reported carbon catalysts as cathodes.

Materials	Peak power density($mW \cdot cm^{-2}$)	Specific capacity ($mAh \cdot g^{-1}$)	References
F/P-N-C-950	138	821	This work
F-CHNS-900	130	——	[14]
BNF-LCF	99	791.5	[15]
NBF-CNW	175	——	[16]
TD-CFs	——	555	[17]
NBCNT-10	173	——	[18]
NCN-1000-5	207	672	[19]
N-GRW	65	873	[20]
HPC(MV-c-PN)	80	——	[21]
N-S-Cs-900	136	——	[22]
N-rGO	139	783	[23]
N-PHCP-900	185	——	[24]
D-NCNS	154	815	[25]

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