Supporting information

## N-doped porous carbon spheres as metal-free electrocatalyst for

## oxygen reduction reaction

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Fig. S1. The images of fabrication procedure and samples of NUFS and NPCS-900



Fig. S2. SEM images of (a, b, c) NPCS-800 and (d, e, f) NPCS-1000 under different magnification.



Fig. S3. SEM images of (a, b) solid spheres of UF resin and (c, d) SCS-900 under different magnification.



**Fig. S4.** (a, b) TEM and (c) STEM and corresponding EDS elemental mapping images for (d) C, (e) N and (f) O of NUFS.



**Fig. S5.** (a) XRD pattern of NPCS-900, (b) the content of N species distribution in NPCS-900, high-resolution XPS spectra with deconvolution of (c) C1s and (d) O1s of NPCS-900.



Fig. S6. CV curves of NPCS-900 and Pt/C in  $O_2$ - (solid line) or  $N_2$ -(dash line) saturated (a) 0.1 M KOH and (b) 0.1 M HClO<sub>4</sub> respectively.

Catalysts	Data				
	BET Surface area	BJH Desorption BJH Desorption		Adsorption	
	(m²/g)	cumulative volume	average pore diameter	average pore	
		of pores (cm³/g)	(4V/A) (nm)	diameter (4V/A	
				by BET) (nm)	
NPCS-800	459.7	0.985	19.2	9.5	
NPCS-900	656.5	0.915	15.7	6.7	
NPCS-1000	692.8	0.857	14.2	6.1	
SCS-900	81.0	0.040	9.7	3.8	

**Table S1**. The parameters obtained from BET surface area and pore size distribution measurement of NPCS-X and

 SCS-900.

 Table S2. The composition of the as-fabricated catalysts from XPS measurement.

Element Atomic %	NPCS-800	NPCS -900	NPCS -1000	SCS -900	
C	85.04	91.1	90.86	93.26	
Ν	8.67	5.36	3.12	4.87	
0	6.29	3.54	6.02	1.87	

## Table S3. The N species distribution of NPCS-X and SCS-900.

N species (%)	NPCS-800	NPCS -900	NPCS -1000	SCS -900
Pyridinic N	25.4	23.9	12.4	22.8
Pyrrolic N	28.1	5.3	8.9	4.6
Graphitic N	31.0	57.6	61.6	57.4
Oxidized-N	15.5	13.2	17.1	15.2

Electrocatalysts	E <sub>onset</sub> (V)	E <sub>1/2</sub> (V)	j <sub>limiting</sub> (mA cm <sup>-2</sup> )
NPCS-800	0.95	0.83	5.8
NPCS-900	0.99	0.87	6.7
NPCS-1000	0.94	0.85	5.6
SCS-900	0.93	0.73	4.8
Pt/C	0.99	0.86	5.7

 Table S4.
 The ORR parameters of the electrocatalysts estimated from LSV curves in Fig.4a in 0.1 M KOH.

Table S5. The ORR parameters the electrocatalysts estimated from LSV curves in Fig.5a in 0.1 M  $HClO_4$ .

Electrocatalysts	E <sub>onset</sub> (V)	E <sub>1/2</sub> (V)	j <sub>limiting</sub> (mA cm <sup>-2</sup> )
NPCS-800	0.82	0.64	5.6
NPCS-900	0.86	0.73	6.3
NPCS-1000	0.76	0.58	5.2
SCS-900	0.55	0.28	4.2
Pt/C	0.93	0.80	6.1