

**Supplementary Information for**

Nitrogen, sulfur and phosphorus-codoped carbon with tunable nanostructure as efficient electrocatalyst for the oxygen reduction reaction

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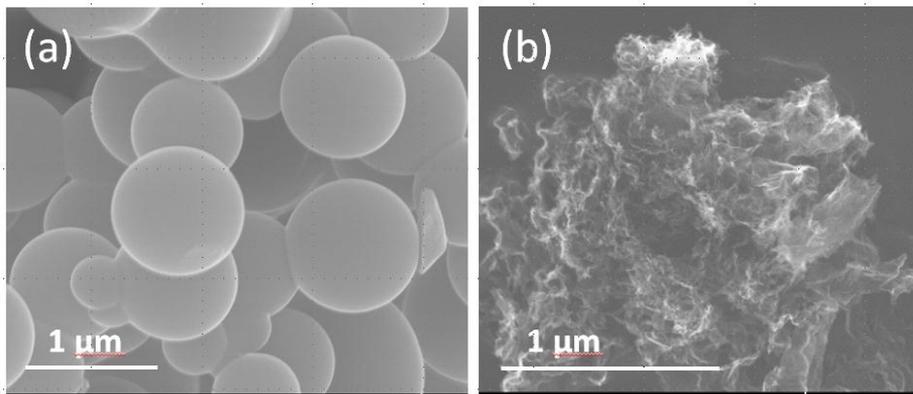
## Experimental details

### Preparation of N-PC-1.

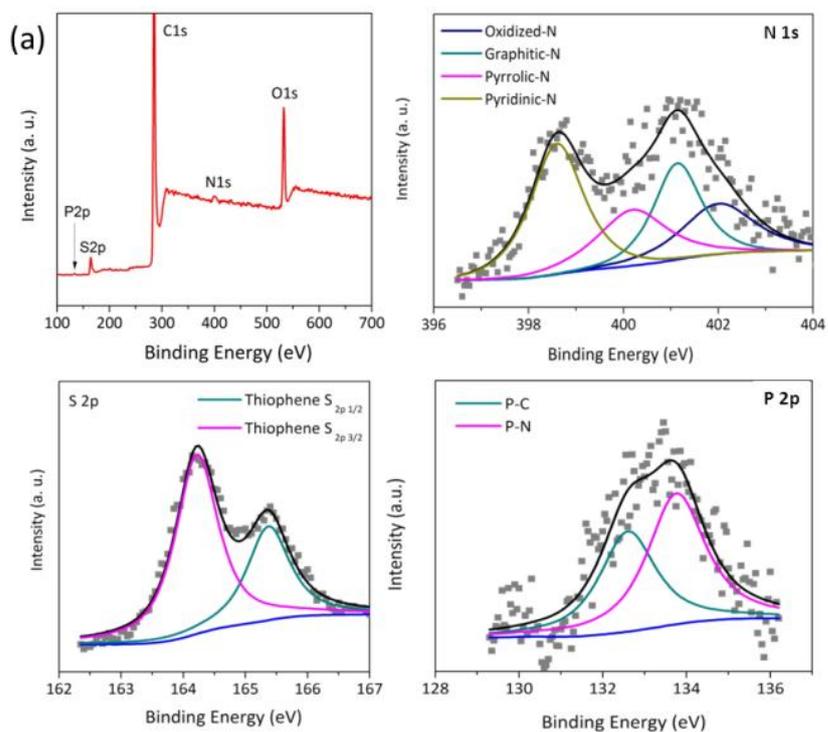
The melamine-doped polymeric nanospheres were prepared using a recipe reported by Zhou et al.<sup>1</sup> Briefly, 1.125 g of resorcinol and 1.658 g of formaldehyde water solution (37 wt%) were dissolved in 19.5 mL of distilled water and then stirred for more than 1 h. Meanwhile, 1.288 g of melamine and 2.488 g of formaldehyde water solution were dissolved in 60 mL of distilled water at 80 C. The solution was stirred vigorously until the solution became clear and slowly cooling down to 40 C. Subsequently, the two solutions were mixed and stirred for 30 min. in which the molar ratio of melamine to resorcinol is 1:1. Then, the mixed solution was transferred in a Teflon lined steel autoclave and treated at 120 C for 24 h. After polymerization, the obtained yellowish resins (MR) were freeze-dried in vacuum overnight. Then, the carbon catalyst N-PC-1 was obtained by pyrolyzing MR at 900 °C for 40 min under N<sub>2</sub> atmosphere.

### Reference.

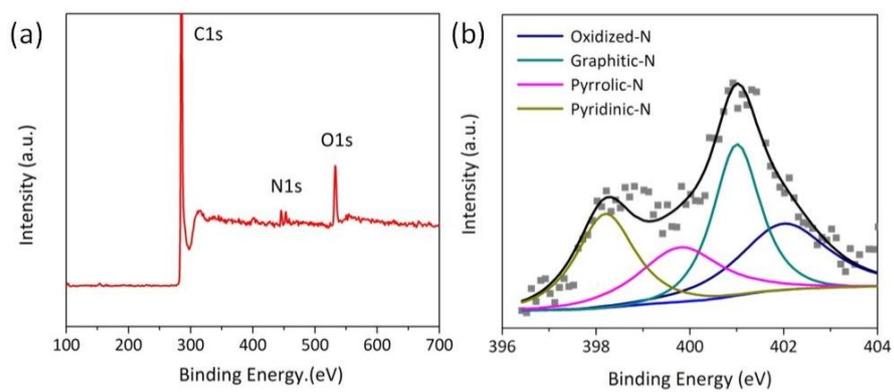
1. H. Zhou, S. Xu, H. Su, M. Wang, W. Qiao, L. Ling, et al. Facile preparation and ultra-microporous structure of melamine–resorcinol–formaldehyde polymeric microspheres. *Chem. Commun.* **2013**, 49 (36), 3763–5.



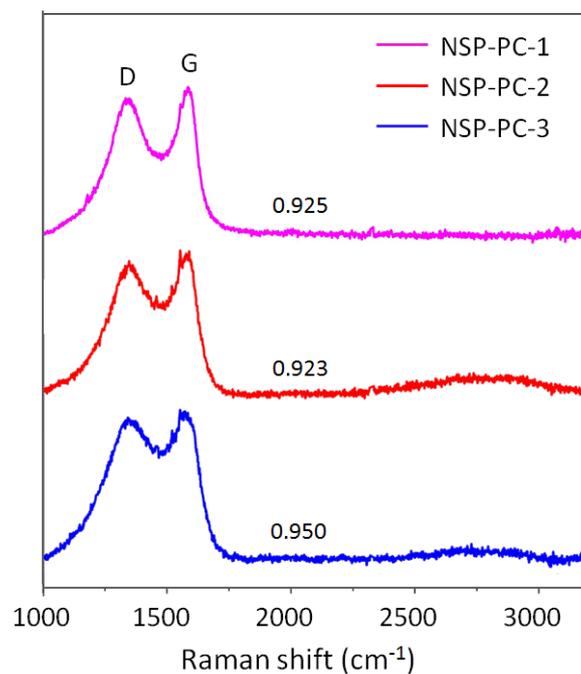
**Figure S1.** SEM images of (a) N-PC-1, (b) NSP-PC-3.



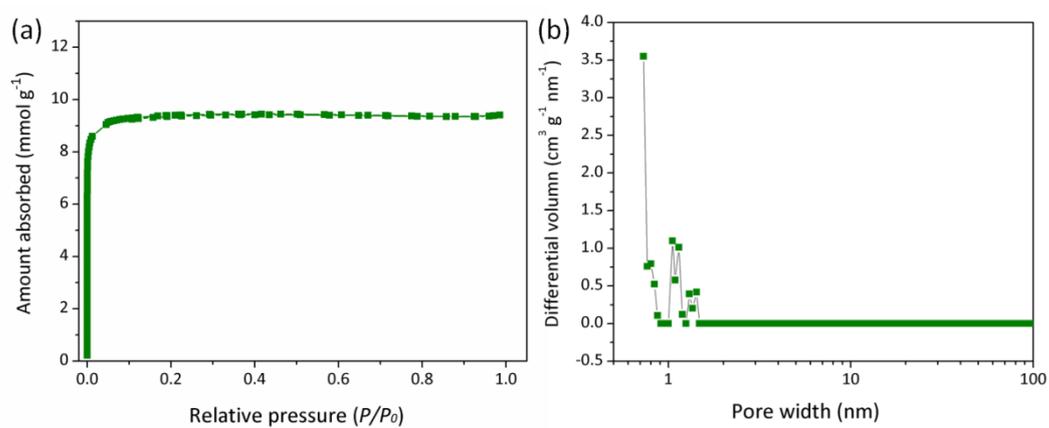
**Figure S2.** XPS spectra of NSP-PC-1.



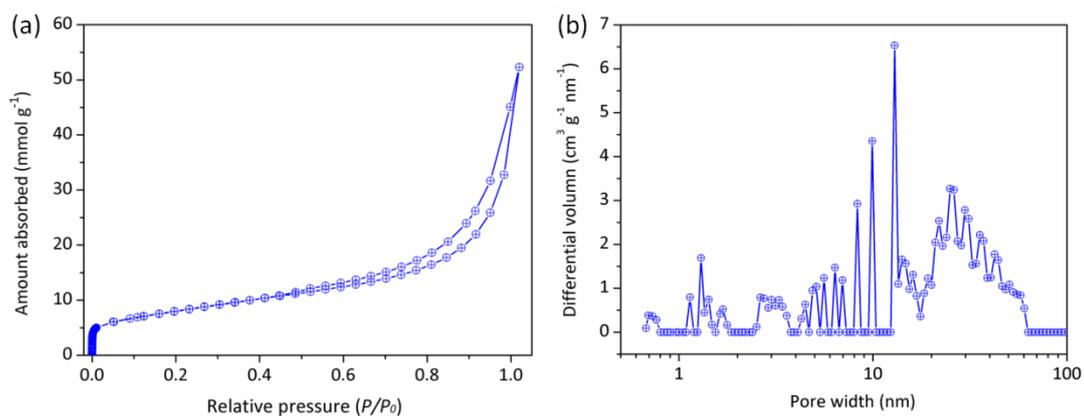
**Figure S3.** XPS spectra of N-PC-1.



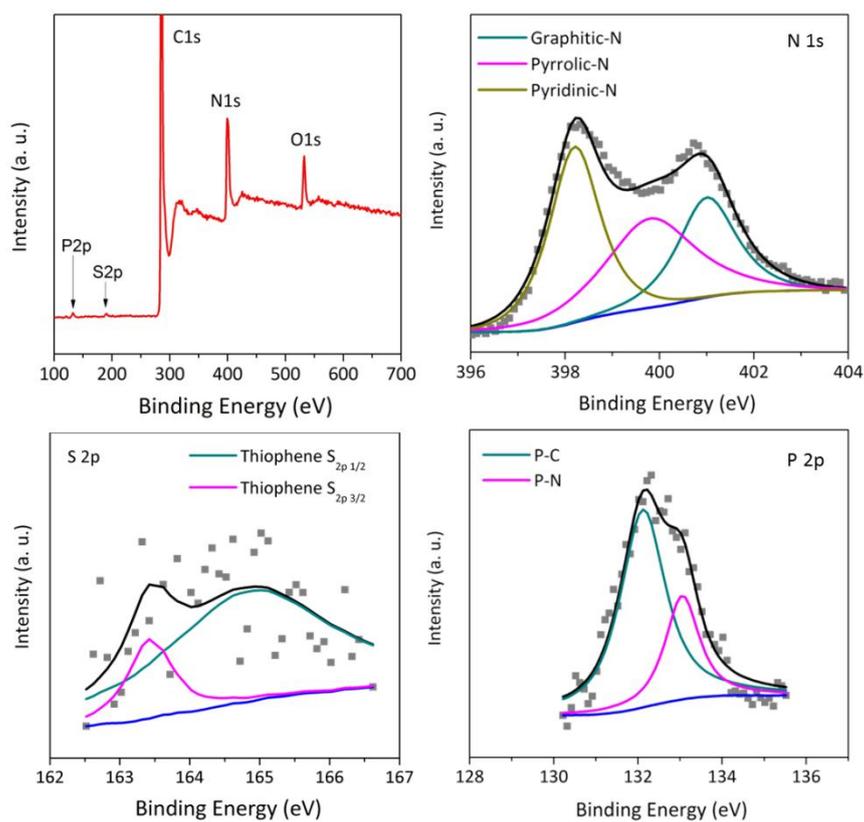
**Figure S4.** Raman spectra of NSP-PC-1, NSP-PC-2 and control catalyst NSP-PC-3.



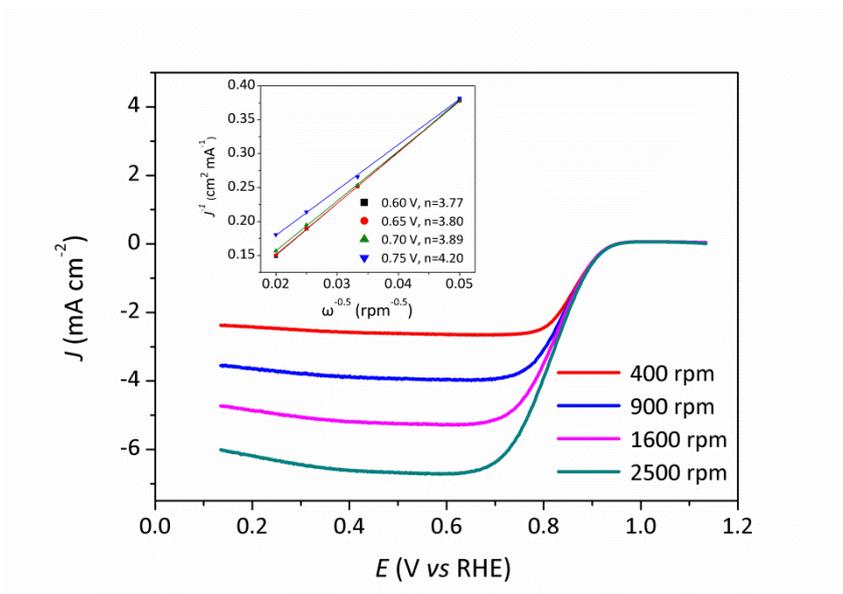
**Figure S5.** (a)  $N_2$  adsorption–desorption isotherm and (a) pore size distribution of NSP-PC-1 calculated using NLDFIT method.



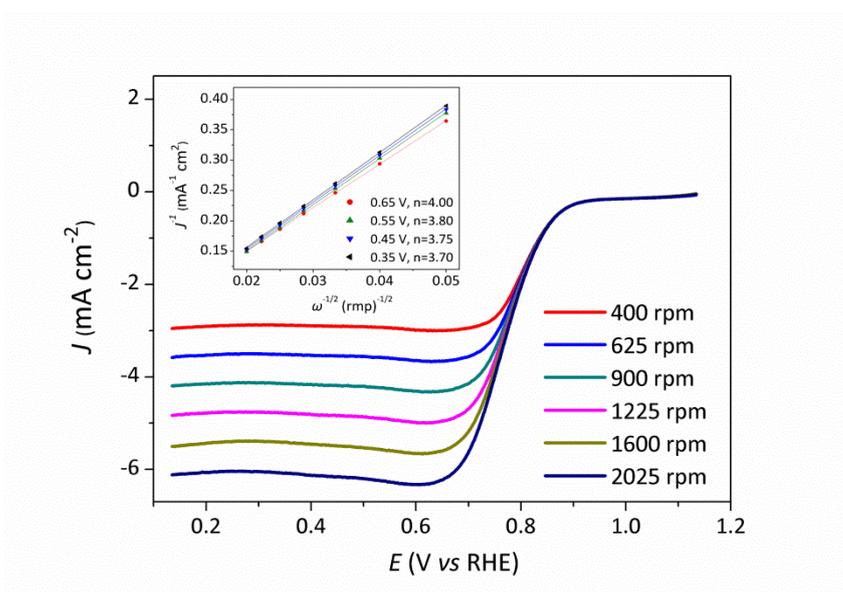
**Figure S6.** (a) N<sub>2</sub> adsorption–desorption isotherm and (a) pore size distribution of control catalyst NSP-PC-3 calculated using NLDFT method.



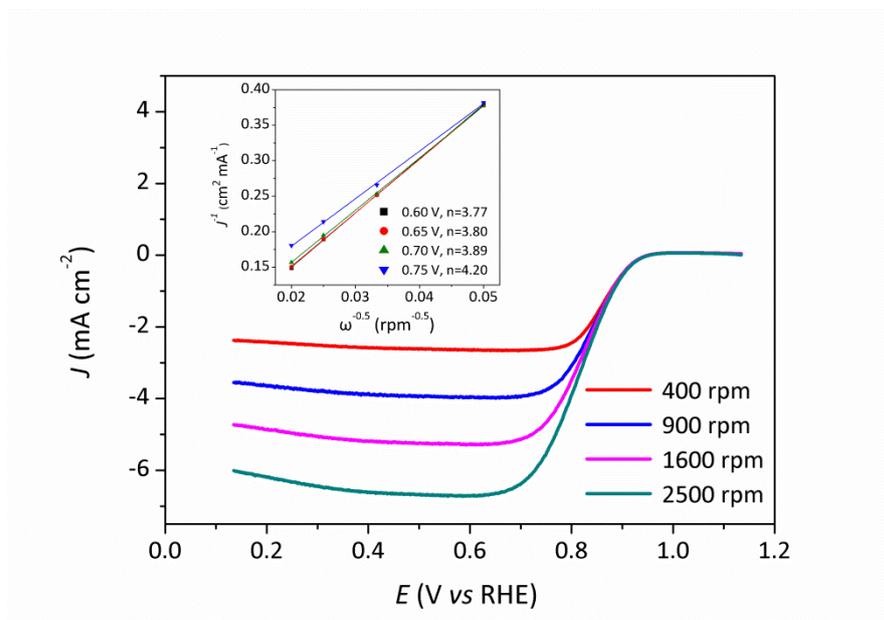
**Figure S7.** XPS spectra of NSP-PC-3.



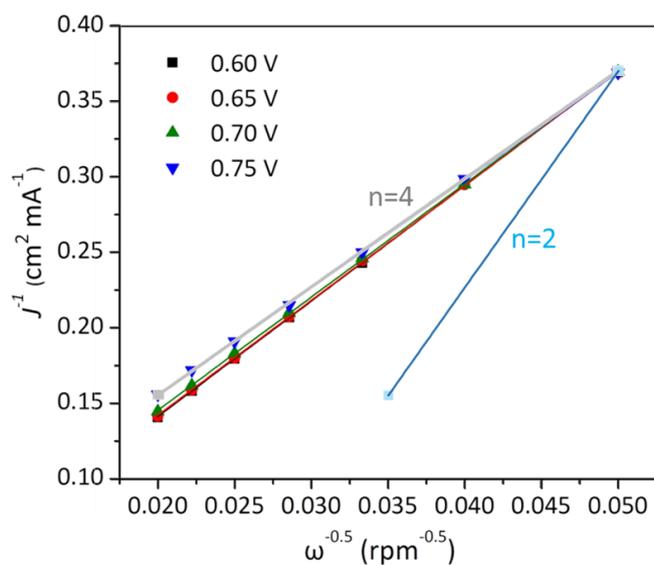
**Figure S8.** LSV curves of N-PC-1 at different rotation speeds in 0.1 M KOH solution at a scanning rate of  $10 \text{ mV s}^{-1}$ . The inset shows the K–L plot.



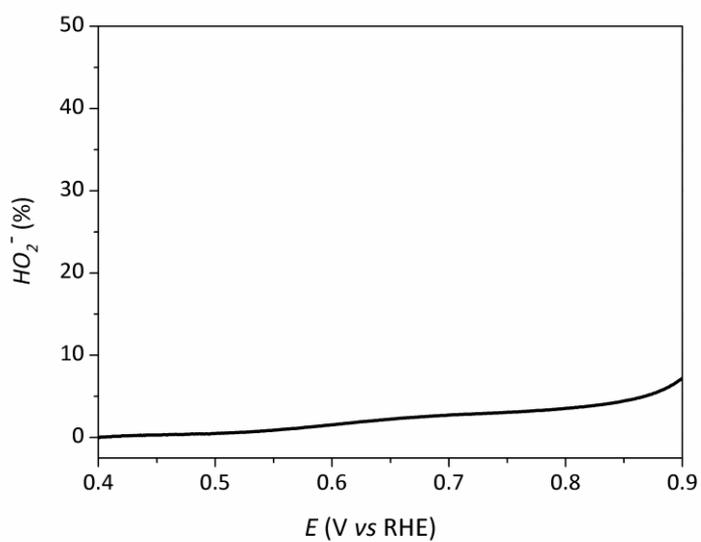
**Figure S9.** LSV curves of NSP-PC-1 at different rotation speeds in 0.1 M KOH solution at a scanning rate of  $10 \text{ mV s}^{-1}$ . The inset shows the K–L plot.



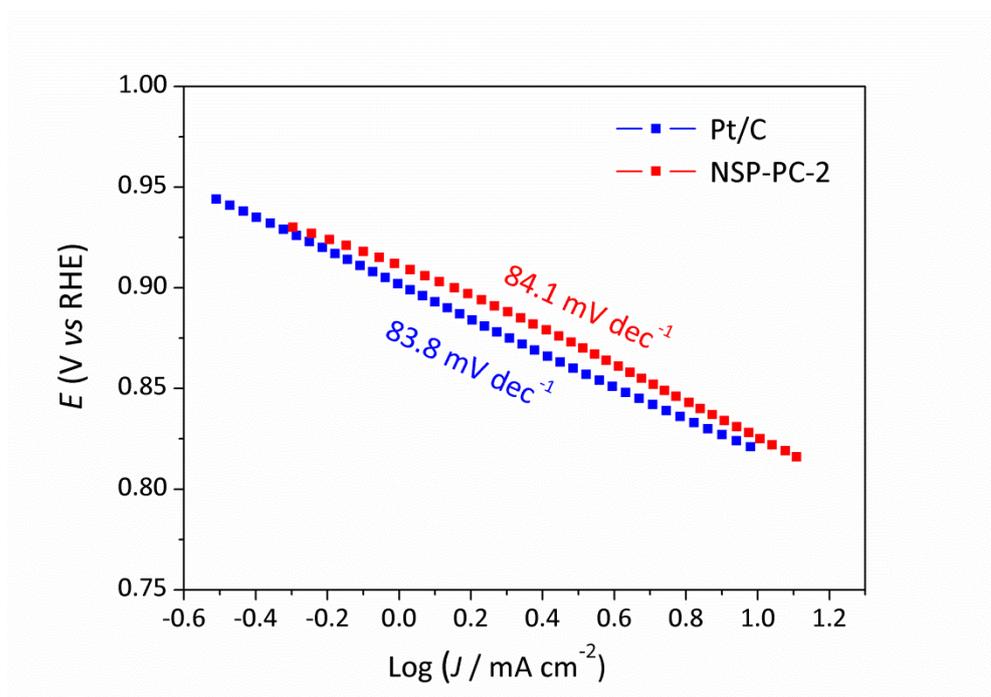
**Figure S10.** LSV curves of NSP-PC-3 at different rotation speeds in 0.1 M KOH solution at a scanning rate of  $10 \text{ mV s}^{-1}$ . The inset shows the K–L plot.



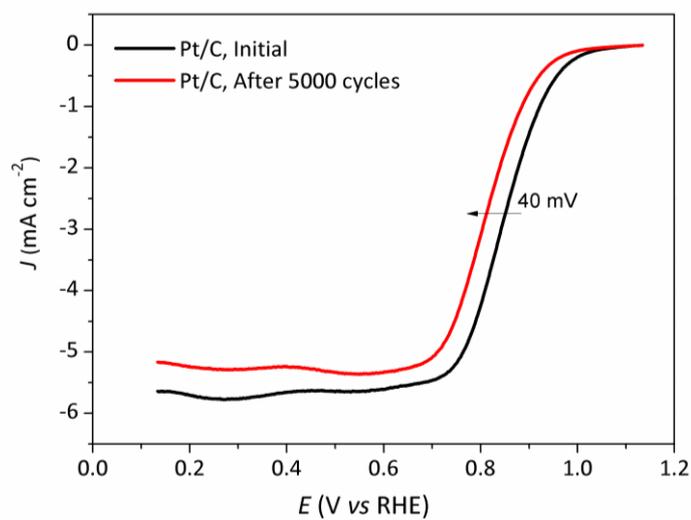
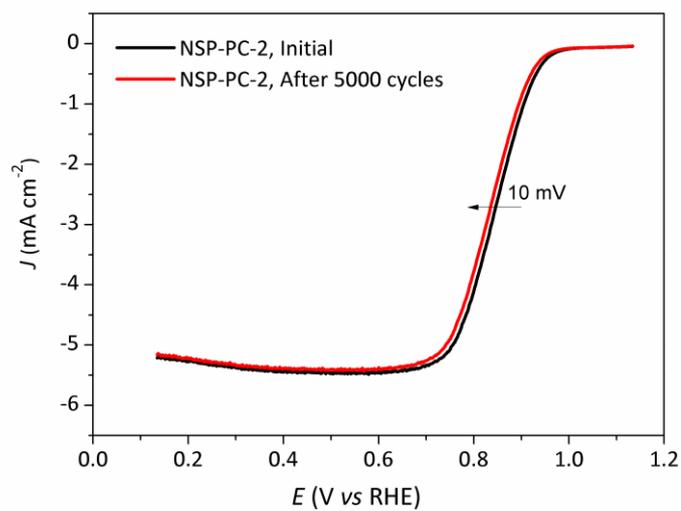
**Figure S11.** The Koutecky–Levich (K-L) plots for NSP-PC-2 at different potentials. For a clear comparison, the theoretical K-L plots for 2 electrons and 4 electron-transfer were plotted in gray and light blue, respectively.



**Figure S12.** Peroxide yield calculated at various potentials for NPS-PC-2 based on the corresponding RRDE data.



**Figure S13.** Tafel plots of NSP-PC-2 and Pt/C.



**Figure S14.** LSV curves of NSP-PC-2 (up) and Pt/C (down) measured during cycling durability tests at 1600 rpm in O<sub>2</sub>-saturated 0.1 M KOH (cycling tests were carried out in a potential window of 0.6–1.0 V vs. RHE with 50 mV s<sup>-1</sup>).

**Table S1.** Contents of C, O, N, P, S in catalysts NSP-PC-1, NSP-PC-2 and control catalysts N-PC-1, NSP-PC-3, as determined by XPS analysis.

<b>Sample</b>	<b>C (at.%)</b>	<b>O (at.%)</b>	<b>N (at.%)</b>	<b>P (at.%)</b>	<b>S (at.%)</b>
<b>N-PC-1</b>	89.49	7.70	2.81	-	-
<b>NSP-PC-1</b>	69.29	22.86	3.75	0.1	4.0
<b>NSP-PC-2</b>	82.79	6.57	9.05	1.0	0.6
<b>NSP-PC-3</b>	75.18	5.29	18.26	1.0	0.27