

The electronic supplementary information for:

## Efficient ORR Electrocatalytic Activity of Peanut Shell-Based Graphitic Carbon Microstructures

Yanling Wu,<sup>a</sup> Yanli Chen,<sup>\*a</sup> Huiqiu Wang,<sup>a</sup> Chiming Wang,<sup>b</sup> Ansheng Wang,<sup>a</sup> Shuai Zhao,<sup>a</sup> Xiyu Li,<sup>a</sup> Daofeng Sun<sup>\*a</sup> and Jianzhuang Jiang<sup>\*a,b</sup>

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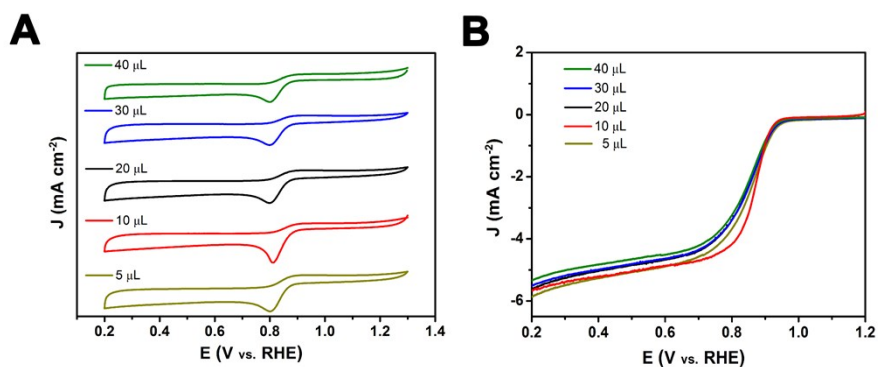
<sup>a</sup> College of Science, China University of Petroleum (East China), Qingdao 266580, China. E-mail: yanlichen@upc.edu.cn

<sup>b</sup> Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China. E-mail: jianzhuang@ustb.edu.cn

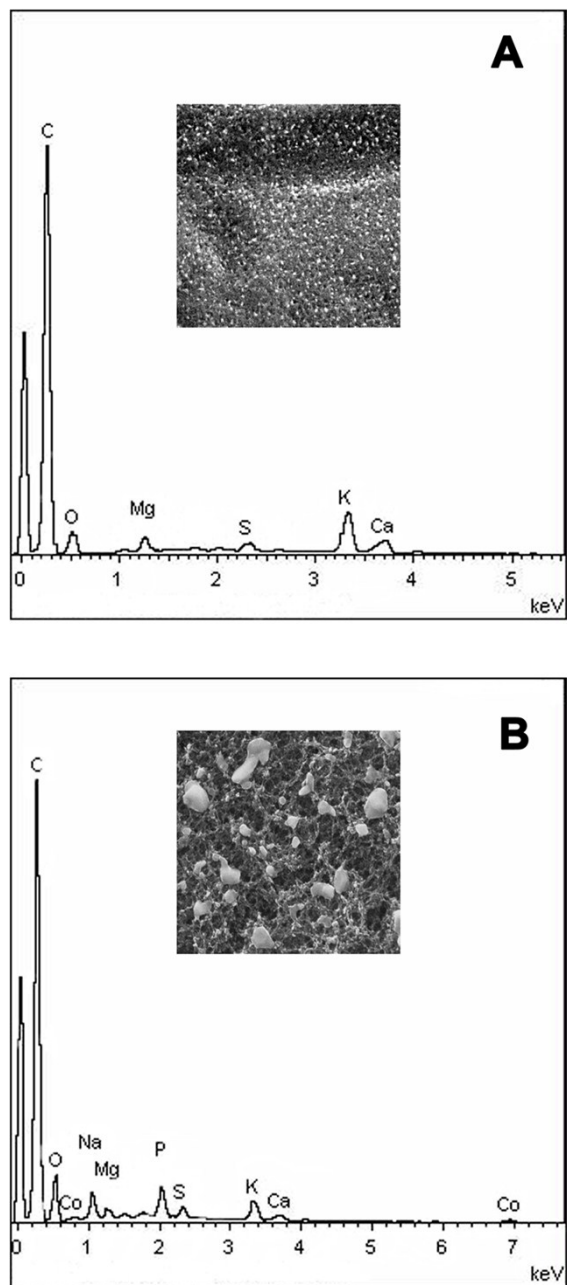
### Corresponding Author

\*E-mail: [yanlichen@upc.edu.cn](mailto:yanlichen@upc.edu.cn) (Y. Chen) and [jianzhuang@ustb.edu.cn](mailto:jianzhuang@ustb.edu.cn) (J. Jiang).

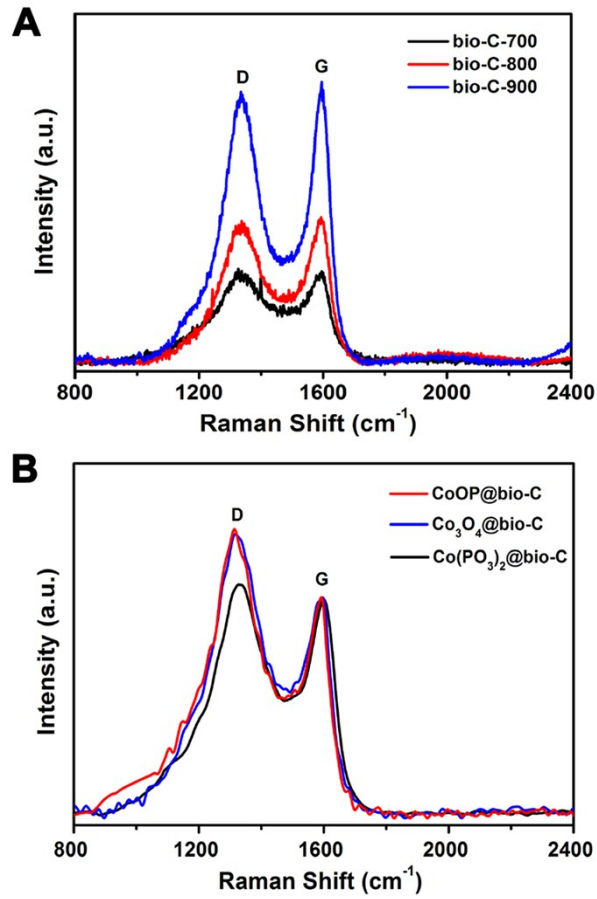
Fig. S1-S19, Table S1-S3



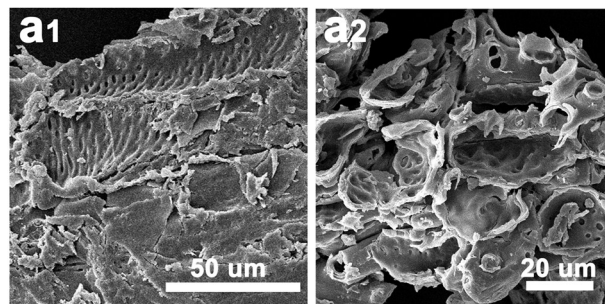
**Fig. S1** (A) CVs of the CoOP@bio-C catalyst under different quantities of Nafion in  $\text{O}_2$ -saturated 0.1 M KOH electrolyte; (B) LSV curves of CoOP@bio-C under different quantities of Nafion at  $10 \text{ mV s}^{-1}$  and a rotating speed of 1600 rpm, respectively.



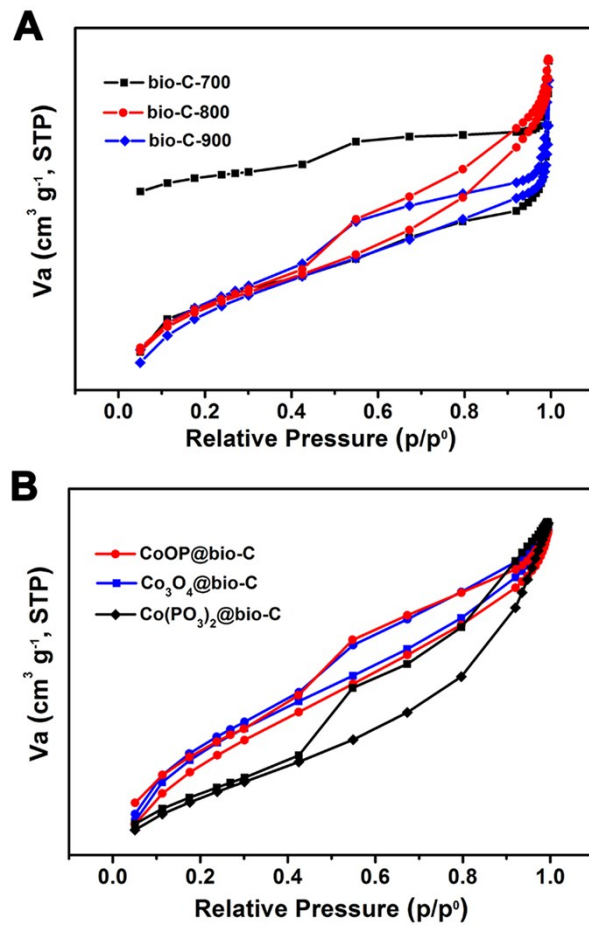
**Fig. S2** SEM and the corresponding EDS image of (A) bio-C-800 and (B) CoOP@bio-C, respectively.



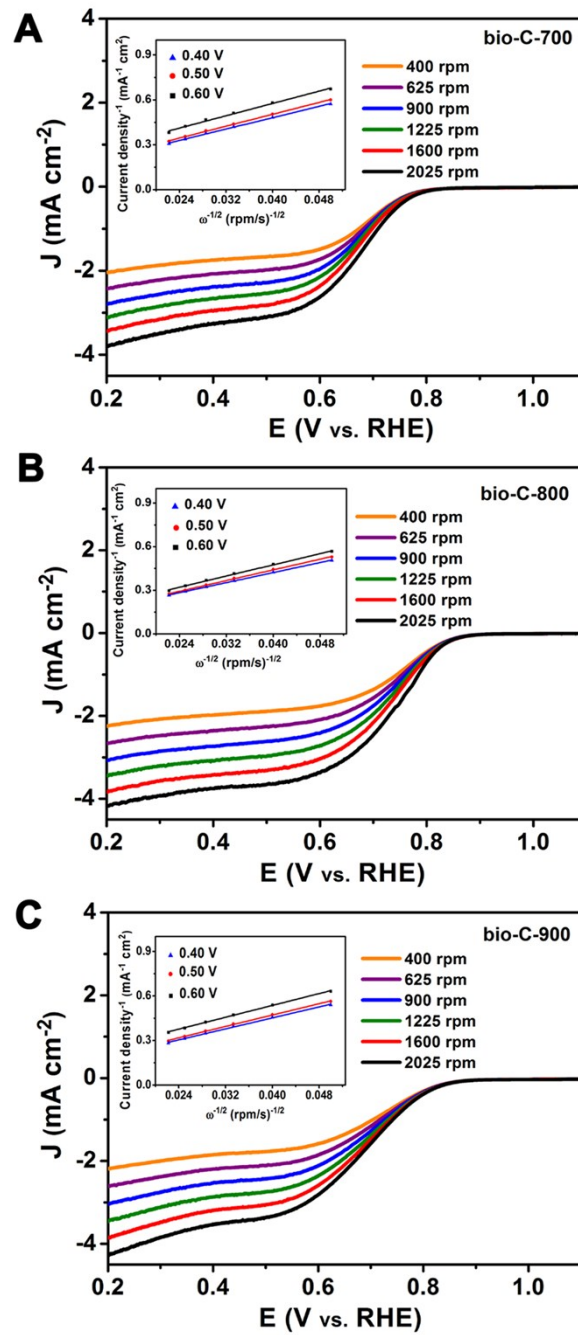
**Fig. S3** Raman spectra of (A) the bio-C-700, bio-C-800, bio-C-900 and (B) CoOP@bio-C, Co<sub>3</sub>O<sub>4</sub>@bio-C, Co(PO<sub>3</sub>)<sub>2</sub>@bio-C, respectively.



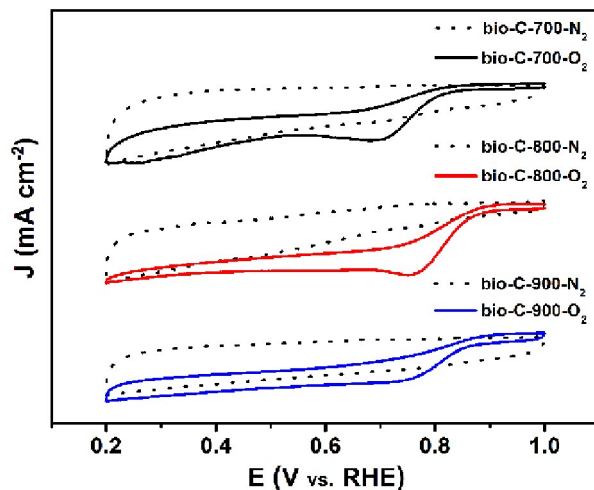
**Fig. S4** SEM image of the blank peanut shell power.



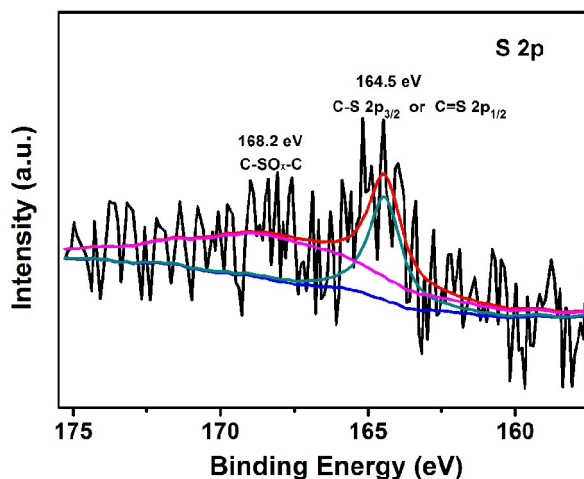
**Fig. S5**  $\text{N}_2$  adsorption/desorption isotherms of (A) the bio-C-700, bio-C-800, bio-C-900 and (B) the CoOP@bio-C,  $\text{Co}_3\text{O}_4$ @bio-C,  $\text{Co}(\text{PO}_3)_2$ @bio-C, respectively.



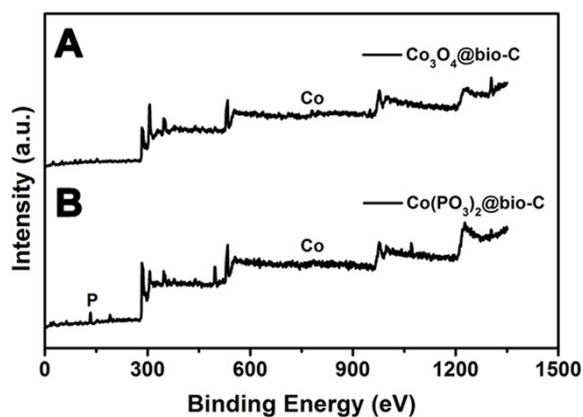
**Fig. S6** LSV curves at various rotating rates of the (A) bio-C-700, (B) bio-C-800 and (C) bio-C-900 in O<sub>2</sub>-saturated 0.1 M KOH electrolyte with a sweep rate of 10 mV s<sup>-1</sup>, respectively. (inset: corresponding K-L plots at various potentials)



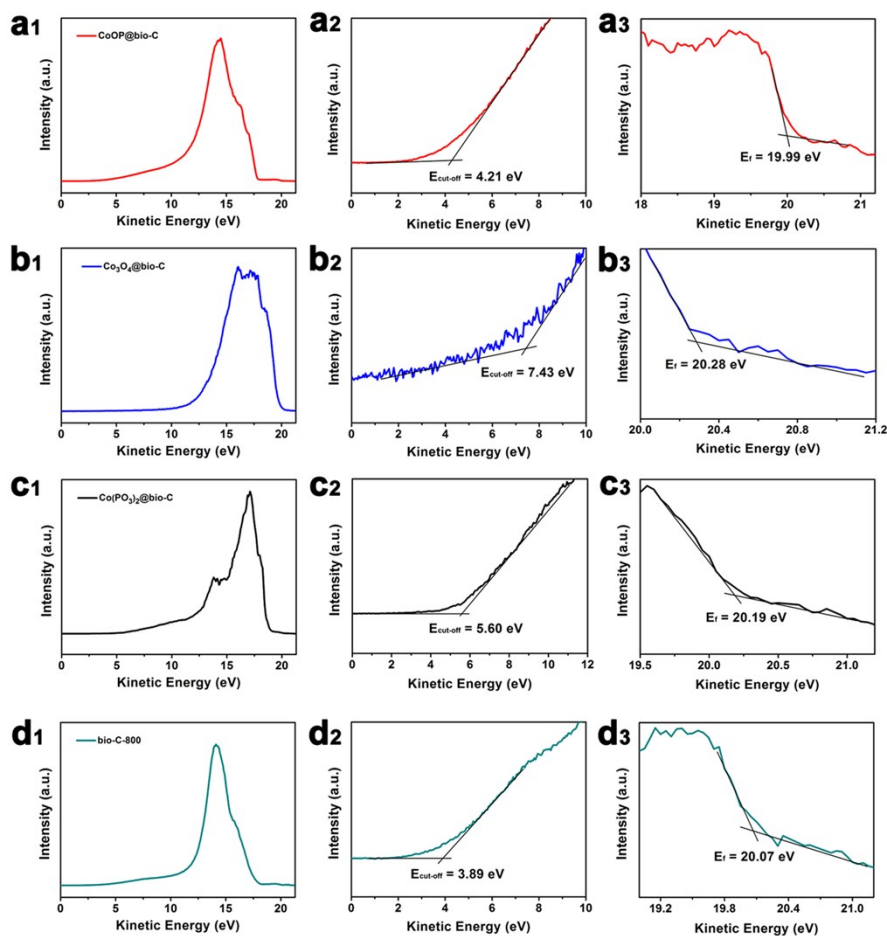
**Fig. S7** CVs of the bio-C-700, bio-C-800 and bio-C-900 catalysts in  $O_2$ -saturated (solid lines) and  $N_2$ -saturated (dot lines) 0.1 M KOH at  $10 \text{ mV s}^{-1}$ , respectively.



**Fig. S8** High-resolution XPS spectra of the S 2p core level for CoOP@bio-C.

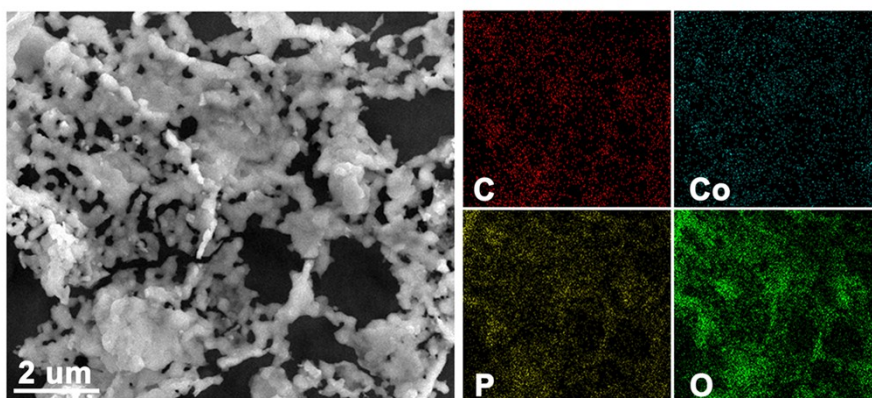


**Fig. S9** XPS survey spectra of the (A)  $Co_3O_4@bio-C$  and (B)  $Co(PO_3)_2@bio-C$  composites.



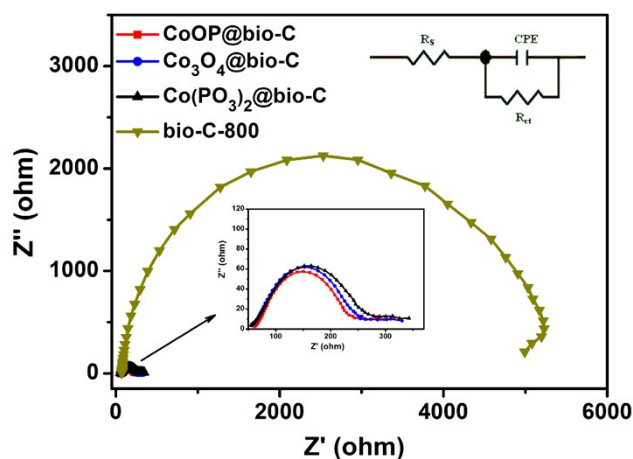
**Fig. S10** Ultraviolet photoelectron spectroscopy (UPS) measurements of CoOP@bio-C (a<sub>1</sub>, a<sub>2</sub> and a<sub>3</sub>), Co<sub>3</sub>O<sub>4</sub>@bio-C (b<sub>1</sub>, b<sub>2</sub> and b<sub>3</sub>), Co(PO<sub>3</sub>)<sub>2</sub>@bio-C (c<sub>1</sub>, c<sub>2</sub> and c<sub>3</sub>) and bio-C-800 (d<sub>1</sub>, d<sub>2</sub> and d<sub>3</sub>) (UV excitation by He I = 21.2 eV). The sample for UPS measurement was prepared by depositing a thin film (8 nm) on a small plate of SiO<sub>2</sub>/Si substance (size: 1.5 cm × 1.5 cm). The work function of samples can be calculated by using the following equation.

$$\Phi \text{ (work function)} = h\nu - |E_{\text{cut-off}} - E_f| \quad (3)$$

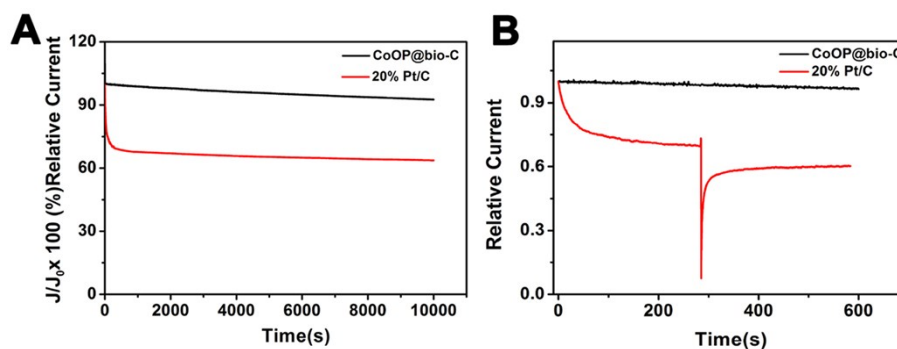


**Fig. S11** SEM image of CoOP@bio-C used in the EDS mapping revealing the elemental distribution of C, Co, P and O.

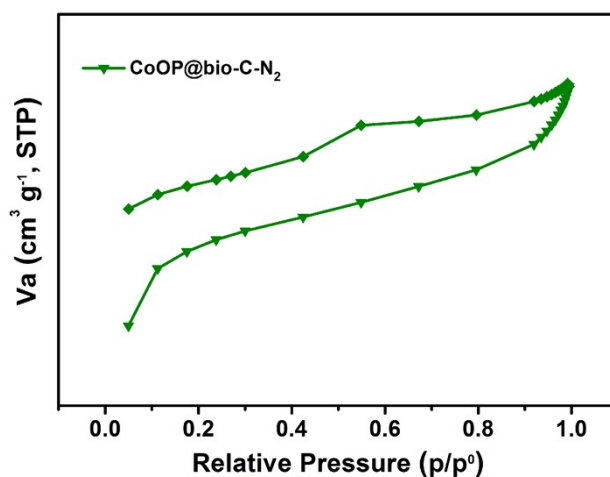




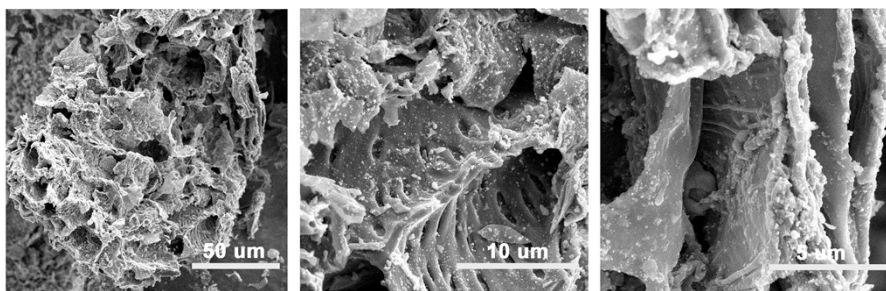
**Fig. S12** Nyquist plots of CoOP@bio-C, Co<sub>3</sub>O<sub>4</sub>@bio-C, Co(PO<sub>3</sub>)<sub>2</sub>@bio-C and bio-C-800 catalysts-modified electrodes in 0.1 M KOH solution in the frequency range of 0.1–10000 Hz, respectively. (inset: corresponding equivalent circuit)



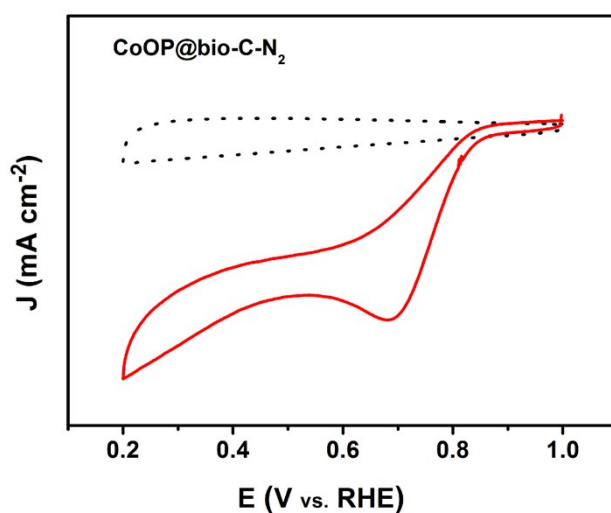
**Fig. S13** (A) Amperometric *i-t* curves of CoOP@bio-C and 20 wt% Pt/C and (B) upon the addition of 3 M methanol in O<sub>2</sub>-saturated 0.1 M KOH solution with the rotation speed of 1600 rpm.



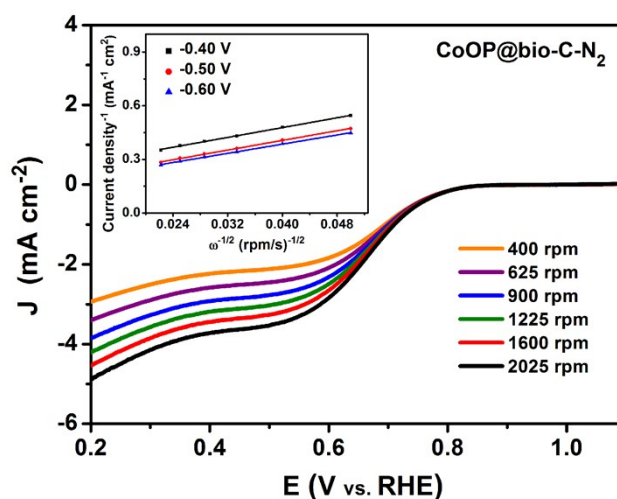
**Fig. S14** N<sub>2</sub> adsorption/desorption isotherms of the CoOP@bio-C-N<sub>2</sub>.



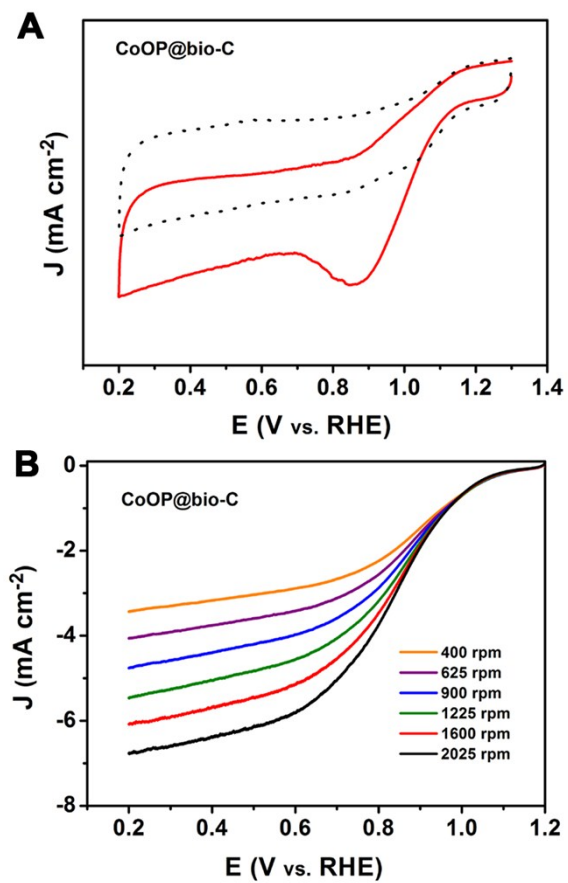
**Fig. S15** SEM images of the CoOP@bio-C-N<sub>2</sub> sample observed at the different amplification times.



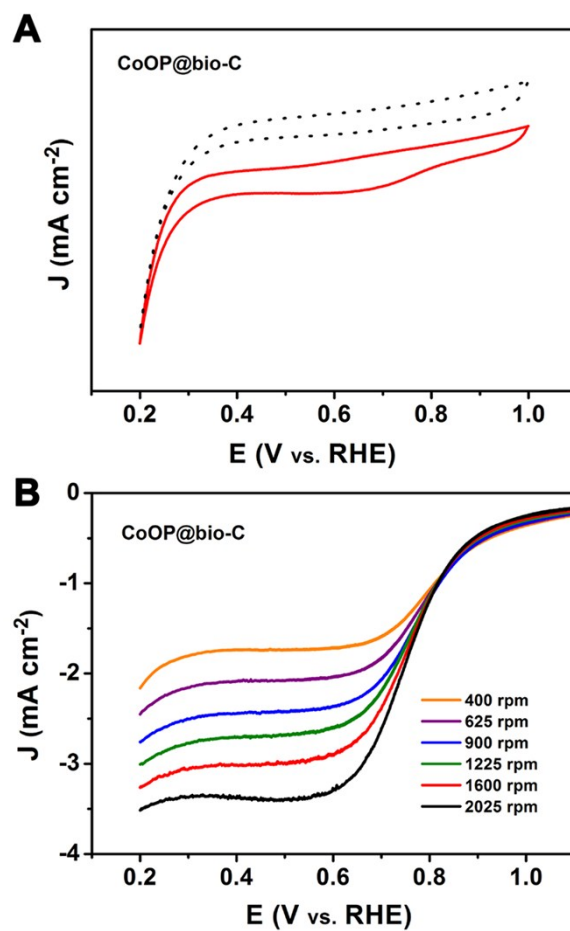
**Fig. S16** CV curve of the CoOP@bio-C-N<sub>2</sub> catalyst in O<sub>2</sub>-saturated (solid line) and N<sub>2</sub>-saturated (dot line) 0.1 M KOH electrolyte.



**Fig. S17** LSV curves at various rotating rates of the CoOP@bio-C-N<sub>2</sub> catalyst in O<sub>2</sub>-saturated 0.1 M KOH electrolyte. (inset: corresponding K–L plots at various potentials)



**Fig. S18** (A) CVs of CoOP@bio-C in O<sub>2</sub>-saturated (solid lines) and N<sub>2</sub>-saturated (dash lines) PBS solution at 10 mV s<sup>-1</sup>. (B) LSV curves of CoOP@bio-C at various rotating speeds.



**Fig. S19** (A) CVs of CoOP@bio-C in O<sub>2</sub>-saturated (solid lines) and N<sub>2</sub>-saturated (dash lines) 0.5 M H<sub>2</sub>SO<sub>4</sub> media at 10 mV s<sup>-1</sup>. (B) LSV curves of CoOP@bio-C at various rotating speeds.

**Table S1** Comparison of the ORR performance for CoOP@bio-C catalysts at 1600 rpm in 0.1 M KOH.

Catalysts	Half-wave potential (V)	Current density J (mA cm <sup>-2</sup> )	Onset potential (V)	Tafel slope (mV/dec <sup>-1</sup> )	Electron transfer number	Reference
CoOP@bio-C	0.81	5.67	0.91	57	3.93	This work
urchin-like CoP NCs	0.70	4.50	0.80	--	--	<i>Nano Lett.</i> , 2015 [1]
Co-NC@CoP-NC	0.78	--	0.89	--	--	<i>J. Mater. Chem. A</i> , 2016 [2]
NCS-800	0.75	4.60	0.82	--	--	<i>Energy Environ. Sci.</i> , 2014 [3]
N-CNAs	0.79	4.35	0.92	--	--	<i>Small</i> , 2014 [4]
Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> C-N	0.84	3.75	0.96	--	--	<i>Energy Environ. Sci.</i> , 2016 [5]
Co@Co <sub>3</sub> O <sub>4</sub> @C	0.81	4.65	0.93	--	--	<i>Energy Environ. Sci.</i> , 2015 [6]
WHC-700	0.88	4.40	0.98	--	--	<i>Nanoscale</i> , 2015 [7]
NPC-800	0.76	5.30	0.94	--	--	<i>Phys. Chem. Chem. Phys.</i> , 2016 [8]
Co <sub>9</sub> S <sub>8</sub> @CNS900	0.83	5.60	0.95	--	--	<i>Adv. Mater.</i> , 2016 [9]
3D-HPG	0.84	5.50	0.93	--	--	<i>Nano Energy</i> , 2016 [10]
CaI-CoZIF-VXC72	-0.16	5.92	--	35	4.0	<i>Adv. Mater.</i> , 2017 [12]
AC-U-P	-0.21	5.40	0.98	--	3.7	<i>Appl. Catal. B Environ.</i> , 2017 [13]
NC@CoPx/PyCNTs-900	-0.20	5.50	0.92	85	3.8	<i>Carbon</i> , 2018 [14]

**Table S2** Surface areas of the bio-C-700, bio-C-800, bio-C-900, CoOP@bio-C, CoOP@bio-C-N<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>@bio-C and Co(PO<sub>3</sub>)<sub>2</sub>@bio-C, respectively.

Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
bio-C-700	95.6
bio-C-800	653.9
bio-C-900	461.7
<b>CoOP@bio-C</b>	<b>671.4</b>
CoOP@bio-C-N <sub>2</sub>	248.9
Co <sub>3</sub> O <sub>4</sub> @bio-C	366.2
Co(PO <sub>3</sub> ) <sub>2</sub> @bio-C	324.4

**Table S3** The ORR performance of the bio-C-700, bio-C-800, bio-C-900, CoOP@bio-C, CoOP@bio-C-N<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>@bio-C and Co(PO<sub>3</sub>)<sub>2</sub>@bio-C in alkaline media at 1600 rpm, respectively.

Sample	Onset potential (V)	Half wave potential (V)	Current density J (mA cm <sup>-2</sup> )	Tafel slope (mV dec <sup>-1</sup> )	Electron transfer number
bio-C-700	0.73	0.71	3.43		2.95
bio-C-800	0.83	0.75	3.84		3.23
bio-C-900	0.81	0.69	3.86		3.02
<b>CoOP@bio-C</b>	<b>0.91</b>	<b>0.81</b>	<b>5.70</b>		<b>3.93</b>
CoOP@bio-C-N <sub>2</sub>	0.79	0.68	4.49		3.19
Co <sub>3</sub> O <sub>4</sub> @bio-C	0.86	0.78	5.20		3.86
Co(PO <sub>3</sub> ) <sub>2</sub> @bio-C	0.85	0.77	4.14		3.47
Pt/C	0.97	0.83	4.28		3.94 [15]

## Notes and references

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