

## Supporting Information

### Facile *in situ* fabrication of biomorphic Co<sub>2</sub>P-Co<sub>3</sub>O<sub>4</sub>/rGO/C as efficient electrocatalyst for oxygen reduction reaction

Xingmei Guo,<sup>a</sup> Cheng Qian,<sup>a</sup> Xiaohan Wan,<sup>a</sup> Wei Zhang,<sup>a</sup> Haowei Zhu,<sup>a</sup> Junhao Zhang,<sup>\*a</sup> Hongxun Yang,<sup>a</sup> Shengling Lin,<sup>a</sup> Qinghong Kong<sup>b</sup> and Tongxiang Fan<sup>\*c</sup>

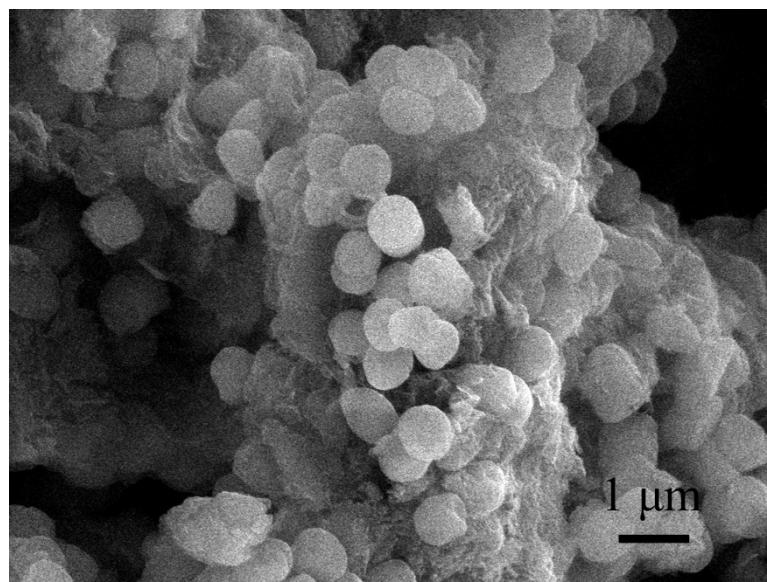
<sup>a</sup>School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, China

Email: [jhzhang6@just.edu.cn](mailto:jhzhang6@just.edu.cn)

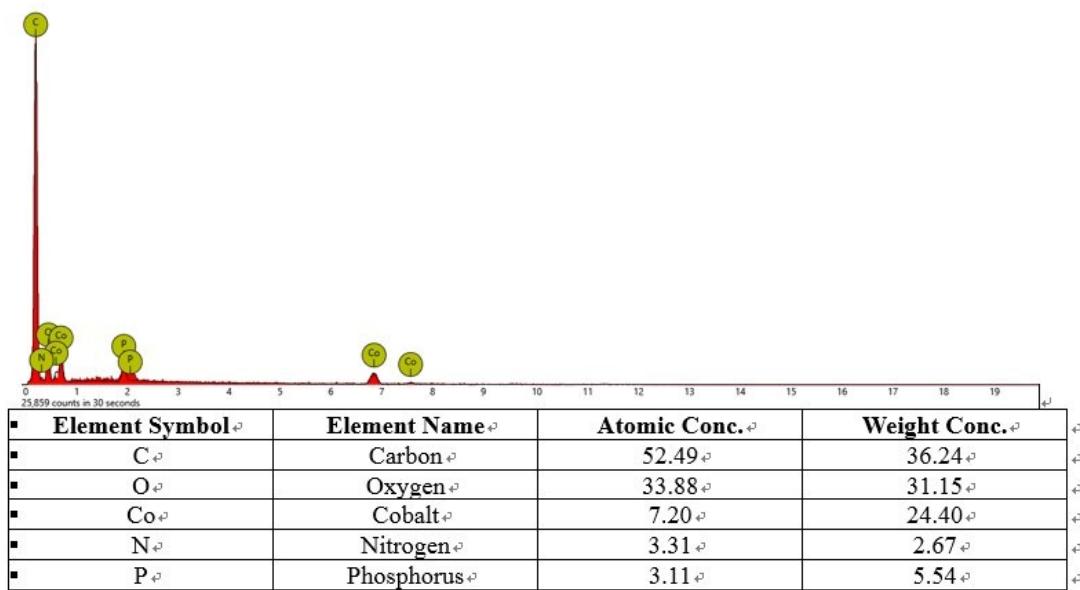
<sup>b</sup>School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China.

<sup>c</sup>School of Materials Science and Technology, Shanghai Jiaotong University, Shanghai 200240, China

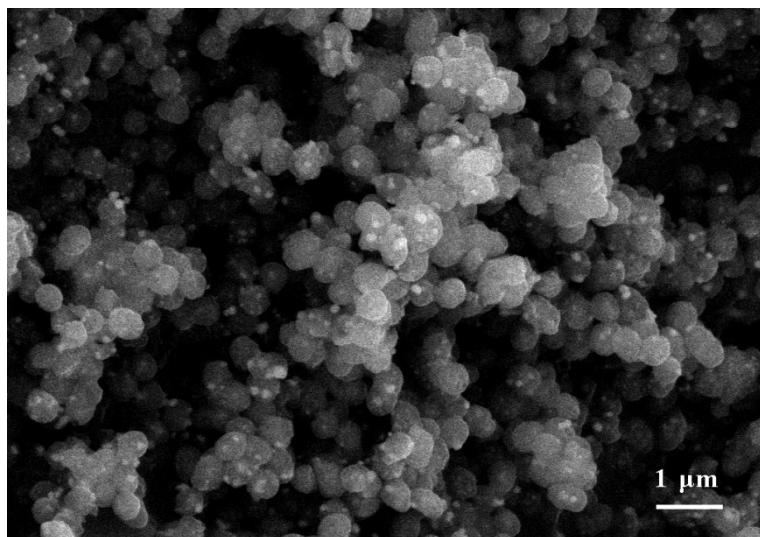
Email: [txfan@sjtu.edu.cn](mailto:txfan@sjtu.edu.cn)



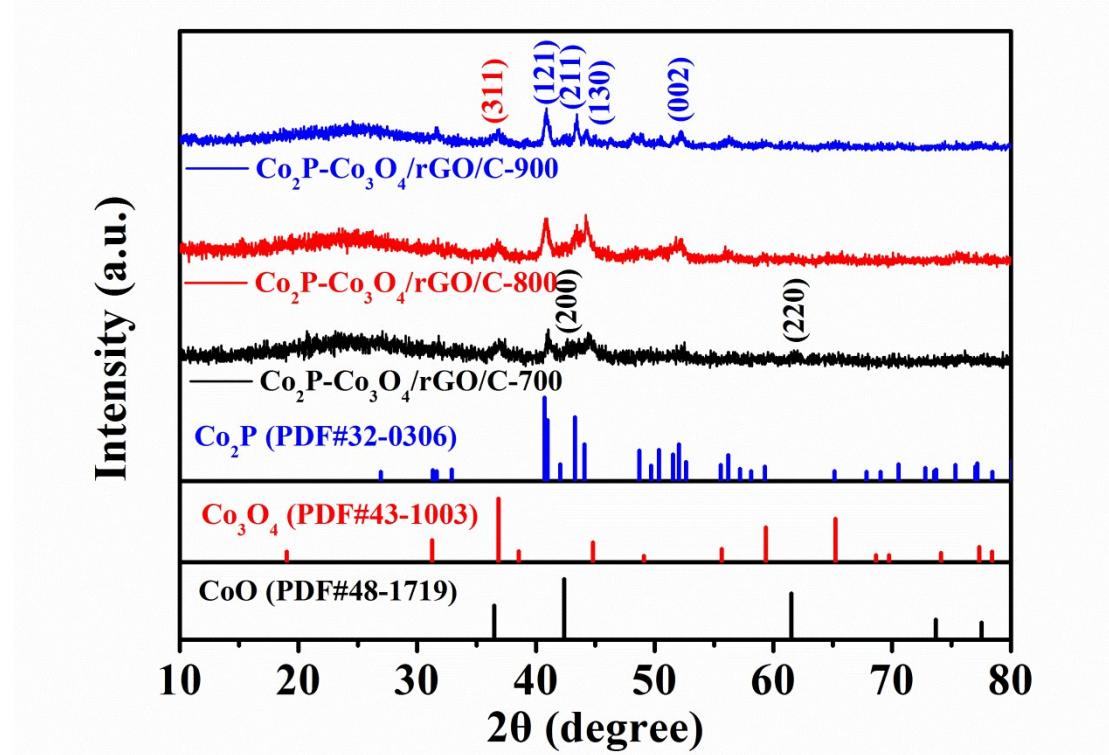
**Fig. S1** FESEM image of *Streptococcus thermophiles* adsorbed with precursor and GO.



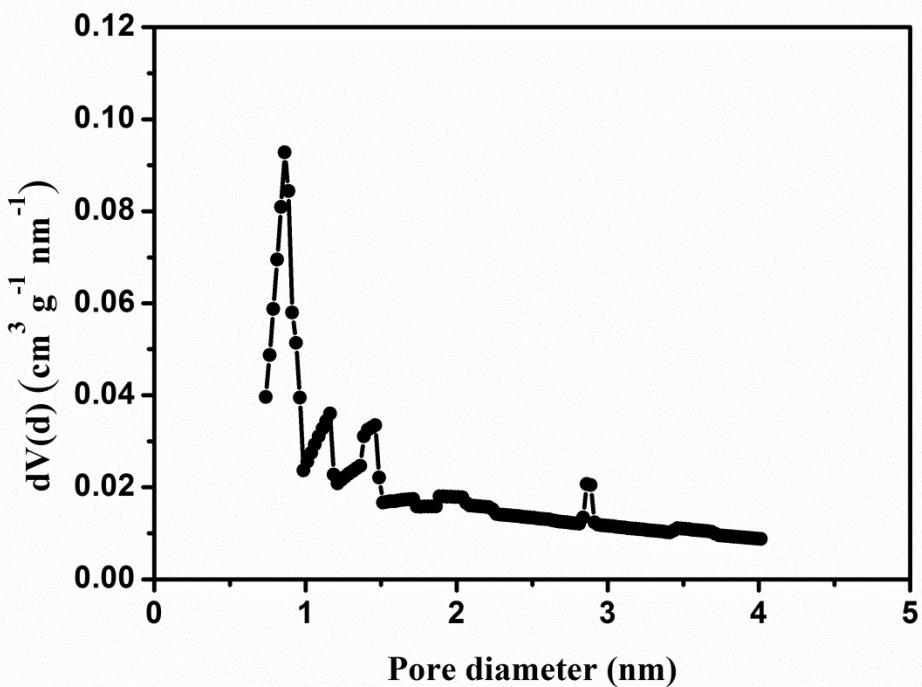
**Fig. S2** EDX spectrum and detailed elemental data of  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{rGO/C}$ .



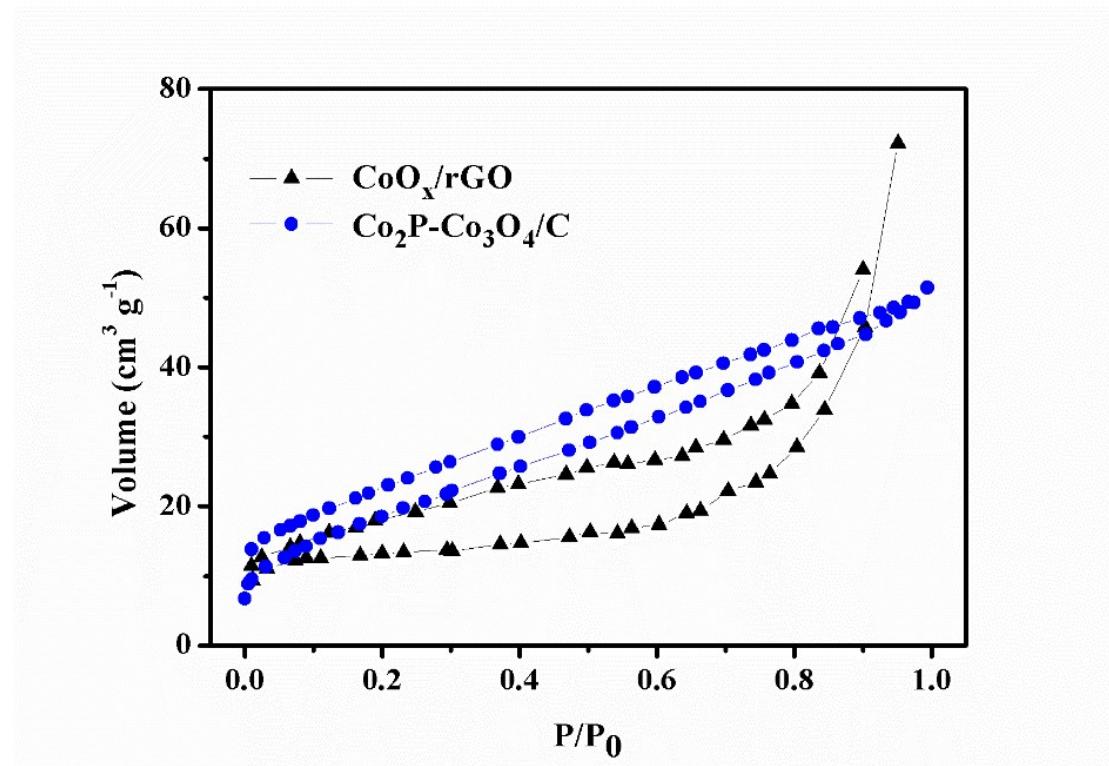
**Fig. S3** FESEM image of biomorphic  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{C}$  sample.



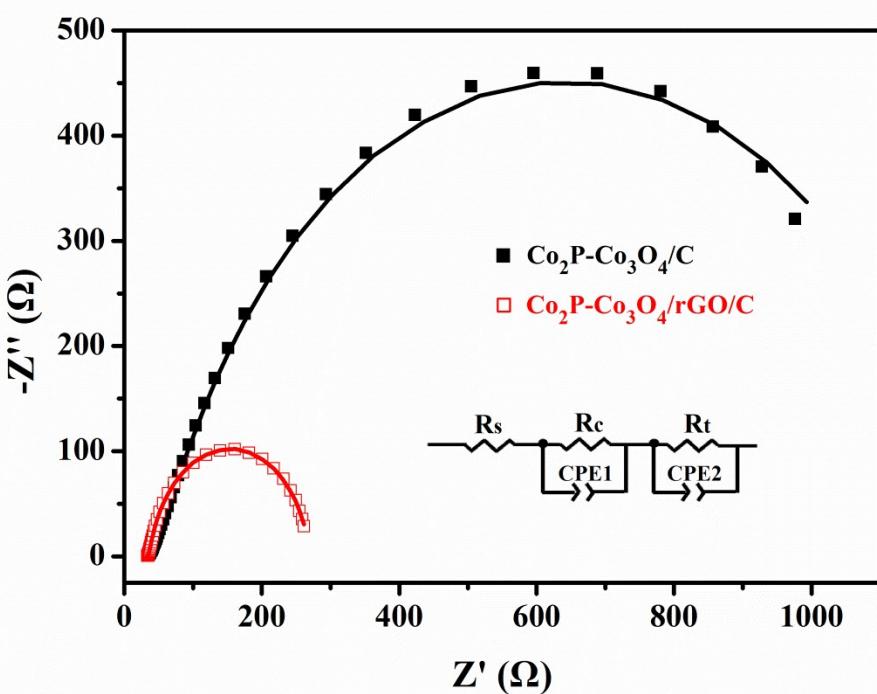
**Fig. S4** XRD patterns of  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{rGO/C}$  with different calcining temperatures.



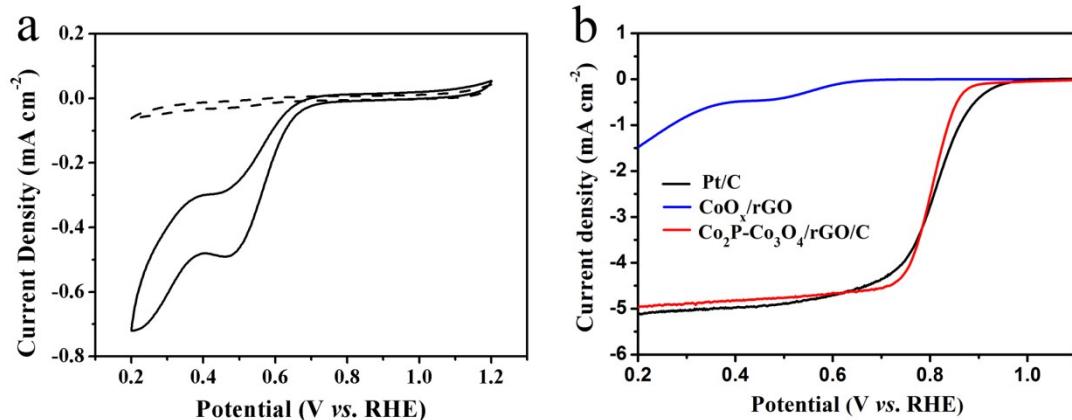
**Fig. S5** Micropore size distribution of  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{rGO}/\text{C}$  calculated through HK method.



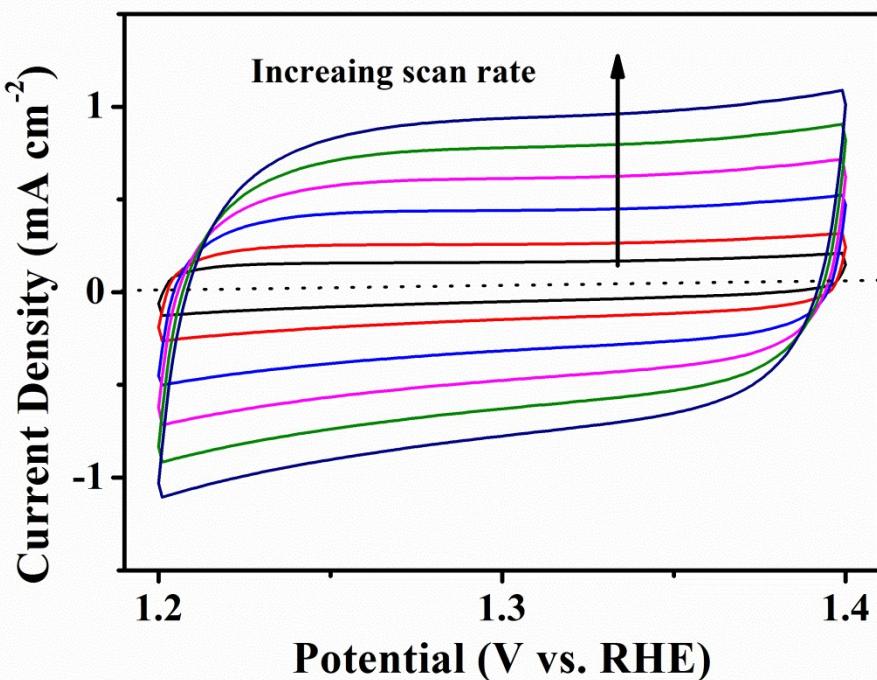
**Fig. S6**  $\text{N}_2$  adsorption/desorption isotherms of  $\text{CoO}_x/\text{rGO}$  and  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{C}$ .



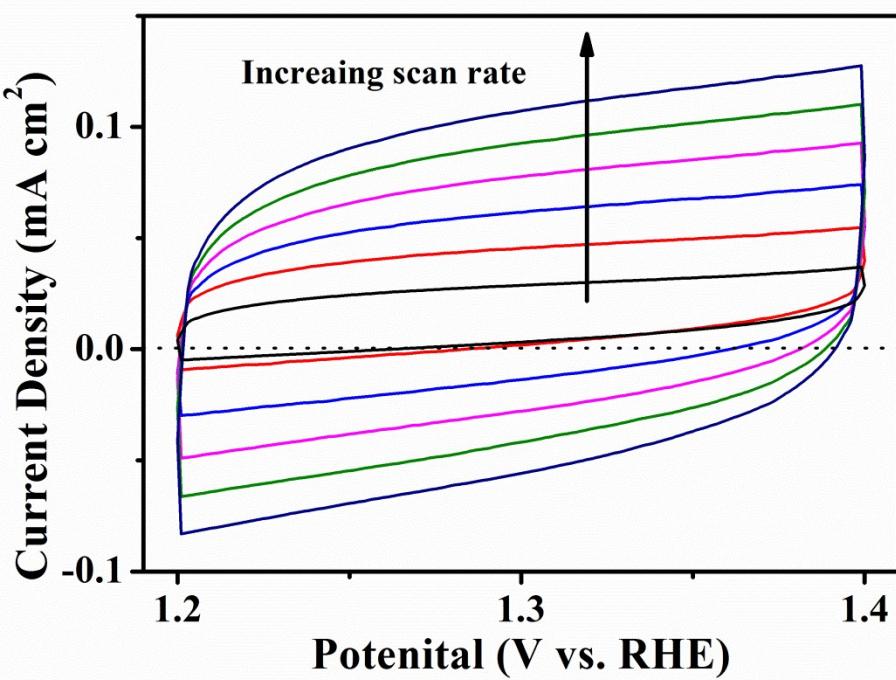
**Fig. S7** Actual and fitting Nyquist plots for ORR at 0.85 V vs. RHE on  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{C}$  and  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{rGO}/\text{C}$ . Inset: the equivalent circuit.



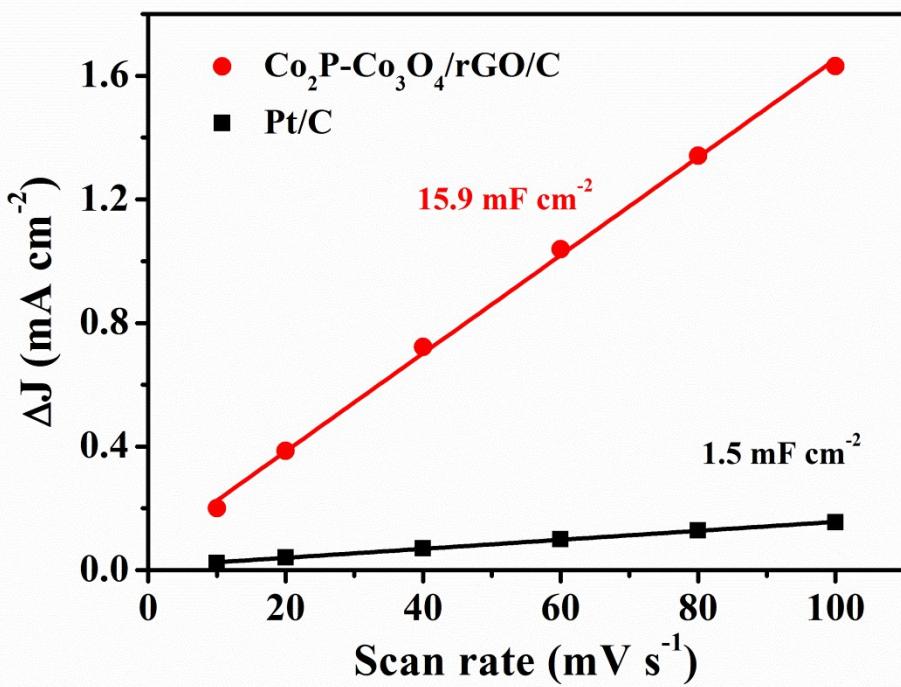
**Fig. S8** (a) CV curves of  $\text{CoO}_x/\text{rGO}$  in oxygen (solid line) and nitrogen (dotted line) saturated KOH solution. (b) LSV curves of  $\text{CoO}_x/\text{rGO}$ ,  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{rGO}/\text{C}$  and Pt/C in oxygen saturated KOH solution at a rotation speed of 1600 rpm.



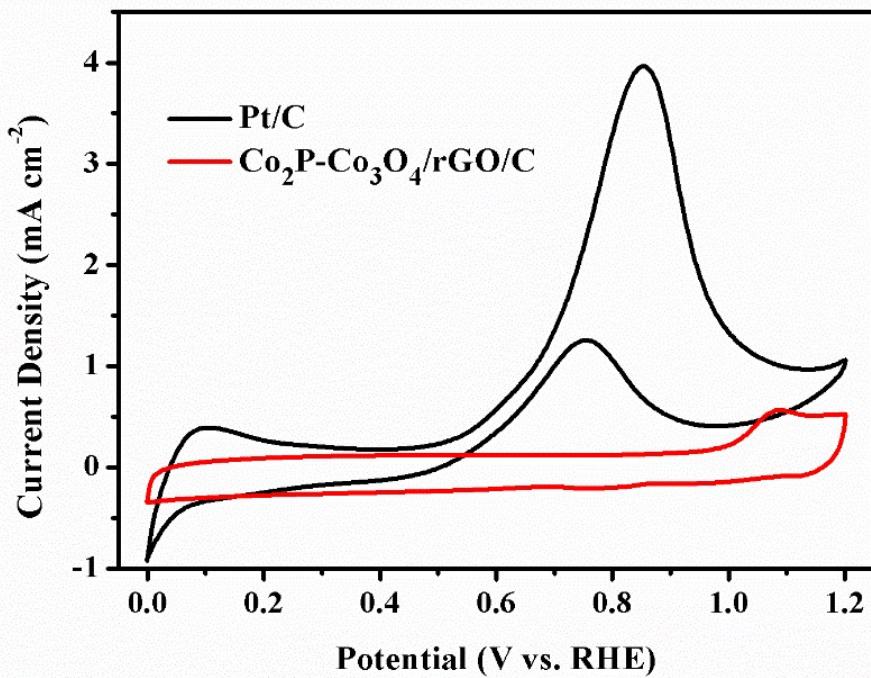
**Fig. S9** CV curves of  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{rGO}/\text{C}$  in the potential range of 1.2-1.4 V vs. RHE with scan rates increasing from 10 to 100  $\text{mV s}^{-1}$ .



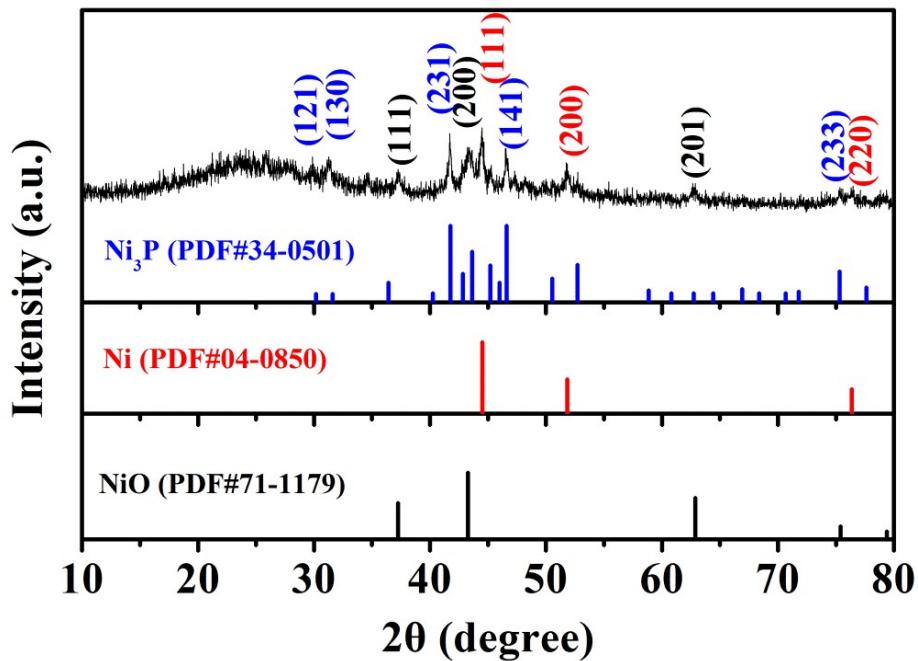
**Fig. S10** CV curves of Pt/C in the potential range of 1.2-1.4 V vs. RHE with scan rates increasing from 10 to 100  $\text{mV s}^{-1}$ .



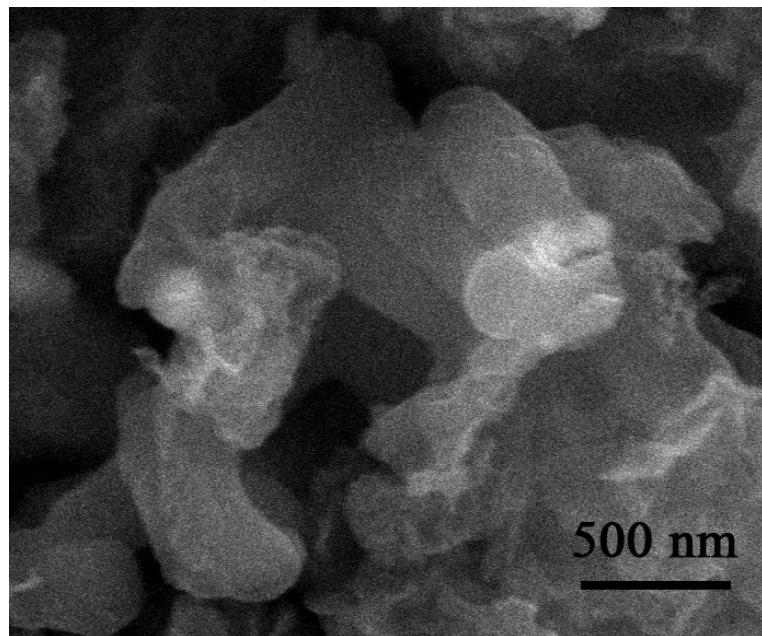
**Fig. S11** Current density differenced at 1.35 V vs. RHE as a function of scan rates.



**Fig. S12** CV curves of  $\text{Co}_2\text{P}-\text{Co}_3\text{O}_4/\text{rGO/C}$  and Pt/C in  $0.1 \text{ mol L}^{-1}$  KOH containing  $0.1 \text{ mol L}^{-1}$  methanol at a scan rate of  $50 \text{ mV s}^{-1}$ .



**Fig. S13** XRD pattern of the as-synthesized  $\text{NiP}_x/\text{NiO}_x/\text{rGO}/\text{C}$  using *Lactobacillus bulgaricus* as template and phosphorous source.



**Fig. S14** SEM image of the as-synthesized  $\text{NiP}_x/\text{NiO}_x/\text{rGO}/\text{C}$  using *Lactobacillus bulgaricus* as template and phosphorous source.

**Table S1** Simulated parameters of Nyquist plots for the ORR on Co<sub>2</sub>P-Co<sub>3</sub>O<sub>4</sub>/C and Co<sub>2</sub>P-Co<sub>3</sub>O<sub>4</sub>/rGO/C.

Samples	R <sub>s</sub> <sup>a</sup> [Ω cm <sup>-2</sup> ]	CPE1 <sup>d</sup> [Ω cm <sup>-2</sup> ]	n <sub>1</sub>	R <sub>C</sub> <sup>b</sup> [Ω cm <sup>-2</sup> ]	CPE2 <sup>e</sup> [Ω cm <sup>-2</sup> ]	n <sub>2</sub>	R <sub>t</sub> <sup>c</sup> [Ω cm <sup>-2</sup> ]
Co <sub>2</sub> P-Co <sub>3</sub> O <sub>4</sub> /C	6.83	0.021	0.47	41.16	0.004	0.87	202.6
Co <sub>2</sub> P-Co <sub>3</sub> O <sub>4</sub> /rGO/C	6.66	0.145	0.40	2.36	0.007	0.92	45.18

<sup>a</sup>electrolyte resistance;

<sup>b</sup>catalyst film intrinsic resistance;

<sup>c</sup>charge transfer resistance for ORR;

<sup>d,e</sup>constant phase element.

**Table S2** Performance comparison of recent works on cobalt phosphide based ORR catalysts.

Samples	Catalyst loading [mg cm <sup>-2</sup> ]	E <sub>onset</sub> [V]	E <sub>1/2</sub> [V]	Tafel slope [mV dec <sup>-1</sup> ]	J <sub>L</sub> [mA cm <sup>-2</sup> ]	Ref.
Co <sub>2</sub> P@CNF	0.20	0.92	0.80	77.10	5.27	1
Co <sub>2</sub> P/NPC	N/A	N/A	0.82	69.8	N/A	2
Co <sub>2</sub> P NRs	N/A	N/A	0.77	N/A	4.60	3
Co <sub>2</sub> P@CoNPG	0.20	0.90	0.81	69.0	6.68	4
HCNT-Co <sub>2</sub> P	N/A	0.84	0.77	N/A	N/A	5
BNC/Co <sub>2</sub> P	0.21	0.92	0.82	N/A	N/A	6
Co <sub>x</sub> P-CNTs	N/A	0.84	0.76	N/A	N/A	7
Urchin-like CoP	0.28	0.80	0.70	51.0	4.50	8
Co/CoP-HNC	0.19	0.94	0.83	59.4	N/A	9
CoP NCs	0.20	0.92	0.86	72.1	4.64	10
Co <sub>2</sub> P-Co <sub>3</sub> O <sub>4</sub> /rGO/C -800	0.20	0.91	0.80	58.2	4.96	This work

## References

1. J. Gao, J. Wang, L. Zhou, X. Cai, D. Zhan, M. Hou, L. Lai, *ACS Appl. Mater. Interfaces*, 2019, **11**, 10364-10372.
2. Y. Yu, J. Ma, C. Chen, Y. Fu, Y. Wang, K. Li, Y. Liao, L. Zheng, X. Zuo, *ChemCatChem*, 2019, **11**, 1722-1731.
3. V.V.T. Doan-Nguyen, S. Zhang, E.B. Trigg, R. Agarwal, J. Li, D. Su, K.I. Winey, C.B.

Murray, *ACS Nano*, 2015, **9**, 8108-8115.

4. H. Jiang, C. Li, H. Shen, Y. Liu, W. Li, J. Li, *Electrochim. Acta*, 2017, **231**, 344-353.
5. K. Chen, X. Huang, C. Wan, H. Liu, *RSC Adv.*, 2015, **5**, 92893-92898.
6. C. Han, X. Bo, Y. Zhang, M. Li, A. Wang, L. Guo, *Chem. Commun.*, 2015, **51**, 15015-15018.
7. K. Chen, X. Huang, C. Wan, H. Liu, *Chem. Commun.*, 2015, **51**, 7891-7894.
8. H. Yang, Y. Zhang, F. Hu, Q. Wang, *Nano Lett.*, 2015, **15**, 7616-7620.
9. Y. Hao, Y. Xu, W. Liu, X. Sun, *Mater. Horiz.*, 2018, **5**, 108-115.
10. H. Li, Q. Li, P. Wen, T. B. Williams, S. Adhikari, C. Dun, C. Lu, D. Itanze, L. Jiang, D. L. Carroll, G. L. Donati, P. M. Lundin, Y. Qiu, S. M. Geyer, *Adv. Mater.*, 2018, **30**, 1705796.