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Significantly boosted oxygen electrocatalysis with cooperation between cobalt and iron porphyrins†

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Developing electrocatalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) is of great importance. Herein, Co tetrakis(pentafluorophenyl)porphyrin (Co-P) and Fe chloride tetrakis(pentafluorophenyl)porphyrin (Fe-P) were loaded on carbon nanotubes (CNTs) for combining the electrocatalytic advantages of both Co-P and Fe-P. The resultant (Co-P)_{0.5}(Fe-P)_{0.5}@CNT composite displayed significantly boosted activity for the selective four-electron ORR with a half-wave potential of 0.80 V *versus* reversible hydrogen electrode (RHE) and for the OER with a potential of 1.65 V *versus* RHE to obtain 10 mA cm⁻² current density in 0.1 M KOH. A Zn-air battery assembled from $(Co-P)_{0.5}(Fe-P)_{0.5}$ @CNT exhibited a small charge-discharge voltage gap of 0.74 V at 2 mA cm⁻², a high power density of 174.5 mW cm⁻² and a good rechargeable stability (>120 cycles).

Globally increasing energy demands and environmental concerns have prompted extensive and intensive research studies on clean energy conversion and storage systems.^{1–4} The electrocatalytic ORR and OER play important roles in energy conversion and storage devices.^{5–10} In particular, the ORR is a key process involved in fuel cells and/or metal–air batteries.^{11–16} Pt/C, as the most active four-electron ORR catalyst, is usually used in fuel cells.¹⁷ However, the high cost and low natural abundance of Pt, and also the deactivation and thus the unsatisfied stability of Pt/C in an electrocatalytic process have forced researchers to find highly efficient and robust ORR electrocatalysts made from Earth-abundant transition metal elements.^{18–29}

In the past decade, extensive efforts have been made to make ORR electrocatalysts from transition metal macrocyclic complexes, such as porphyrins,^{21,23,27,30-33} phthalocyanines,^{34–39} and corroles.^{19,20,22,40–43} Among these

complexes, metal porphyrins have attracted increasing interest as ORR catalysts. As inspired by cytochrome *c* oxidases (*Cc*Os), which have heme active sites for the selective 4e ORR, a variety of Fe and Co porphyrins have been synthesized and studied as catalysts for the ORR.^{21,31–33,44–49} In general, Fe porphyrins usually show high selectivity for the 4e ORR although they require high overpotentials to achieve considerable activities. On the other hand, Co porphyrins typically catalyze the 2e ORR with much higher activities at relatively much smaller overpotentials.^{32,40} Theoretical calculations indicated that the poor 4e ORR activity of Co porphyrins was due to the difficulty in transferring its 3d electrons to the π^* orbital of the O₂ adducts to weaken the O–O bond.⁵⁰

In order to achieve the electrocatalytic ORR with high activity and selectivity, we herein report a simple strategy by combining the advantages of both Fe and Co porphyrins. Fe and Co complexes of tetrakis(pentafluorophenyl)porphyrin (denoted as Fe-P and Co-P, respectively) were loaded on CNTs through simple adsorption to form $(Co-P)_x(Fe-P)_y$ (CNT (x + y)= 1) hybrids. The strong electron-withdrawing pentafluorophenyl substituents will make porphyrins easier to be reduced, which will usually decrease the overpotentials for catalytic reduction reactions. We show that (Co-P)0.5(Fe-P)0.5@CNTs display high activity and selectivity for the 4e ORR, which is a result of having both Co-P and Fe-P on CNTs. As a practical demonstration, a Zn-air battery assembled using (Co-P)0.5(Fe-P)0.5@CNT showed a comparable performance to that with Pt/ C. This work provides a simple strategy to significantly boost the ORR activity and selectivity by combining two metal porphyrins, which is valuable to be extended to other catalyst systems.

The reaction of tetrakis(pentafluorophenyl)porphyrin with Co and Fe salts in dimethylformamide afforded **Co-P** and **Fe-P**, respectively.⁵¹ High quality crystals of **Co-P** (Fig. S2†) and **Fe-P** (Fig. S3†) were obtained, and their structures were characterized by the single crystal X-ray diffraction method. The purity of the bulk samples of **Co-P** and **Fe-P** was confirmed by high-resolution mass spectrometry (HRMS, Fig. S4 and S5,† respectively) and UV-vis spectroscopy (Fig. S6†).

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Fig. 1 (a) SEM image of unmodified CNTs. (b) SEM image, (c) HAADF-STEM image, and (d-f) the corresponding elemental mapping images of $(Co-P)_{0.5}(Fe-P)_{0.5}$ @CNT.

After loading Co-P and Fe-P on CNTs through physical adsorption (Fig. 1a and b), the resultant hybrids were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which showed the absence of aggregated particles of metal porphyrins. The high-angle annular dark-field transmission electron microscopy (HAADF-STEM) image of (Co-P)0.5(Fe-P)0.5(CNTs (Fig. 1c) and the corresponding energy dispersive X-ray (EDX) elemental mapping images of N (Fig. 1d), Fe (Fig. 1e) and Co (Fig. 1f) clearly confirmed the adsorption and uniform distribution of metal porphyrins on the surfaces of CNTs. The EDX analysis indicated a Co/Fe elemental ratio close to 1:1 in the (Co-P)0.5(Fe- $P_{0.5}$ (Fig. S7[†]). This ratio was also confirmed by inductively coupled plasma mass spectrometry (ICP-MS, Table S1⁺). In addition, the X-ray photoelectron spectroscopy (XPS) analysis of $(Co-P)_{0.5}(Fe-P)_{0.5}$ @CNT showed signals attributed to N 1s (398.7 eV), Co 2p (796.8 and 780.6 eV) and Fe 2p (724.2 and 710.8 eV), further confirming the presence of Co-P and Fe-P on CNTs (Fig. S8[†]).

Electrocatalytic ORR studies were carried out in 0.1 M KOH solution. As shown in Fig. 2a, the cyclic voltammograms (CVs) of Co-P@CNT and Fe-P@CNT showed catalytic ORR currents with peak potentials at 0.71 and 0.64 V versus RHE (all potentials reported in this work are with reference to RHE unless otherwise noted), respectively. Notably, the CV of (Co-P)_{0.5}(Fe-P)_{0.5}@CNT showed a catalytic ORR wave with a peak potential of 0.70 V, which was almost identical to the activity of Co-P@CNT. Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) measurements were then carried out in O2saturated 0.1 M KOH aqueous solution. As shown in Fig. 2b, the linear sweep voltammetry (LSV) of (Co-P)_{0.5}(Fe-P)_{0.5}@CNT displayed an ORR wave with the half-wave potential $E_{1/2} = 0.80$ V, which is very close to that of Co-P@CNT (0.81 V) and is anodically shifted as compared to unmodified CNTs (0.70 V) and Fe-P@CNT (0.73 V). Being used as a reference, commercial Pt/ C (20 wt%) displayed ORR activity with a half-wave potential of



Fig. 2 (a) CVs, (b) RDE polarization data (at a rotation rate of 1600 rpm) and (c) Tafel slopes of CNTs, **Co**-P@CNT, **Fe**-P@CNT, **(Co**-P)_{0.5}(**Fe**-P)_{0.5}@CNT and 20% Pt/C in 0.1 M KOH solution. RDE polarization data of **Co**-P@CNT (d), **Fe**-P@CNT (e), and **(Co**-P)_{0.5}(**Fe**-P)_{0.5}@CNT (f) at different rotation rates. Inset: K-L plot of j^{-1} versus ω^{-1} .

0.86 V. The Tafel slope of $(Co-P)_{0.5}(Fe-P)_{0.5}$ @CNT (70.1 mV per decade) is smaller than that of Co-P@CNT (83.6 mV per decade) and Fe-P@CNT (98.2 mV per decade), indicating good kinetics during the ORR (Fig. 2c). In RDE measurements, the *n* value was calculated from the K-L analysis, giving *n* = 3.33 for Co-P@CNT, 3.98 for Fe-P@CNT, and 3.95 for $(Co-P)_{0.5}(Fe-P)_{0.5}$ @CNT (Fig. 2d-f).

In addition, the *n* value was also evaluated by using RRDE measurements. In RRDE, the H₂O₂ yielded during the catalytic ORR was calculated to be 73.2% for CNTs, 36.5% for Co-P@CNT, 5.9% for Fe-P@CNT, 5.1% for (Co-P)0.5(Fe- $P_{0.5}$ (CNT, and 0.5% for Pt/C (Fig. 3a). Based on these results, the average *n* values were evaluated, giving n = 2.54 for CNTs, *n* = 3.27 for Co-P(a)CNT, n = 3.88 for Fe-P(a)CNT, n = 3.89 for $(Co-P)_{0.5}(Fe-P)_{0.5}$ (Contraction (Co-P)_{0.5} (Fe-P)_{0.5} results were consistent with those obtained from the K-L analysis. Furthermore, we changed the ratio of Co-P and Fe-P loaded on CNTs to make (Co-P)0.3(Fe-P)0.7@CNT and (Co- $P_{0.7}(Fe-P)_{0.3}$ (CNT. Under the same conditions, these two composites displayed relatively poorer ORR activity and 4e selectivity than (Co-P)_{0.5}(Fe-P)_{0.5}@CNT (Fig. S9-11[†]). By comparing with Co porphyrin and Fe porphyrin alone when loaded on carbon substrates, $(Co-P)_{0.5}$ (Fe-P)_{0.5} (CNT shows the best ORR performance (Table S2[†]). The durability tests are shown in Fig. 3c. After 10 h of controlled potential electrolysis, the



Fig. 3 (a) RRDE measurements and (b) *n* values for CNTs, Co-P@CNT, Fe-P@CNT, (Co-P)_{0.5}(Fe-P)_{0.5}@CNT and 20% Pt/C measured in O₂-saturated 0.1 M KOH solution at 1600 rpm with RRDE. (c) Controlled potential electrolysis of GC electrodes coated with (Co-P)_{0.5}(Fe-P)_{0.5}@CNT and Pt/C. (d) LSVs of (Co-P)_{0.5}(Fe-P)_{0.5}@CNT tested in O₂-saturated 0.1 M KOH electrolyte at 1600 rpm with a scan rate of 5 mV s⁻¹.

electrocatalytic ORR currents with Pt/C and $(Co-P)_{0.5}$ (Fe-P)_{0.5}@CNT decreased by 17% and 6%, respectively.

Moreover, the hybrid $(Co-P)_{0.5}(Fe-P)_{0.5}$ (CONT was also active for the electrocatalytic OER by reaching 10 mA cm⁻² current density at an overpotential of 420 mV in 0.1 M KOH (Fig. 3d). As a practical demonstration, this bifunctional electrocatalyst was used to assemble a rechargeable Zn-air battery (Fig. 4a). As shown in Fig. 4b, the battery with $(Co-P)_{0.5}(Fe P_{0.5}$ (a) CNT displayed a higher discharge current than that with Pt/C. The peak power density of the battery with (Co-P)_{0.5}(Fe- $P_{0.5}$ (CNT is 174.5 mW cm⁻², which is larger than that with Pt/C (75.8 mW cm⁻²). The specific capacity was tested at a discharge current density of 20 mA cm⁻² and was normalized to the mass of Zn (Fig. 4c). The specific capacity of the battery with $(Co-P)_{0.5}(Fe-P)_{0.5}$ (CNT was found to be 752.2 mA h g⁻¹, which is higher than that with Pt/C (720.5 mA h g^{-1}). As shown in Fig. 4d, the open circuit voltage is 1.49 V for (Co- $P_{0.5}(Fe-P)_{0.5}$ (BCNT, whereas it is 1.45 V for Pt/C. Moreover, the battery with $(Co-P)_{0.5}(Fe-P)_{0.5}$ (CNT exhibited good cyclic stability and its initial voltage gap during charging-discharging was 0.74 V, which is smaller than that with Pt/C (0.98 V), (Co-P)_{0.3}(Fe-P)_{0.7}@CNT (0.80 V), and (Co-P)_{0.7}(Fe-P)_{0.3}@CNT (0.82 V) at 2 mA cm⁻² (Fig. 4e and S12[†]). The durability is shown in Fig. 4f, indicating that the Zn-air battery with (Co- $P_{0.5}(Fe-P)_{0.5}$ @CNT displayed a stable performance over 40 h.

In conclusion, we reported the electrocatalytic ORR features of a hybrid with both **Co-P** and **Fe-P** loaded on CNTs. The resultant (**Co-P**)_{0.5}(**Fe-P**)_{0.5}@CNT displayed high 4e ORR activity and selectivity with a half-wave potential of 0.80 V, which is superior to **Co-P** and **Fe-P** alone when loaded on CNTs. It is suggested that O₂ may be first reduced at the **Co-P**



Fig. 4 (a) Diagram of the Zn-air battery. (b) Charge and discharge polarization data, (c) discharge data at 20 mA cm⁻², (d) open circuit plots, (e) galvanostatic discharge-charge cycle data at 2 mA cm⁻² of $(Co-P)_{0.5}(Fe-P)_{0.5}@CNT$ and 20% Pt/C. (f) The long-time cycling of a rechargeable Zn-air battery using $(Co-P)_{0.5}(Fe-P)_{0.5}@CNT$ at 2 mA cm⁻².

sites and the generated partially reduced O_2 species can be further reduced at the **Fe–P** sites, achieving both high activity and selectivity for the 4e ORR. This work provides a new strategy by combining different molecular catalysts to achieve cascade reactions, which is valuable to be explored in other electrocatalytic processes.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 D. K. Dogutan and D. G. Nocera, Acc. Chem. Res., 2019, 52, 3143-3148.
- 2 X. Fang, S. Kalathil and E. Reisner, *Chem. Soc. Rev.*, 2020, **49**, 4926–4952.
- 3 J. Pan, C. Chen, L. Zhuang and J. Lu, *Acc. Chem. Res.*, 2012, **45**, 473-481.
- 4 B. Zhang and L. Sun, Chem. Soc. Rev., 2019, 48, 2216–2264.
- 5 W. Zhang, W. Lai and R. Cao, *Chem. Rev.*, 2017, **117**, 3717–3797.
- 6 H. Lei, X. Li, J. Meng, H. Zheng, W. Zhang and R. Cao, ACS Catal., 2019, 9, 4320–4344.
- 7 M. L. Pegis, C. F. Wise, D. J. Martin and J. M. Mayer, *Chem. Rev.*, 2018, **118**, 2340–2391.
- 8 Q. Zhao, Z. Yan, C. Chen and J. Chen, *Chem. Rev.*, 2017, 117, 10121–10211.
- 9 Y. Liu, Y. Han, Z. Zhang, W. Zhang, W. Lai, Y. Wang and R. Cao, *Chem. Sci.*, 2019, 10, 2613–2622.
- 10 L. Xu, H. T. Lei, Z. Y. Zhang, Z. Yao, J. F. Li, Z. Y. Yu and R. Cao, *Phys. Chem. Chem. Phys.*, 2017, **19**, 9755–9761.
- 11 L. An, B. Huang, Y. Zhang, R. Wang, N. Zhang, T. Dai, P. Xi and C. H. Yan, *Angew. Chem., Int. Ed.*, 2019, **58**, 9459–9463.
- 12 Z. Lu, W. Xu, J. Ma, Y. Li, X. Sun and L. Jiang, Adv. Mater., 2016, 28, 7155–7161.
- 13 L. Jiao, G. Wan, R. Zhang, H. Zhou, S. H. Yu and H. L. Jiang, Angew. Chem., Int. Ed., 2018, 57, 8525– 8529.
- 14 X. Jia, C. Liu, Z. G. Neale, J. Yang and G. Cao, *Chem. Rev.*, 2020, **120**, 7795–7866.
- 15 B.-Q. Li, S.-Y. Zhang, B. Wang, Z.-J. Xia, C. Tang and Q. Zhang, *Energy Environ. Sci.*, 2018, **11**, 1723–1729.
- 16 W. Yang, X. Liu, X. Yue, J. Jia and S. Guo, J. Am. Chem. Soc., 2015, 137, 1436–1439.
- 17 Y. Nie, L. Li and Z. Wei, *Chem. Soc. Rev.*, 2015, 44, 2168–2201.
- 18 C. Zhu and S. Dong, Nanoscale, 2013, 5, 1753-1767.
- 19 L. Xie, X. Li, B. Wang, J. Meng, H. Lei, W. Zhang and R. Cao, Angew. Chem., Int. Ed., 2019, 58, 18883– 18887.
- 20 J. Meng, H. Lei, X. Li, W. Zhang and R. Cao, J. Phys. Chem. C, 2020, 124, 16324–16331.
- 21 Y. Liu, G. Zhou, Z. Zhang, H. Lei, Z. Yao, J. Li, J. Lin and R. Cao, *Chem. Sci.*, 2020, **11**, 87–96.
- 22 J. Meng, H. Lei, X. Li, J. Qi, W. Zhang and R. Cao, ACS Catal., 2019, 9, 4551-4560.
- 23 C. Zhang, H. Yang, D. Zhong, Y. Xu, Y. Wang, Q. Yuan,
 Z. Liang, B. Wang, W. Zhang, H. Zheng, T. Cheng and
 R. Cao, *J. Mater. Chem. A*, 2020, 8, 9536–9544.
- 24 Y.-H. Wang, B. Mondal and S. S. Stahl, *ACS Catal.*, 2020, **10**, 12031–12039.
- 25 C. W. Machan, ACS Catal., 2020, **10**, 2640–2655.
- 26 Y. M. Zhao, G. Q. Yu, F. F. Wang, P. J. Wei and J. G. Liu, Chem. - Eur. J., 2019, 25, 3726-3739.
- 27 G. Passard, D. K. Dogutan, M. Qiu, C. Costentin and D. G. Nocera, ACS Catal., 2018, 8, 8671–8679.

- 28 L. Li, X. Feng, Y. Nie, S. Chen, F. Shi, K. Xiong, W. Ding, X. Qi, J. Hu, Z. Wei, L.-J. Wan and M. Xia, ACS Catal., 2015, 5, 4825–4832.
- 29 R. Zhang, L. Wang, Y.-H. Ma, L. Pan, R. Gao, K. Li, X. Zhang and J.-J. Zou, *J. Mater. Chem. A*, 2019, 7, 10010– 10018.
- 30 Q. Lin, X. Bu, A. Kong, C. Mao, F. Bu and P. Feng, Adv. Mater., 2015, 27, 3431–3436.
- 31 H. Tang, H. Yin, J. Wang, N. Yang, D. Wang and Z. Tang, Angew. Chem., Int. Ed., 2013, 52, 5585–5589.
- 32 R. Zhang and J. J. Warren, *J. Am. Chem. Soc.*, 2020, **142**, 13426–13434.
- 33 Y. Zhou, Y.-F. Xing, J. Wen, H.-B. Ma, F.-B. Wang and X.-H. Xia, Sci. Bull., 2019, 64, 1158–1166.
- 34 Z. Zhang, J. Sun, F. Wang and L. Dai, Angew. Chem., Int. Ed., 2018, 57, 9038–9043.
- 35 Y. Jiang, Y. Lu, X. Lv, D. Han, Q. Zhang, L. Niu and W. Chen, ACS Catal., 2013, 3, 1263–1271.
- 36 K. Chen, K. Liu, P. An, H. Li, Y. Lin, J. Hu, C. Jia, J. Fu, H. Li, H. Liu, Z. Lin, W. Li, J. Li, Y. R. Lu, T. S. Chan, N. Zhang and M. Liu, *Nat. Commun.*, 2020, **11**, 4173.
- 37 Z. Li, Z. Zhuang, F. Lv, H. Zhu, L. Zhou, M. Luo, J. Zhu,
 Z. Lang, S. Feng, W. Chen, L. Mai and S. Guo, *Adv. Mater.*,
 2018, 30, e1803220.
- 38 W. Liu, K. Wang, C. Wang, W. Liu, H. Pan, Y. Xiang, D. Qi and J. Jiang, *J. Mater. Chem. A*, 2018, 6, 22851–22857.
- 39 R. Cao, R. Thapa, H. Kim, X. Xu, M. G. Kim, Q. Li, N. Park, M. Liu and J. Cho, *Nat. Commun.*, 2013, 4, 2076.
- 40 S. Liu, K. Mase, C. Bougher, S. D. Hicks, M. M. Abu-Omar and S. Fukuzumi, *Inorg. Chem.*, 2014, **53**, 7780–7788.
- 41 J. Tang, Z. Ou, R. Guo, Y. Fang, D. Huang, J. Zhang, J. Zhang, S. Guo, F. M. McFarland and K. M. Kadish, *Inorg. Chem.*, 2017, **56**, 8954–8963.
- 42 A. Friedman, L. Landau, S. Gonen, Z. Gross and L. Elbaz, *ACS Catal.*, 2018, **8**, 5024–5031.
- 43 A. Mahammed and Z. Gross, *Isr. J. Chem.*, 2016, **56**, 756–762.
- J. P. Collman, N. K. Devaraj, R. A. Decreau, Y. Yang,
 Y. L. Yan, W. Ebina, T. A. Eberspacher and C. E. Chidsey, *Science*, 2007, 315, 1565–1568.
- 45 A. Hosseini, C. J. Barile, A. Devadoss, T. A. Eberspacher, R. A. Decreau and J. P. Collman, *J. Am. Chem. Soc.*, 2011, 133, 11100–11102.
- 46 M. L. Rigsby, D. J. Wasylenko, M. L. Pegis and J. M. Mayer, J. Am. Chem. Soc., 2015, 137, 4296–4299.
- 47 C. T. Carver, B. D. Matson and J. M. Mayer, *J. Am. Chem. Soc.*, 2012, **134**, 5444–5447.
- 48 S. Samanta, P. K. Das, S. Chatterjee, K. Sengupta,
 B. Mondal and A. Dey, *Inorg. Chem.*, 2013, 52, 12963– 12971.
- 49 S. Bhunia, A. Rana, P. Roy, D. J. Martin, M. L. Pegis, B. Roy and A. Dey, *J. Am. Chem. Soc.*, 2018, **140**, 9444–9457.
- 50 S. Sun, N. Jiang and D. Xia, *J. Phys. Chem. C*, 2011, **115**, 9511–9517.
- 51 H. Lei, Y. Wang, Q. Zhang and R. Cao, J. Porphyrins Phthalocyanines, 2020, 24, 1361–1371.