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Confined Bimetallic Phosphide within P, N Co-doped Carbon Layers

towards Boosted Bifunctional Oxygen Catalysis

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Fig. S1 XRD patterns of control samples CMP@PC, MP@PNC and CP@PNC.



Fig. S2 (a) TEM image and (b) magnified TEM image of CMP@PNC.



Fig. S3 HRTEM image of CMP@PNC.



Fig. S4 (a) SEM image and (b) magnified SEM image of CMP@PNC.



Fig. S5 SEM images of (a) CMP@PC, (b) PNC, (c) CP@PNC, (d) MP@PNC.



Fig. S6 TEM images of (a) CMP@PC, (b) PNC, (c) CP@PNC, (d) MP@PNC.



Fig. S7 EDX spectrum coupled with TEM for CMP@PNC.



Fig. S8 EDX spectrum coupled with SEM for CP@PNC.



Fig. S9 EDX spectrum coupled with SEM for MP@PNC.

It can be identified from the EDX spectrum that Mn, Co, P, C, N, O coexisted in CMP@PNC (Fig. S7, signal of Cu came from the test substrate), and the content of C dominated in this hybrid. The EDX spectra of control samples show that Mn, P, N, C, O coexisted in MP@PNC (Fig. S9) and Co, P, C, N, O coexisted in CP@PNC (Fig. S8), signals of Pt and Si came from the test substrates.



Fig. S10 XPS fitting spectrum of C 1s of CMP@PNC.



Fig. S11 Raman spectra of rGO and P, N co-doped carbon.

the Raman spectra of PNC and initial carbon template GO show two splitted D-band (1337 cm⁻¹) and G-band (1579 cm⁻¹), the increased intensity ratio (I_D/I_G) of D- and G-band of PNC (0.99) indicates more defects than that of GO (0.91).^{1,2}



Fig. S12 XPS fitting spectrum of N 1s of CMP@PNC



Fig. S13 XPS spectrums of MP@PNC. (a) survey spectrum; (b) spectrum of Co 2p; (c) spectrum of P 2p; (d) spectrum of N 1s; (e) spctrum of C 1s; (f) spectrum of O 1s.

It can be seen that Mn, P, C, N, O existed in MP@PNC (Fig. S13a), which is in line with the EDX spectrum result of MP@PNC (Fig. S9). Combining with XRD pattern, TEM and SEM images (Fig. S1, S5d, S6d), we suggest the existence of amorphous Mn based phosphides in MP@PNC. Mn 2p, P 2p, N 1s and C 1s XPS lines (Fig. S13b-d) show similar shapes with CMP@PNC, with a decrease intensity of P 2p_{3/2} and P 2p_{1/2} peaks (probably due to its undetectable low crystallinity signal).³



Fig. S14 XPS spectra of CP@PNC. (a) survey spectrum; (b) spectrum of Co 2p; (c) spectrum of P 2p; (d) spectrum of N 1s; (e) spctrum of C 1s; (f) spectrum of O 1s.
The coexistence of Co, P, C, N, O in CP@PNC is proved by XPS survey spectrum (Fig. S14a), agreeing with EDX spectrum of CP@PNC (Fig. S8). The Co 2p, N 1s, C 1s curves show similar sharps with CMP@PNC (Fig. S14b, d, e), and P 1s has obvious P 2p_{3/2} and P 2p_{1/2} peaks. Combining with the XRD pattern (Fig. S1), TEM and SEM images (Fig. S5c, S6c), the existence of CoP nanoparticles in CP@PNC can be strongly confirmed.



Fig S15 Co K-edge (a) XANES and (c) EXAFS oscillation functions, Mn K-edge (b) XANES and (d) EXAFS oscillation functions.



Fig. S16 Thermogravimetric analysis curves of the initial CMP@PNC and acid-leached

CMP@PNC.



Fig. S17 TEM images of the acid-leached CMP@PNC.

To confirm the accessibly defective carbon of CMP@PNC, thermogravimetric analyses were recorded on the initial CMP@PNC and acid-leached CMP@PNC (stirred with 1 M HNO₃ solution under 50 °C for 7 h), as shown in Fig. S16. Before 400 °C, the mass loss is attributed to the removal of water and hydroxy groups probably adsorbed on the surface of the composite. The continuous mass loss from 400 °C to 800 °C is caused by the burning of carbon and oxidation of phosphide to oxides.⁴ Therefore, the content of Co/Mn based compositions are about 50 wt% and 9 wt%, respectively in CMP@PNC and acid-leached CMP@PNC hybrid. This result suggests that HNO₃ solution has dissolved most of metal compounds, further provide the existence of accessible defects in carbon. TEM images of the acid-leached CMP@PNC clearly show the absence of CoMnP₄ nanoparticles (Fig. S17), a number of pore can also be observed. Based on the above analyses, we can conclude that the carbon of CMP@PNC are accessibly defective, which can provide fully contact between CoMnP₄, P, N co-doped carbon and electrolyte.



Fig. S18 (a) CV curves of CMP@PNC, CMP@PC, PNC, 20 wt% Pt/C and (b) CP@PNC, MP@PNC in O_2 -saturated 0.1 M KOH measured with a scan rate of 5 mV s⁻¹.



Fig. S19 LSV curves of CP@PNC and MP@PNC in O2-saturated 0.1 M KOH with a rate

of 5 mV s⁻¹.



Fig. S20 LSV curves of (a) CMP@PC, (b) PNC, (c) CP@PNC, (d) MP@PNC measured at different rotation speeds in O_2 -saturated 0.1 M KOH with a scan rate of 5 mV s⁻¹.



Fig. S21 K-L plots of CMP@PNC, CMP@PC, PNC, CP@PNC, MP@PNC, 20 wt% Pt/C. (inset: the kinetic-limited current densities of CP@PNC and MP@PNC at 0.5 V (vs.

RHE)).



Fig. S22 RRDE polarization curves of CMP@PNC and 20 wt% Pt/C at the rotating rate

of 1600 rpm.



Fig. S23 RRDE polarization curves of CMP@PNC and CMP@PC, PNC, CP@PNC,

MP@PNC measured at the rotating rate of 1600 rpm.



Fig. S24 Tafel plots of CP@PNC and MP@PNC calculated from LSV curves.



Fig. S25 I-t curves of CMP@PNC and 20 wt% Pt/C at 0.65 V (vs. RHE).



Fig. S26 TEM images of CMP@PNC a) before and b) after cycles.



Fig. S27 TEM images of CMP@PC a) before and b) after cycles.



Fig. S28 ORR methanol crossover tolerance test of CMP@PNC and 20 wt% Pt/C at

0.65 V vs. RHE.



Fig. S29 LSV curves of CP@PNC, MP@PNC in N₂-saturated 0.1 M KOH measured with

a scan rate of 5 mV s⁻¹.



Fig. S30 Tafel plots of CP@PNC and MP@PNC calculated from LSV curves.



Fig. S31 (a-e) Cyclic voltammetry curves of different samples with different scan rates at the potential range from 1.10 to 1.30 V vs. RHE upon OER catalysis for the determination of the double layer capacitance. (f) The corresponding capacitive current densities at 1.20 V vs. RHE plotted as a function of scan rates and the calculated double layer capacitances.



Fig. S32 The polarization curves of CMP@PNC and control samples before (a) and

after (b) ECSA correction.



Fig. S33 The LSV polarization curves for CMP@PNC before and after 7000 cycles.



Fig. S34 I-t curves of CMP@PNC at 1.55 V (vs. RHE).



Fig. S35 XPS spectrum comparisons of (a) Co 2p before and after OER, (b) Mn 2p before and after OER.

It can be observed that an obvious peak shift and the disappear of satellite peak (Fig. S35a), suggesting the increased oxidation state from Co^{2+} to $Co^{3+}.^{5,6}$ The obvious peak shift from 641.3 eV to 643.0 eV (Fig. S35b) suggested the oxidation from Mn^{3+} to $Mn^{4+}.^{7,8}$ And there a negligible signal of phosphides in P 2p spectrum (Fig. S35c) after OER, indicating the phosphides have changed. The above results indicate the transformation of $CoMnP_4$ to corresponding oxyhydroxides during OER process.⁹



Fig. S36 ORR and OER performcances examined in 0.1 M KOH solution. (a) ORR polarization curves of initial CMP@PNC and acid leached CMP@PNC; (b) OER polarization curves of initial CMP@PNC and acid leached CMP@PNC; (c) (d) Tafel slopes of each catalyst calculated form ORR and OER polarization, respectively; (e) LSV polarization curves showing the bifunctional ORR/OER activities of initial CMP@PNC and acid leached CMP@PNC.



Fig. S37 LSV curves showing the bifunctional ORR/OER activities of CP@PNC and MP@PNC.

Catalyst	E _{OER} (V) ^a	E _{ORR} (V) ^b	ΔΕ (V) ^c	Ref.
	10 mA cm ⁻²	-3 mA cm ⁻²	(E _{OER-} E _{ORR)}	
NGM-Co	1.700	0.750	0.950	10
N-Co ₉ S ₈ /G	1.640	0.760	0.880	11
Co@Co ₃ O ₄ /NC-1	1.650	0.800	0.850	12
NiCo ₂ S ₄ /N-CNT	1.600	0.800	0.800	13
CoO _{0.87} S _{0.13} /GN	1.590	0.830	0.760	4
NiFe-LDH/Co,N-CNF	1.645	0.893	0.752	14
S,N-Fe/N/C-CNT	1.600	0.850	0.750	15
CMP@PNC	1.560	0.810	0.750	this work

Table S1. Comparison of bifunctional performance of CMP@PNC with differentreported elecrtocatalysts.

^(a) The potential at OER current density of 10 mA cm⁻²; ^(b) The potential at ORR current density of -3 mA cm⁻²; ^(c) Potential difference calculated between E_{OER} and

EORR.

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