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## Introduction

Developing energy conversion and storage technologies has been targeted as an essential approach to meet the increasingly urgent energy issues and sustainable utilizations.1 Electrochemical oxygen-involving reactions including the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) play a vital role in renewable energy applications, such as regenerative fuel cells, metal-air batteries and solar fuel synthesis reactions.<sup>2-4</sup> However, both the ORR and OER are thermodynamically uphill reactions and have sluggish kinetics arising from the efficiency-limiting multi-electron transfer pathways.<sup>5</sup> As reported, noble metal based catalysts (such as Pt/ C, RuO<sub>2</sub>, IrO<sub>2</sub>, etc.) are highly effective in triggering the ORR or OER, but their low natural reserves and poor stability severely hinder their practical applications.<sup>6-9</sup> Therefore, developing economical and high-efficiency non-precious metal based bifunctional catalysts has recently become a hot topic of energy research.<sup>10</sup> In this regard, various non-precious metal catalysts, including carbon materials and  $MX_{\nu}$  (M = transition metal Fe,

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# Confined bimetallic phosphide within P, N co-doped carbon layers towards boosted bifunctional oxygen catalysis<sup>†</sup>

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Rational design of bifunctional oxygen electrocatalysts with high activity and low cost is crucial but still challenging for the development of rechargeable energy storage devices. In this work, a novel bimetallic phosphide confined within P, N co-doped carbon layers is achieved through a space-confinement phosphorization strategy. Electrochemical measurements demonstrate that the obtained bimetallic phosphide nanoparticle-containing hybrid can serve as a highly efficient bifunctional oxygen reduction and evolution reaction (ORR/OER) catalyst. It delivers a small potential difference of 0.75 V in 0.1 M KOH solution along with long-term catalytic durability, superior to most of the non-precious metal catalysts reported to date. The detailed synchrotron-based spectra results combined with structural characterizations reveal that the constructed hierarchical structure endows the confined bimetallic phosphide catalyst with abundant catalytic sites and stable spatial structure, thereby achieving remarkable electrocatalytic performance. This work opens up a facile way to design effective and durable bifunctional oxygen electrocatalysts for practical applications in renewable energy production, especially in rechargeable metal-air batteries and regenerative fuel cells.

Ni, Co, and Mn; X = S, O, N, and P), have been studied.<sup>11-15</sup> Among these reported candidates, heteroatom-functionalized (*e.g.* N, S, P, Fe, Co, Mn, *etc.*) carbon nanomaterials have drawn extensive interest due to their distinctive electronic structures.<sup>16-21</sup> For example, Zhang *et al.* reported that N, P codoped carbon foam exhibited excellent ORR catalytic activity due to its defective structures and edge effects.<sup>22</sup> It has also been demonstrated that dual-doped carbon materials could exhibit better electrocatalytic activities than mono-doped ones, because of their increased spin density and optimized oxygen adsorption sites.<sup>23,24</sup>

Meanwhile, transition metal phosphides (TMPs) are gradually dedicated towards oxygen-involving electrocatalytic processes with high activity and stability.<sup>25–27</sup> For example, Li *et al.* reported that Co<sub>2</sub>P anchored to Co, N, P tri-doped graphene could display a high OER activity in 0.1 M KOH.<sup>28</sup> More recently, bimetallic phosphide-based catalysts have attracted much research attention due to their tunable compositions. Our previous work has reported a bulk amorphous NiFeP material with outstanding OER performance.<sup>29</sup> It has been testified that the coexistence of double transition metal elements could help to tune the electronic structures of catalysts for achieving enhanced OER performance.<sup>30,31</sup>

Herein, by integrating the advantages of dual-doped carbon materials and bimetallic phosphides, we rationally designed a novel hierarchical structure in which CoMnP<sub>4</sub> nanoparticles were confined within P, N co-doped defective carbon layers

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(recorded as CMP@PNC) *via* a space-confinement phosphorization strategy. It is demonstrated that the confined bimetallic phosphide based hybrid could not only achieve higher catalytic activity than most of the reported bifunctional oxygen catalysts (Table S1†), but also exhibited long-term durability due to the obstructed aggregation of CoMnP<sub>4</sub> nanoparticles during the electrochemical cycling process. This work suggests a promising way to approach highly practicable bifunctional oxygen catalysts.

### Materials and methods

#### Synthesis of CMP@PNC

Typically, graphene oxide was synthesized by a modified Hummers method.<sup>32</sup> 30 mg graphene oxide (GO) was dispersed in deionized water by sonication for 15 min, and then 0.15 mmol CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.15 mmol MnCl<sub>2</sub>·4H<sub>2</sub>O were added into the above GO solution, and the resulting solution was kept stirring for another 10 min. Subsequently, 8.67 mL propylene oxide (PO) was dropwise added into the above solution. After stirring for 22 h, the products were collected by centrifugation and freeze drying. Then, the obtained sample was re-dispersed in Tris buffer-containing KOH solution with a pH of  $\sim$ 8.5, and stirred for 5 h to get a uniform precursor solution. A certain amount of dopamine hydrochloride salt (DA) was added into the liquid precursor with stirring for 24 h, and after washing and freeze drying, dark powders were obtained. Finally, red phosphorus and the dark samples were placed in a quartz tube under a N2 atmosphere and heated at 800 °C for 3 h with a ramp rate of 5  $^{\circ}$ C min<sup>-1</sup>. GO was annealed at 800  $^{\circ}$ C for 3 h with a ramp rate of 5  $^{\circ}$ C min<sup>-1</sup> in a N<sub>2</sub> atmosphere to obtain reduced graphene oxide (rGO). The control samples were also achieved under the same abovementioned synthesis conditions, consisting of CMP@PC (no dopamine hydrochloride salt procedure), PNC (no metal salts), CP@PNG (no Mn salt) and MP@PNG (no Co salt).

#### Material characterization

Scanning electron microscopy (SEM, 15 kV, JEOL, JSM-6700F) and transmission electron microscopy (TEM, JEOL, JEM2010) coupled with energy-dispersive X-ray spectroscopy (EDX) measurements were carried out to analyze the morphology and structure. The crystal structure was characterized by X-ray Diffraction (XRD, Philips X'Pert Pro Super diffractometer equipped with Cu K $\alpha$  radiation,  $\lambda = 1.54178$  Å). Raman spectra were collected on an XploRA Raman spectrometer with 532 nm wavelength incident laser light. X-ray photoelectron spectroscopy (XPS, Mg K $\alpha$  = 1249.5 eV source) was carried out to analyze the elements' chemical states and compositions in Hefei Light Source (HLS). Co and Mn K-edge X-ray absorption structure (XAS) spectra were measured at the 14W1 beam-line in Shanghai Synchrotron Radiation Facility (SSRF). Thermogravimetric analyses (TGA, DTG-60H) were performed for the estimation of carbon contents in the obtained samples by heating the samples from room temperature to 800 °C at 5 °C min<sup>-1</sup> in an air atmosphere.

#### **Electrochemical measurements**

A CHI660E electrochemical workstation was used for all electrochemical measurements with a standard three-electrode system, which comprised Pt foil as a counter electrode, Ag/ AgCl (saturated with 3.0 M KCl) as a reference electrode, and a rotating disk electrode (RDE) as a working electrode. O<sub>2</sub>saturated 0.1 M KOH and N2-saturated 0.1 M KOH solutions served as electrolytes for the ORR and OER, respectively. To fabricate the working electrode, 2 mg catalyst was dispersed into the mixed solution containing 500 µL absolute ethanol and 15 µL Nafion solution (5 wt%) to get uniform ink by sonication. Then the ink (15  $\mu$ L) was transferred onto the polished glassycarbon electrode (GCE) and naturally dried (loading density  $\sim$  $0.30 \text{ mg cm}^{-2}$ ). The activation of the working electrode was achieved by cyclic voltammetry (CV) cycles, and the linear sweep voltammetry (LSV) curves were obtained at a scan rate of 5 mV  $s^{-1}$ . The ORR polarization curves were obtained in a potential range of -0.1-1.0 V under various rotating speeds (225-1600 rpm), while the OER polarization curves were collected at 1600 rpm from 1.0-1.7 V. The ORR and OER stability of the samples were measured by current-time (i-t) responses at 0.65 V (vs. RHE) and 1.55 V (vs. RHE) over 20 h, respectively. The ORR methanol crossover test was carried out through the i-t response at 0.65 V (vs. RHE) with 3 M methanol addition. Koutechy-Levich eqn (1)-(3) were utilized for the calculation of kinetic current density.

$$\frac{1}{J} = \frac{1}{J_{\rm L}} + \frac{1}{J_{\rm K}} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_{\rm K}}$$
(1)

$$B = 0.62nFC_0(D_0)^{2/3}v^{-1/6}$$
(2)

$$J_{\rm K} = nFkC_0 \tag{3}$$

where J,  $J_{\rm K}$ , and  $J_{\rm L}$  represent the measured current density, and the kinetic and diffusion-limited current density, respectively;  $\omega$  represents the angular velocity; F is the Faraday constant (96 485 C mol<sup>-1</sup>);  $C_0$  and  $D_0$  are the bulk concentration  $(1.2 \times 10^{-6} \text{ mol cm}^{-3})$  and diffusion coefficient of  $O_2$  in 0.1 M KOH ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), respectively;  $\nu$  is the kinematic viscosity of the electrolyte; k is the electron-transfer rate constant; n is the total electron transfer number during the ORR.

A rotating ring disk electrode (RRDE) configuration was used for detecting the electron transfer number and  $H_2O_2$  yield. The disk electrode was scanned at a rate of 5 mV s<sup>-1</sup> and the Pt-ring potential was constant at 1.5 V ( $\nu$ s. RHE). The electron transfer number (*n*) and hydrogen peroxide yield (%  $H_2O_2$ ) were calculated with eqn (4) and (5):

$$V_0 H_2 O_2 = 200 \frac{I_r/N}{I_d + I_r/N}$$
 (4)

$$n = 4 \frac{I_{\rm d}}{I_{\rm d+I_r/N}} \tag{5}$$

where  $I_d$ ,  $I_r$ , and N are the disk current, ring current, and current collection efficiency (N = 0.37), respectively. The

electrochemically active surface areas were measured by CV measurements in the non-faradaic potential range from 1.10 to 1.30 V *vs.* RHE at different scan rates (20–100 mV s<sup>-1</sup>). The double layer capacitance ( $C_{dl}$ ) was calculated by plotting the charge current density gap ( $\Delta j = j_{anodic} - j_{cathodic}$ ) at 1.20 (*vs.* RHE) against the scan rate, and the linear slope is equivalent to double the  $C_{dl}$ .

## Results and discussion

The preparation process of CMP@PNC is schematically depicted in Scheme 1. The synthesis process begins with the formation of the mixed transition metal hydroxides  $(CoMn(OH)_r)$  on graphene oxide (GO) under a weakly propylene oxide (PO)mediated alkaline environment (GO@CoMn(OH)<sub>x</sub>).<sup>33</sup> Subsequently,  $GO(OCOMn(OH)_x)$  is coated with polydopamine (PDA) layers (GO@CoMn(OH)x@PDA), followed by the phosphorization treatment at high temperature. As a result, PDA is carbonized and codoped with P and N (PNC), and GO is reduced and codoped with P from red phosphorus vapour and N from PDA decomposition; meanwhile the  $CoMn(OH)_r$  layers are completely converted into CoMnP<sub>4</sub> nanoparticles which are coated with thin PNC shells and anchored into another twodimensional (2D) PNC layers. The control samples synthesized with the lack of dopamine hydrochloride salt (CMP@PC), transition metal Co and Mn salts (PNC), transition metal Co salt (MP@PNC) or Mn salt (CP@PNC) are also obtained (see more details in the Experimental section).

The phase compositions of the as-prepared samples were first explored by X-ray diffraction (XRD) measurements (Fig. 1a). Obviously, the PNC shows a wide XRD peak (26.0°) assigned to the graphitic carbon without any other peaks.<sup>22</sup> The XRD pattern of CMP@PNC also shows a wide graphitic carbon peak, and other distinct peaks which can be assigned to CoMnP<sub>4</sub> (JCPDS no. 26-0475). In detail, these peaks occurring at 31.5°, 36.4°, 40.7°, 48.5°, and 52.0° are indexed to the crystal planes of (020), (120), (111), (220), and (211) of CoMnP<sub>4</sub>, respectively. The broad peaks imply the small size of the samples.<sup>29</sup> The control sample CMP@PC shows only two peaks (40.7° and 52.0°) corresponding to standard CoMnP<sub>4</sub> except a graphitic carbon peak. And the XRD pattern of CP@PNC coincides well with that of CoP (JCPDS no. 29-0497), while the MP@PNC has no other



Scheme 1 Illustration of the synthesis route to confined bimetallic phosphide based hybrid CMP@PNC.



**Fig. 1** (a) XRD patterns of CMP@PNC and PNC; (b) TEM image of CMP@PNC; (c) HRTEM image of CMP@PNC (inset: a magnified image of the marked area with a red circle); (d) SEM image of CMP@PNC; (e– j) the EDX-mapping images of CMP@PNC coupled with SEM.

peaks except for the graphitic carbon peak probably due to low crystallinity (Fig. S1<sup>†</sup>).<sup>34</sup>

Transmission electron microcopy (TEM) and scanning electron microscopy (SEM) measurements were carried out to analyse the morphologies and microstructures of different samples. Typical TEM images (Fig. 1b and S2<sup>†</sup>) of CMP@PNC identify that numerous nanoparticles (average diameter of  $\sim 20$ nm) were uniformly anchored into the carbon layers. High resolution TEM (HRTEM, Fig. 1c) observation shows interplanar spacings of 0.28 and 0.22 nm and an interfacial angle of 67°, which can be well indexed to the (020) and (111) crystal planes of CoMnP<sub>4</sub>. An obvious carbon shell wrapping the  $CoMnP_4$  nanoparticles can also be observed (Fig. S3<sup>†</sup>), further confirming the obtainment of CoMnP<sub>4</sub> nanoparticles wrapped by carbon shells. SEM images of CMP@PNC (Fig. 1d, S4<sup>†</sup>) reveal an integrated and uniform nanosheet architecture, demonstrating the homogeneous coating of nanosized CoMnP<sub>4</sub> nanoparticles. TEM and SEM images of the control samples were also collected (Fig. S5 and S6<sup>†</sup>). In contrast, a considerable number of particles with a large diameter throughout the nanosheets and serious aggregation can be observed for CMP@PC, while CP@PNC and MP@PNC show a similar morphology to CMP@PNC. The above results suggest that the PDA layers play a positive role in inhibiting the aggregation and growth of particles. Energy-dispersive X-ray spectroscopy coupled with SEM (SEM-EDX) mapping (Fig. 1e-j) indicates the homogeneous distribution of C, N, P, Mn, and Co in the entire CMP@PNC. This was further testified by TEM-EDX spectra (Fig. S7, for control samples see Fig. S8 and S9<sup>†</sup>).

The elemental composition and bonding configuration of the obtained samples were analyzed in detail through synchrotron-based X-ray photoelectron spectroscopy (XPS) measurements. Fig. 2a shows the XPS survey spectrum of CMP@PNC, confirming the coexistence of C, N, P, O, Co, and Mn in the entire CMP@PNC, which is in accordance with the aforementioned EDX analysis. The high resolution Co 2p XPS spectrum in Fig. 2b displays the typical  $Co^{2+}$  peaks located at 871.8 eV and 785.5 eV (satellite peak).<sup>35</sup> The Mn 2p XPS line in Fig. 2c exhibits two main peaks centered at 641.3 eV and



Fig. 2 (a) XPS survey spectrum of CMP@PNC; (b) XPS fitting lines of Co  $2p_{3/2}$  of CMP@PNC; (c) XPS fitting lines of Mn  $2p_{3/2}$  of CMP@PNC; (d) XPS fitting lines of P 2p of CMP@PNC; Fourier-transformed EXAFS spectra collected at (e) the Co K-edge and (f) the Mn K-edge.

643.0 eV, corresponding to the Mn<sup>3+</sup> and Mn<sup>4+</sup> and one attendant Mn<sup>3+</sup> satellite peak at 645.5 eV.<sup>36,37</sup> As for the P 2p XPS spectrum (Fig. 2d), the peaks at 129.8 eV and 130.8 eV can be assigned to P  $2p_{3/2}$  and P  $2p_{1/2}$  respectively, and the peak located at 132.2 eV can be assigned to the P-C bonds.28,38 Another peak identified at 134.0 eV is attributed to the P-O bonds stemming from the superficial oxidation of carbon layers in air.<sup>17,39</sup> The C 1s spectrum shows five peaks at 283.6 eV for C-P, 284.7 eV for C-C, 285.8 eV for C-N, 287.0 eV for C-O, and 290.5 eV for C=O (Fig. S10<sup>†</sup>), and the existing peaks for C-N and C-P suggest that N and P atoms have been doped into the carbon lattice effectively.40,41 The Raman spectrum of PNC verified the increased defects again (Fig. S11<sup>†</sup>). The N 1s spectrum shows three peaks at 398.6 eV, 400.5 eV, and 401.7 eV, which can be associated with pyridinic/metal-coordinated N, pyrrolic N, and graphitic N, respectively (Fig. S12<sup>†</sup>). Additional XPS spectra of MP@PNC and CP@PNC are also exhibited for comparison (Fig. S13 and S14<sup>†</sup>).

In order to further analyse the structures of the obtained samples, synchrotron-based X-ray absorption structure (XAS) spectroscopy was employed. The X-ray absorption near-edge structure (XANES) spectrum of the Co K-edge and the  $k^3\chi(k)$ oscillation curve of CMP@PNC (Fig. S14a and c†) show different shapes from those of CP@PNC, CoO and Co foil. Similarly, the Mn K-edge XANES spectrum and  $k^3\chi(k)$  oscillation curves of CMP@PNC (Fig. S15b and d†) also show significantly different shapes from those of MP@PNC, MnO<sub>2</sub> and Mn foil, implying distinct atomic arrangements. In order to realize direct observations, the Co K-edge extended X-ray absorption fine structure (EXAFS) spectra with  $k^3$ -weighted Fourier-transform of CMP@PNC and related reference samples are compared in Fig. 2e. Obviously, CMP@PNC contains Co–P and Co–Co bonds, which also appear in CP@PNC. Moreover, several weak Co–Mn bonds are observed in CMP@PNC.<sup>42</sup> In the Mn K-edge EXAFS spectra (Fig. 2f), CMP@PNC shows the same Mn–P bond as in MP@PNC, and additional Mn–Co bonds appear in the similar locations of Co–Mn bonds.<sup>43,44</sup> The existence of CoMnP<sub>4</sub> nanoparticles in this hybrid should have been strongly confirmed. Based on the above structure and composition analyses, the successful preparation of CMP@PNC and control samples can be strongly verified.

The electrochemical performances of these samples were first evaluated in 0.1 M KOH electrolyte using the threeelectrode system with a rotating disk electrode (RDE) configuration as the working electrode. Here, the accessibly defective carbon layers (confirmed by thermogravimetric (TG) analysis and TEM images after acid leaching for CMP@PNC (Fig. S16 and S17<sup>†</sup>)) allowed the whole hybrid including CoMnP<sub>4</sub> nanoparticles to immerse in KOH solution. Upon the ORR measurements of CMP@PNC and control samples, the cyclic voltammetries (CVs) were first performed in O2-saturated 0.1 M KOH solution (Fig. S18<sup>†</sup>). Obviously, all samples show sharp reduction peaks, suggesting their efficient oxygen reduction activities. It is worth noting that CMP@PNC can achieve a positive reduction peak at 0.80 V (vs. RHE), a little lower than that of 20 wt% Pt/C (0.85 V vs. RHE).<sup>45</sup> To further investigate the ORR performance, linear sweep voltammograms (LSVs) were recorded at a rotating rate of 1600 rpm (Fig. 3a and S19<sup>+</sup>). In agreement with the CVs, CMP@PNC exhibits an onset potential of  $\sim$ 0.89 V (vs. RHE) and a diffusion-limited current density of  $\sim$ 5.5 mA cm<sup>-2</sup> at 0.0 V (vs. RHE), which is close to those of 20 wt% Pt/C (0.91 V vs. RHE, 5.5 mA cm<sup>-2</sup>) and greater than those of CMP@PC (0.87 V  $\nu s$ . RHE, 5.0 mA cm<sup>-2</sup>), PNC (0.84 V vs. RHE, 4.6 mA cm<sup>-2</sup>), CP(a)PNC (0.87 V vs. RHE, 4.8 mA cm<sup>-2</sup>) and MP@PNC (0.86 V vs. RHE, 4.6 mA cm<sup>-2</sup>). To thoroughly understand the ORR activity of these catalysts, LSV curves ranging from 225 to 1600 rpm were collected (Fig. 3b and S20<sup>+</sup>). The reduction current densities regularly increased with increasing rotation speeds, which is ascribed to the reduced diffusion distance at large velocity.28 Besides, a high kineticlimited current density ( $I_{\rm K}$ ) of 13.34 mA cm<sup>-2</sup> at 0.5 V (vs. RHE) was achieved from Koutecky-Levich (K-L) plots (Fig. S21<sup>†</sup>) for CMP@PNC, and it was close to that of 20 wt% Pt/C (13.70 mA  $cm^{-2}$ ), outperforming those of control samples (Fig. 3c). This superior ORR performance can be ascribed to the abundant active sites in N, P co-doped carbon, which has been proved in previous studies that the P, N co-doped structure can induce positive polarization of carbon atoms to favor the capture of O2 molecules and effectively facilitate the ORR processes.<sup>22,46</sup> The interfacial effect between phosphide nanoparticles and defective carbon layers can also boost the activity of  $C-N_x$  for the ORR through electron transfer from phosphide to carbon layers.47-49

To evaluate the electron transfer number (n), rotating ring disk electrode (RRDE) tests from 0.1–0.8 V (*vs.* RHE) were carried out (Fig. S22 and S23<sup>†</sup>). As displayed in Fig. 3d,



Fig. 3 ORR performance examined in 0.1 M KOH solution. (a) LSV polarization curves of CMP@PNC, CMP@PC, PNC and 20 wt% Pt/C at 1600 rpm. (b) LSV polarization curves of CMP@PNC with different rotation speeds. (c) Kinetic-limited current densities of each catalyst at 0.5 V (vs. RHE) obtained from the corresponding K–L plots. (d) Electron transfer number (*n*) and H<sub>2</sub>O<sub>2</sub> yield from RRDE tests for CMP@PNC and 20 wt% Pt/C; (e) Tafel slopes of each catalyst calculated from LSV curves. (f) The LSV polarization curves for CMP@PNC before and after 7000 cycles.

CMP@PNC shows a prominent *n* value in the range of 3.73–3.98 per oxygen molecule accompanied by a low H<sub>2</sub>O<sub>2</sub> yield of 4.0-1.0%, which is quite close to those of 20 wt% Pt/C. The excellent ORR performance of CMP@PNC can also be attested by the small Tafel slope value of 62 mV  $dec^{-1}$ , recorded at 1600 rpm and a low polarization region. This value is only 3 mV  $dec^{-1}$ higher than that of 20 wt% Pt/C (59 mV dec<sup>-1</sup>) and lower than those of control samples (Fig. 3e and S24<sup>†</sup>), denoting that the first electron reduction of oxygen may be the rate determining step in the ORR process for CMP@PNC.<sup>50</sup> From the mechanism point of view, the small Tafel slope means fast reaction kinetics.51 The polarization curve of CMP@PNC recorded after 7000 cycles shows almost the same onset potential and diffusion-limited current density as that of the initial cycles (Fig. 3f), which is consistent with the chronoamperometric test (Fig. S25,† 96% retention after working at 0.65 V for 22 h). The long-term durability of the CMP@PNC catalyst is clearly higher than that of 20 wt% Pt/C (87%). The initial and recycled TEM images of CMP@PNC and CMP@PC were collected to explore the morphology change (Fig. S26, S27<sup>†</sup>). It can be observed that there is obvious aggregation of nanoparticles in CMP@PC after ORR catalytic cycling, and there is no obvious morphological change in CMP@PNC, indicating that the defective carbon layers can effectively limit the aggregation of CoMnP<sub>4</sub>

nanoparticles in the catalytic process. Moreover, there is no obvious variation in the current density with the addition of 3.0 M methanol for CMP@PNC, while a dramatic current density decrease occurred for 20 wt% Pt/C (Fig. S28†).

The OER performance of these samples was measured in N2saturated 0.1 M KOH electrolyte. In Fig. 4a and S29,† the LSV curve of CMP@PNC was compared with those of other control catalysts without *iR* correction (*i*, current; *R*, resistance), and a potential of  $\sim$ 1.56 V (vs. RHE) at a current density of 10 mA  $cm^{-2}$  can be achieved. The overpotential value of CMP@PNC is 20 mV, 61 mV, 71 mV, and 79 mV lower than those of IrO<sub>2</sub>, CMP@PC, CP@PNC and MP@PNC, respectively. Additionally, the corresponding Tafel slopes were calculated from the polarization curves to investigate the OER catalytic kinetics of the obtained samples. Fig. 4b and S30<sup>†</sup> reveal that the Tafel slope of CMP@PNC is approximately 74 mV dec<sup>-1</sup>, lower than those of  $IrO_2$  (79 mV dec<sup>-1</sup>), CMP@PC (88 mV dec<sup>-1</sup>), PNC (142 mV dec<sup>-1</sup>), CP@PNC (100 mV dec<sup>-1</sup>) and MP@PNC (127 mV dec $^{-1}$ ), suggesting the favorable OER kinetics of the asprepared CMP@PNC. Electrochemically active surface areas (ECSAs) were estimated through CV curves at different scan rates (Fig S31<sup>†</sup>). CMP@PNC shows the highest double-layered capacitance  $(C_{dl})$  of 25.36 mF cm<sup>-2</sup>, suggesting the largest active surface area and more active sites during the electrocatalytic process. The ECSA-corrected OER polarization curves of different samples (Fig. S32<sup>†</sup>) show small disparity in performance compared with pristine curves. Moreover, the durability test of CMP@PNC shows a negligible variation in the LSV curves even after 7000 cycles (Fig. S33†), in line with the chronoamperometric test (95% retention, Fig. S34<sup>†</sup>). These results indicate the high stability of CMP@PNC under alkaline conditions. It has been confirmed that the coexistence of double transition metal elements could help to tune the electronic structures of catalysts for enhanced OER activity.<sup>30,31</sup> The carbon



**Fig. 4** OER performance examined in 0.1 M KOH solution at a rotating rate of 1600 rpm. (a) LSV polarization curves of CMP@PNC, CMP@PC, PNC and IrO<sub>2</sub>. (b) Tafel slopes calculated from LSV curves for CMP@PNC, CMP@PC, PNC and IrO<sub>2</sub>. (c) Schematic of the ORR and OER main performance origins. (d) LSV polarization curves showing the bifunctional ORR/OER activities of different samples.

components could facilitate the transformation of  $CoMnP_4$  into corresponding oxyhydroxides as the true active component (confirmed by Co/Mn/P 2p XPS spectra of CMP@PNC after the OER, Fig. S35†).<sup>52,53</sup> In addition, the small size of CoMnP<sub>4</sub> nanoparticles provides large specific surface areas which can provide more active sites in the catalytic process. The OER and ORR main performance origins are displayed in Fig. 4c, which clearly shows that N, P codoped defective carbon mainly provides active sites for the ORR and bimetallic phosphide CoMnP<sub>4</sub> plays a crucial role in the OER. We also tested the electrocatalytic performance of the acid leached CMP@PNC under the same testing conditions (Fig. S36†), and obviously poor ORR and OER electrocatalytic performances were obtained, indicating the important role of the bimetallic phosphide in the catalytic process.

The bifunctional electrocatalytic activities of all catalysts were studied by the potential difference ( $\Delta E$ ) between the current density of 10 mA cm<sup>-2</sup> for the OER and the current density of -3 mA cm<sup>-2</sup> for the ORR (Fig. 4d, S37†). It is worth noting that the  $\Delta E$  of CMP@PNC is only 0.75 V, which is lower than those of all control catalysts and most of the reported non-precious metal-based oxygen electrocatalysts to date (Table S1†).

Based on the above analysis, the excellent ORR/OER catalytic activities and superior durability of CMP@PNC can be related to the following primary features: (1) bimetallic phosphide CoMnP<sub>4</sub> with a small size can serve as an efficient pre-catalyst for the OER; meanwhile the P, N co-doped structure can effectively facilitate the ORR process; (2) the interfacial effect between CoMnP<sub>4</sub> nanoparticles and P, N co-doped carbon layers can boost ORR processes through electron transfer; (3) the defective carbon layers could provide large and stable spatial structures with highly dispersed defective carbon layer encapsulated nanoparticles, thereby effectively limiting the growth and aggregation of nanoparticles in catalytic cycling as well as facilitating charge transfer in the hybrid.

## Conclusions

A hybrid of bimetallic phosphide nanoparticles and P, N codoped defective carbon layers has been developed as an efficient bifunctional ORR/OER electrocatalyst. Benefitting from the well-designed composition and structure, the hybrid achieved a potential gap of 0.75 V in 0.1 M KOH solution, superior to most of the non-precious metal based catalysts reported to date. Moreover, it has no obvious change in catalytic activity and structure after a long-term test. The superior electrocatalytic performance makes it a promising catalyst in energy conversion devices; meanwhile this work opens up a new avenue to design bifunctional oxygen electrocatalysts.

## Conflicts of interest

There are no conflicts of interest to declare.

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