Co$_2$P Nanoparticle/Multi-Doped Porous Carbon nanosheet for Oxygen Evolution Reaction

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Experimental

Reagents and materials
Cobaltous nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 99% pure), potassium hydroxide (KOH, 90%) and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd used without further purification. Analytical-grade iridium(IV) oxide (IrO$_2$) and 5% Nafion were bought from Macklin and Alfa Aesar, respectively. 2-methylimidazole (Hmim, 99% pure), branched polyethylenimine (PEI, Mw = 10,000 g/mol), and phytic Acid (PA, 50% in water) were supplied by Sigma-Aldrich.

Sample preparation
Firstly, leaf-like ZIF-L was synthesized with a Hmim to cobalt ions molar ratio of 4 at room temperature as previous reported. Typically, 1 mmol of Co(NO$_3$)$_2$·6H$_2$O and 4 mmol of Hmim were dissolved in 5 mL deionized water respectively, and then the aqueous solution of Co(NO$_3$)$_2$ was mixed with the Hmim solution under stirring. After stirring for 2 hours, 0.5 mL PEI with a concentration of 0.05 g/mL was added. ZIF-L/PEI can be obtained 5 minutes later by centrifugation and re-dispersed in ethanol. Finally, 0.1 mL PA solution was introduced into ZIF-L/PEI dispersion. The product ZIF-L/PEI/PA was collected by repeated centrifugation (at 6000 rpm for 20 min) and
washed with water for three times, and then dried in an oven at 70 °C overnight. The ZIF-L/PEI/PA hybrid was then heated in a tube furnace under Ar atmosphere from 50 °C to 700 °C with a heating rate of 2 °C min⁻¹, and maintained at 800 °C for 2 h. The final products were grounded to fine powders, named as Co₂P@CoNPC. As comparisons, the carbonization products of ZIF-L and ZIF-L/PEI are named Co@NC-Z and Co@NC-ZP. Moreover, ZIF-L/PEI/PA hybrids with different volumetric PA addition were also carbonized as catalysts. Catalysts obtained from different ZIF-L/PEI/PA hybrids were named as ZPP₀.₀₅ and ZPP₀.₅ based on volume of PA solution 0.05 and 0.5 mL.

**Materials characterization**

The morphology of the samples were observed by the scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscopic (TEM, JEM-2100F). The crystalline phase was identified by X-ray diffraction (XRD, BRUKER D8 ADVANCE X-ray diffractometer, Cu-Kα X-ray source). X-ray photoelectron spectroscopy (XPS) is recorded on an ESCALab220i-XL spectrometer with a 300W Al Kα X-ray source.

**Electrochemical measurements**

The oxygen evolution reactions (OER) was performed on a CHI760E electrochemical workstation (Shanghai Chenhua, China). Electrodes were prepared by drop-casting ink containing catalyst powder on a glassy carbon electrode. 5 mg of the electrocatalyst sample was sonicated in a mixture of 1 mL deionized water and ethanol (v:v = 1:1) and 10 μl Nafion for 60 min to form a homogeneous catalyst ink (5 mg·mL⁻¹). The activities of catalysts were measured via a conventional three-electrode system, including graphite rod auxiliary electrode and Ag/AgCl reference electrode. The catalyst ink was then coated onto the glassy carbon electrode at a loading of 10 μl and dried at room temperature. The loading of the catalysts for the activity evaluation is calculated to be 0.255 mg·cm⁻². The OER activities of catalysts were measured in O₂-saturated 1 M KOH aqueous solution at 1600 rpm rotation rates and a scan rate of 5 mV·s⁻¹. All results reported in this work were converted to
the RHE scale according to the Nernst equation \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197 \).

**Fig. S1** (A) SEM image, (B) elemental mapping and (C) energy dispersive X-ray (EDX) spectrum of ZIF-L/PEI/PA.

**Fig. S2** Survey XPS spectra of (a) Co@NC-Z, (b) Co@NC-ZP and (c) Co\(_2\)P@CoNPC.

**Fig. S3** Linear scan voltammetry (LSV) of various samples for OER: ZPP\(_{0.05}\) (black) and ZPP\(_{0.5}\) (blue).
Fig. S4 XRD patterns of ZPP$_{0.05}$ (black) and ZPP$_{0.5}$ (blue).

Fig. S5 XRD patterns of Co$_2$P@CoNPC hybrids after stability test.

Fig. S6 SEM images of Co$_2$P@CoNPC hybrids after stability test.
Fig. S7 (A) XPS survey spectra and high-resolution P 2p (B), Co 2p (C) spectra of Co$_2$P@CoNPC hybrids after stability test.

Table S1 Summary of TMP-based electrocatalysts for OER in 1 M KOH.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Overpotential @J$_{10}$/mV</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>“P” sources</th>
<th>Reference</th>
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<td>CoP$_3$ CPs</td>
<td>343</td>
<td>76</td>
<td>Red phosphorus</td>
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<tr>
<td>CoP/NCNHP</td>
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<td>70</td>
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<td>311</td>
<td>78</td>
<td>Phytic acid</td>
<td>This work</td>
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</table>

References

[S7] W. Hong, M. Kitta and Q. Xu, Small Methods, 2018, 2, 1800214.