Supplementary Information

Enhanced oxygen evolution reaction of defective CoP/MOF-integrated electrocatalyst by partial phosphating

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Experimental section

Chemicals

All chemical materials were used without further purification. Co(NO$_3$)$_2$·6H$_2$O (≥98.5%, Xilong Scientific), Cu(NO$_3$)$_2$·3H$_2$O (99.0–102.0%, Kermel), 4,5-Imidazoledicarboxylic acid (≥97.0%, Sigma-aldrich), NaOH (≥96.0%, Tianjin Damao), Sulfur sublimed (≥99.5%, Kermel), Selenium powder (≥99.7%, Zhongqin), 1,4-benzenedicarboxylic acid (≥98.5%, Guangfu), N,N-dimethylformamide (≥99.5%, Rionlon), ethanol (≥99.7%, Rionlon) and NaH$_2$PO$_2$·H$_2$O (≥98.0%, Kermel). The deionized water (DI-water) was used throughout the synthesis.

Synthesis of CoCu-MOF

Co(NO$_3$)$_2$·6H$_2$O (0.57 mmol, 0.1657 g) and Cu(NO$_3$)$_2$·3H$_2$O (0.03 mmol, 0.0072g) were dissolved in DI-water (20 mL) (Solution A). 4,5-Imidazoledicarboxylic acid (0.6 mmol, 0.0936 g) was deprotonated in NaOH solution (28 mL, 0.03 M) (Solution B). Then Solution B was quickly injected into Solution A under vigorous magnetic agitation. After stirring for 2 h, the precipitate was collected and washed with DI-water for several times by centrifugation and further dried overnight at 60 °C. For comparison, Co-MOF was prepared at the same condition except without addition of Cu(NO$_3$)$_2$·3H$_2$O.

Synthesis of D-CoCu-MOF-300

The obtained CoCu-MOF (0.0300 g) was placed in the porcelain boat and annealed at 300 °C for 1 h with a heating rate of 5 °C min$^{-1}$ under flowing N$_2$ atmosphere. For comparison, D-CoCu-MOF-220 and Co$_3$O$_4$/D-CoCu-MOF-380 were prepared only by changing the annealing temperature of 220 °C and 380 °C, respectively.

Synthesis of CoP/D-CoCu-MOF-300

In a typical process, the obtained D-CoCu-MOF-300 (0.0300 g) was placed in the porcelain boat at the downstream side and NaH$_2$PO$_2$·H$_2$O (0.6000 g) was placed in another porcelain boat at the upstream side. The annealing treatment was set as 300 °C for 1 h with a heating rate of 5 °C min$^{-1}$ under flowing N$_2$ atmosphere. For comparison, CoP/CoCu-MOF, CoP/D-CoCu-MOF-220 and CoP/(CoCu)$_2$P$_4$O$_12$ were prepared at the same condition only using different precursor (CoCu-MOF, D-CoCu-MOF-220 and Co$_3$O$_4$/D-CoCu-MOF-380, respectively). And the S-D-CoCu-MOF or S-CoCu-MOF was used Sulfur sublimed (0.600 g) as sulfur source, while Se-D-CoCu-MOF or Se-CoCu-MOF were prepared and so on.

Synthesis of P-D-Co-BDC

The Co-BDC MOFs were prepared according to the reference. Then the P-D-Co-BDC powder was prepared referring to the synthesis of CoP/D-CoCu-MOF-300, except that the presintering temperature was chosen as 420 °C.

Characterization

Thermogravimetric (TG) curves were measured on a thermogravimetric analysis instrument (Netzsch STA 449C), with a heating rate of 5 °C min$^{-1}$ from 25 to 750 °C under N$_2$ atmosphere. The X-ray diffraction (XRD) patterns were recorded on a X-ray
generator diffractometer (Rigaku D/max 2400). Scanning electron microscope (SEM) images and energy dispersive X-ray spectroscopy (SEM-EDS) spectra were photographed on a scanning electron microscope (thermoscientific Apero S). Transmission electron microscope (TEM) images, high resolution TEM (HRTEM) images and energy dispersive X-ray spectroscopy (EDS) mapping were observed on a transmission electron microscope (Philips TecnaiTM G2 F30). Fourier transform infrared spectroscopy (FTIR) spectra were recorded by a spectrometer (Bruker VERTEX 70v FT-IR). The X-ray photoelectron spectroscopy (XPS) spectra were obtained on a spectrophotometer (PHI-5702, C 1s at 284.5 eV).

**Electrochemical measurements**

Electrochemical measurements were conducted on a potentiostat electrochemical workstation (Metrohm, Autolab PGSTAT302N) in 1.0 M KOH solution. A standard three-electrode electrochemical setup was used: a glass carbon (GC, φ=3.0 mm) substrate electrode for the working electrode, a Hg/HgO electrode with 1.0 m KOH filling solution for reference electrodes and a graphite rod for counter electrodes, respectively. The catalyst ink was using 2.5 mg electrocatalyst and 20 μL 5 wt% Nafion solutions, dispersed them into 1 mL of DI-water, and treated with an ultrasonic treatment to form a homogeneous slurry. Then, 6.0 μL as-prepared catalyst ink was deposited onto the clean surface of GC electrode, and the loading is calculated as 0.212 mg cm⁻². The potentials vs. Hg/HgO were converted to the reversible hydrogen electrode by using $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.0591 \text{pH} + 0.098$.

The polarization curves were measured by linear sweep voltammetry (LSV) at a scan rate of 5.0 mV s⁻¹ in the range from 0 to 0.9 V vs Hg/HgO at room temperature. The current density was normalized by the geometric surface area of GC electrode. The electrochemical impedance spectroscopy (EIS) test was measured at a potential of 1.53 V vs RHE, in a frequency range of 0.1-100k Hz with an amplitude of 5.0 mV.

The overpotential was calculated using $\eta = E_{\text{RHE}} - 1.23$. Mass activity $J_m = j_{\text{geo}}/m$. Where $j_{\text{geo}}$ is the measured current at a certain overpotential of 300 mV, and m is the loading mass.

**Reference**

Fig. S1. The XRD patterns of D-CoCu-MOF-300 and CoP/D-CoCu-MOF-300.
Fig. S3. (a) The LSV, (b) Tafel, (c) $C_{\text{dl}}$ and (d) EIS curves of CoCu-MOF, D-CoCu-MOF-220, D-CoCu-MOF-300 and Co$_3$O$_4$/D-CoCu-MOF-380, respectively. Inset: the equivalent circuit.
Fig. S4. (a) The LSV, (b) Tafel, (c) C_{dl} and (d) EIS curves of CoP/CoCu-MOF, CoP/D-CoCu-MOF-220, CoP/D-CoCu-MOF-300 and CoP/(CoCu)$_2$P$_4$O$_{12}$, respectively. Inset: the equivalent circuit.
Fig. S5. (a) The LSV, (b) Tafel, (c) $C_{dl}$ and (d) EIS curves of CoP/D-CoCu-MOF-300 and CoP/D-Co-MOF-300, respectively.
Fig. S6. The SEM images of (a) Co₃O₄/D-CoCu-MOF-380 and (b) CoP/(CoCu)₂P₄O₁₂.
**Fig. S7.** The SEM images CoP/D-Co-MOF-300 at different magnification (a-c), at low test voltage (d).
Fig. S8. The TEM images of (a) CoCu-MOF, (b) D-CoCu-MOF-300 and (c) CoP/CoCu-MOF.
Fig. S9. The TEM images (a, b) and HRTEM images (c) of CoP/(CoCu)$_2$P$_4$O$_{12}$.
Fig. S10. The XPS spectra of CoCu-MOF, D-CoCu-MOF-300, CoP/D-CoCu-MOF-300, CoP/(CoCu)$_2$P$_2$O$_{12}$ and CoP/D-Co-MOF-300.
Fig. S11. The XPS spectra of Co 2p for CoP/CoCu-MOF and CoP/D-CoCu-MOF-300.
Fig. S12. (a) The LSV curves and (b) comparison of overpotential and mass activity for S-CoCu-MOF, S-D-CoCu-MOF, Se-CoCu-MOF and Se-D-CoCu-MOF, respectively.
Fig. S13. (a) The LSV curves and (b) comparison of overpotential and mass activity for Co-BDC, D-Co-BDC, P-Co-BDC and P-D-Co-BDC, respectively.