

Supplementary Information

***In-situ* growth of urchin-like cobalt-chromium phosphide on 3D graphene foam for efficient overall water splitting**

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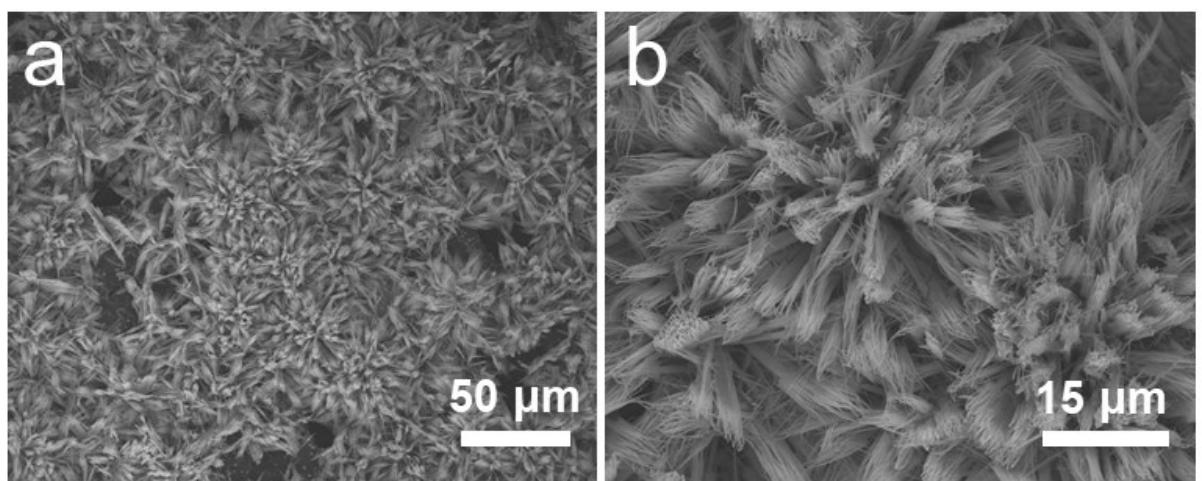


Fig. S1. SEM images of CoP@3DGF.

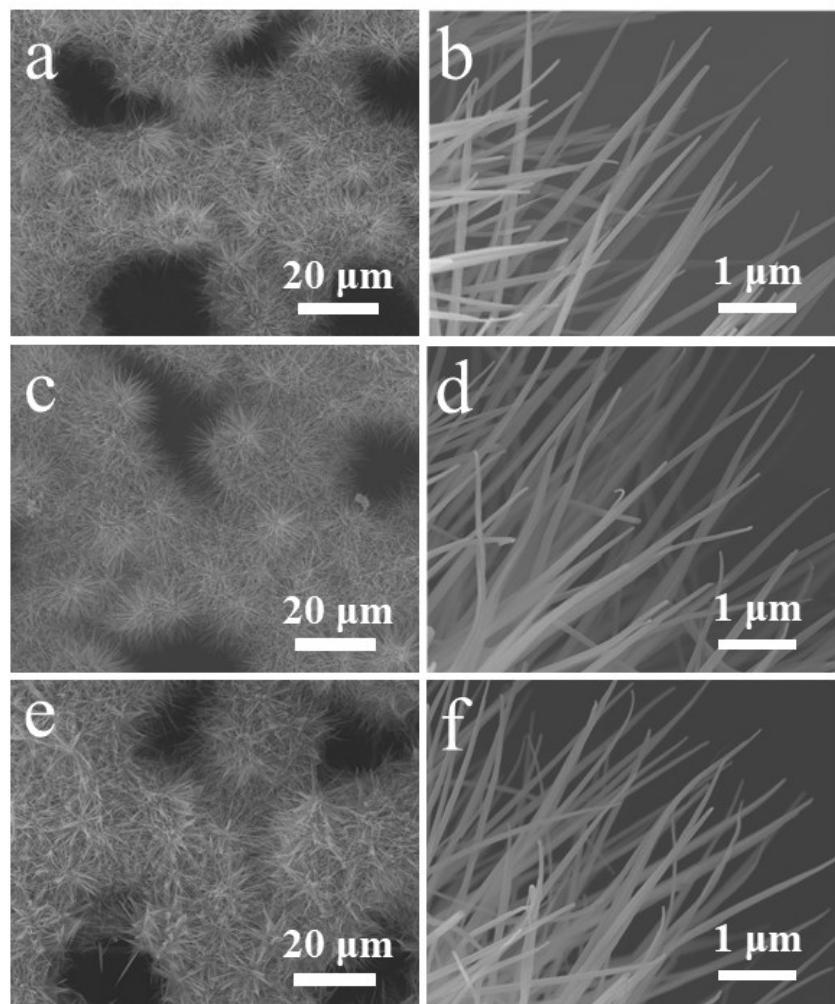


Fig. S2. SEM images of CoCr-P@3DGF with different Co/Cr ratios of (a-b) 1:1, (c-d) 3:1 and (e-f) 4:1.

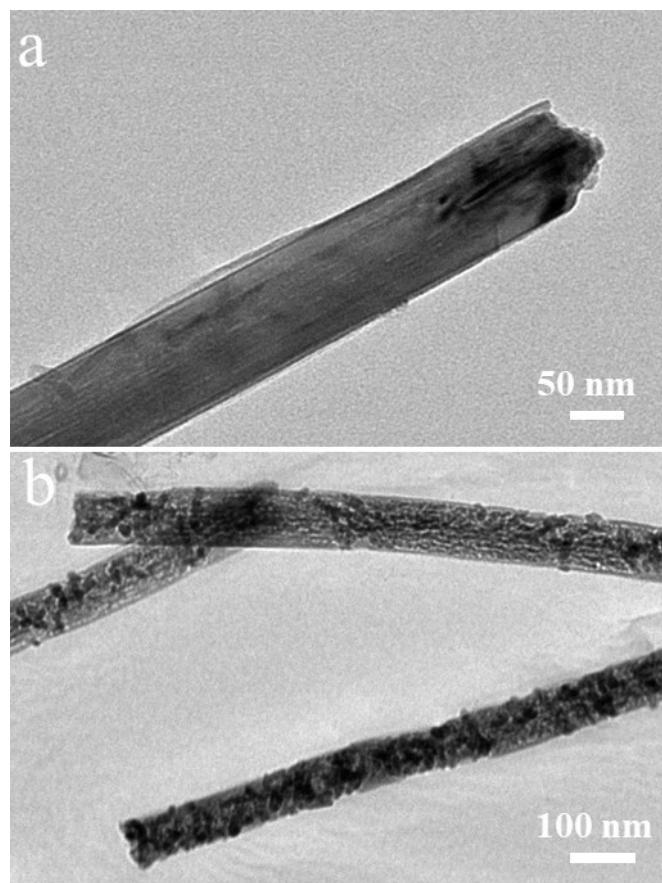


Fig. S3. TEM images of (a) $\text{Co}_2\text{Cr}_1\text{-LDH}@3\text{DGF}$ and (b) $\text{Co}_2\text{Cr}_1\text{-P}@3\text{DGF}$.

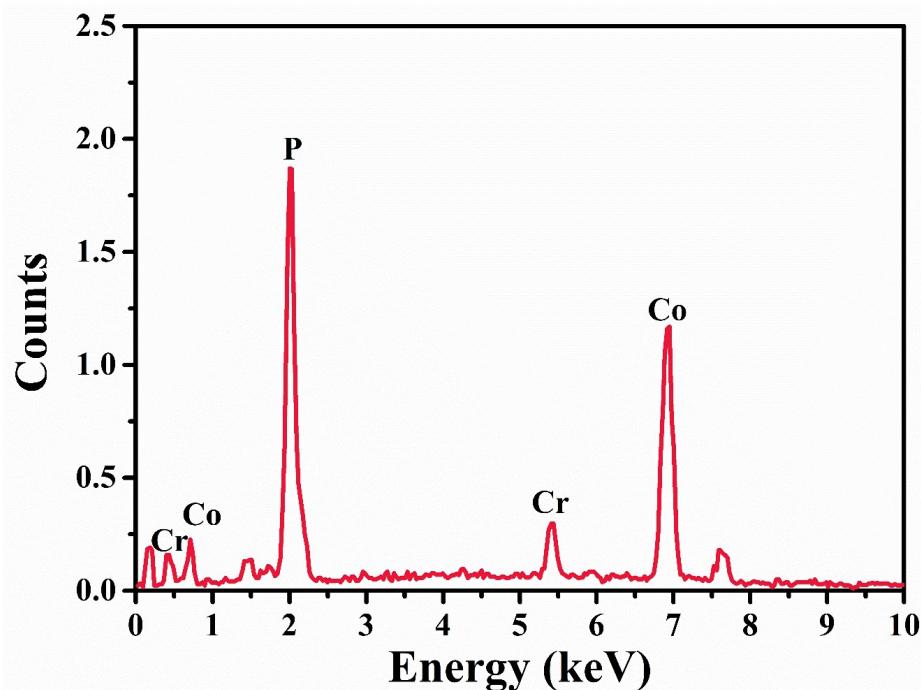


Fig. S4. EDS spectrum of $\text{Co}_2\text{Cr}_1\text{-P}@\text{3DGF}$ composite.

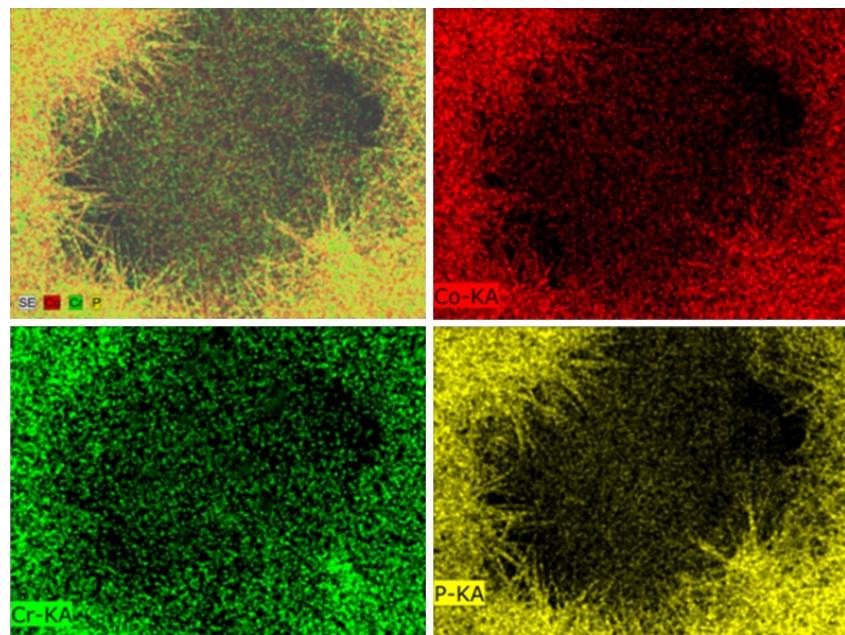


Fig. S5. Element mapping images of $\text{Co}_2\text{Cr}_1\text{-P}@\text{3DGF}$ (red: Co; green: Cr; yellow: P).

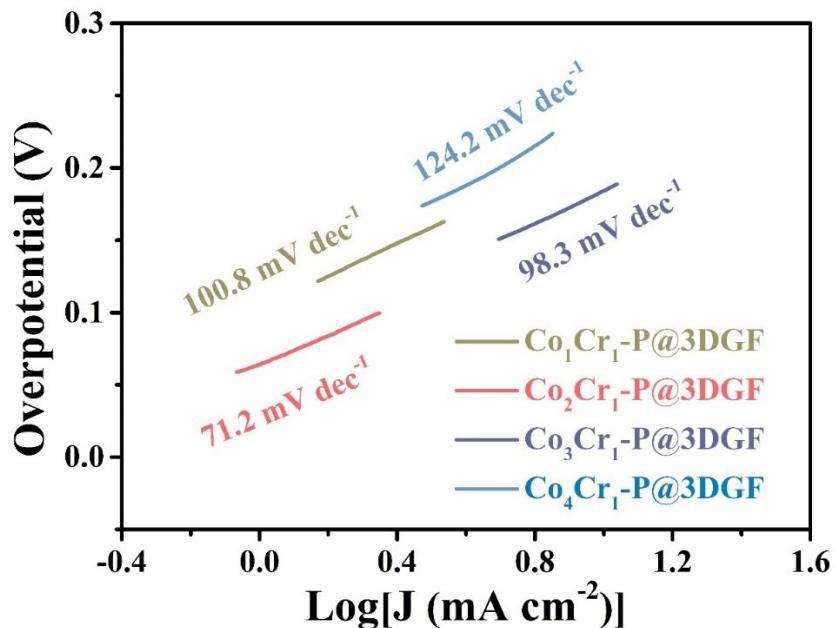


Fig. S6. Tafel curves of CoCr-P@3DGF with different Co/Cr ratios towards HER in 1.0 M KOH.

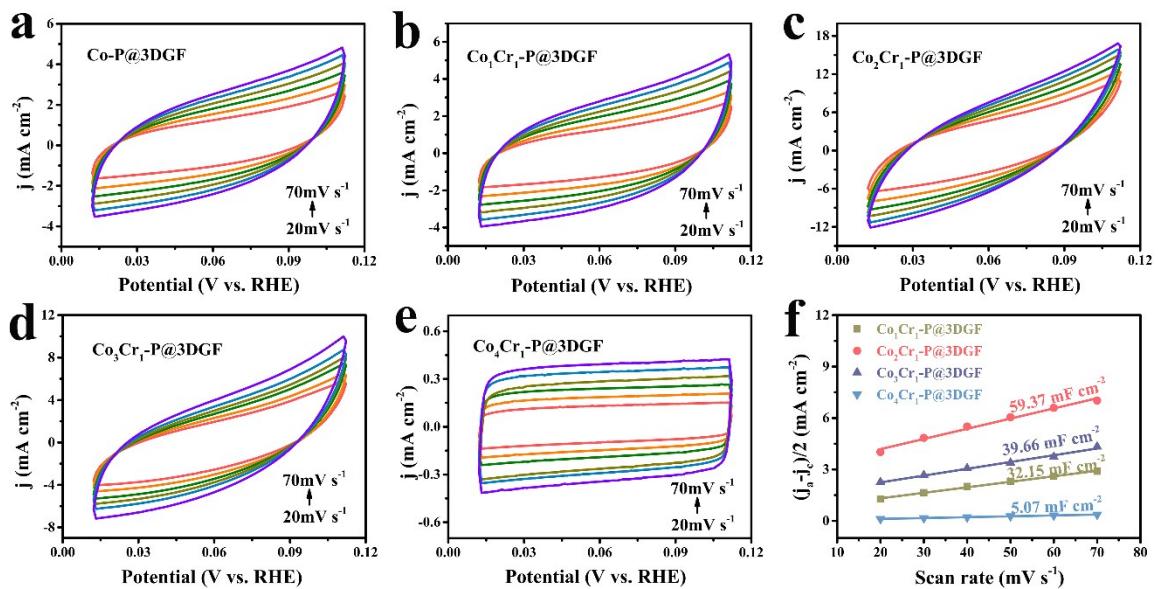


Fig. S7. CV curves of (a) Co-P@3DGF, (b) Co₁Cr₁-P@3DGF, (c) Co₂Cr₁-P@3DGF, (d) Co₃Cr₁-P@3DGF, (e) Co₄Cr₁-P@3DGF with various scan rates in 1.0 M KOH. (f) Double layer capacitances of CoCr-P@3DGF with different Co/Cr ratios.

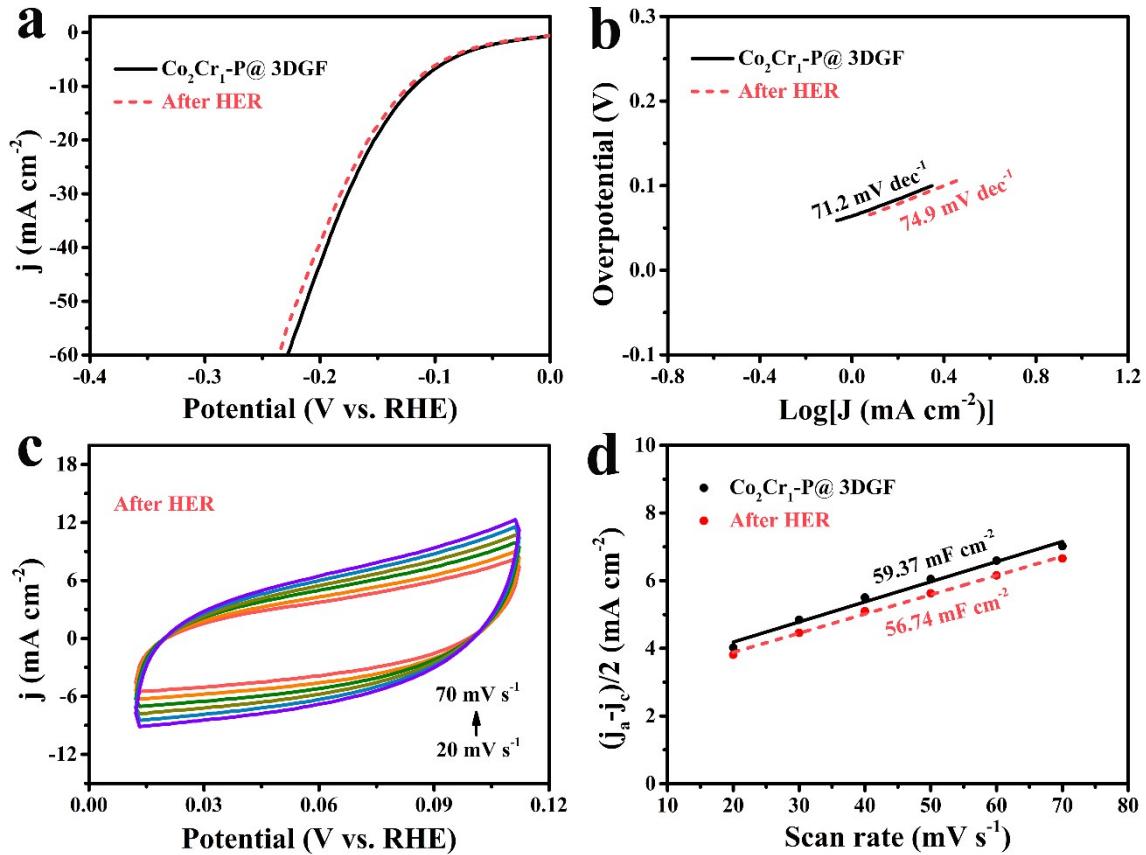


Fig. S8. (a) The polarization, (b) Tafel curves and (c) CV curves of $\text{Co}_2\text{Cr}_1\text{-P}@3\text{DGF}$ after 50 h stability tests for HER reaction in 1.0 M KOH. (d) Double layer capacitances of $\text{Co}_2\text{Cr}_1\text{-P}@3\text{DGF}$ before and after HER reaction.

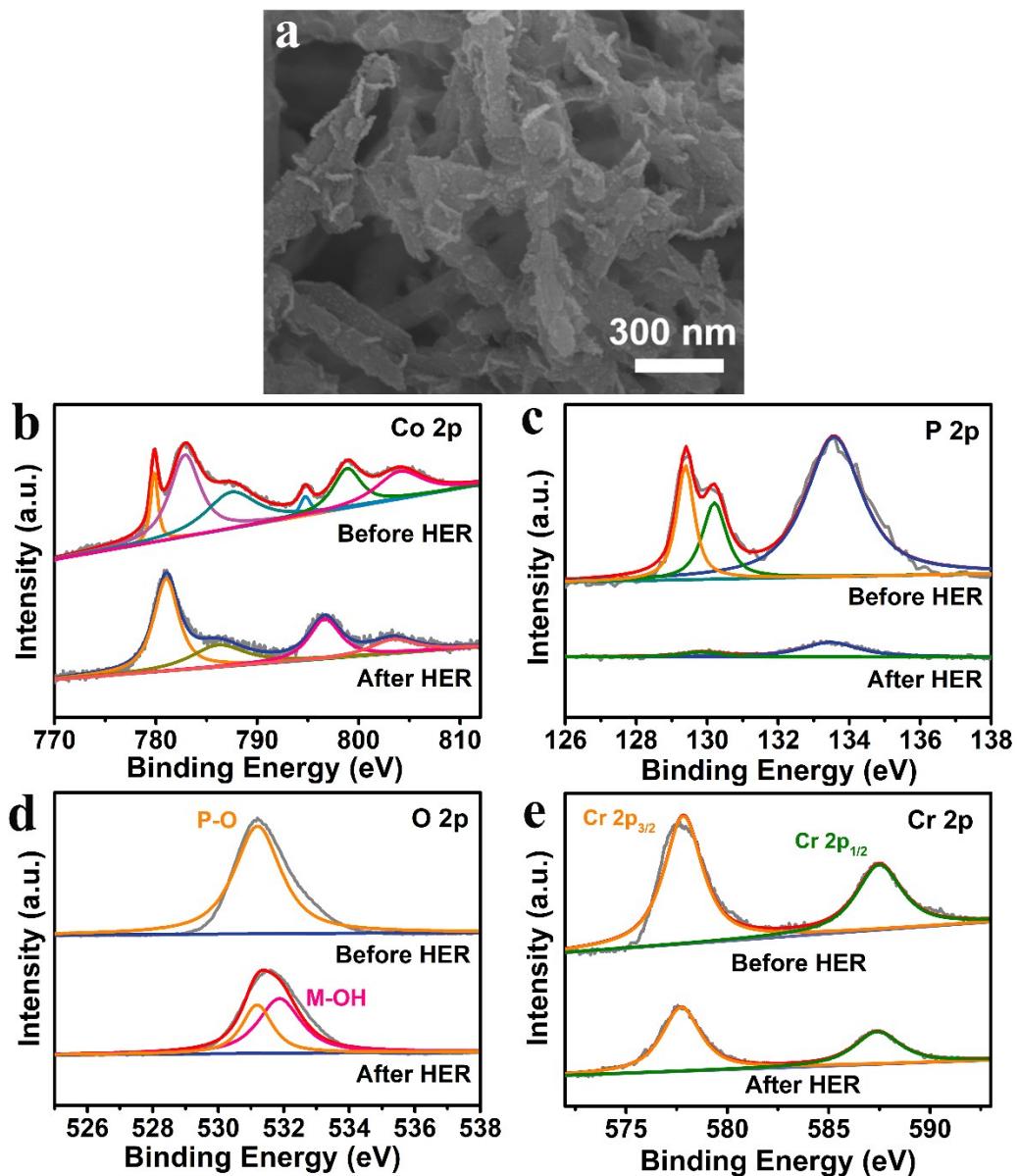


Fig. S9. (a) SEM images of $\text{Co}_2\text{Cr}_1\text{-P}@\text{3DGF}$ after the stability test of HER. High-resolution XPS spectra of $\text{Co}_2\text{Cr}_1\text{-P}@\text{3DGF}$ for (b) Co 2p, (c) P 2p, (d) O 1s, (e) Cr 2p before and after HER test.

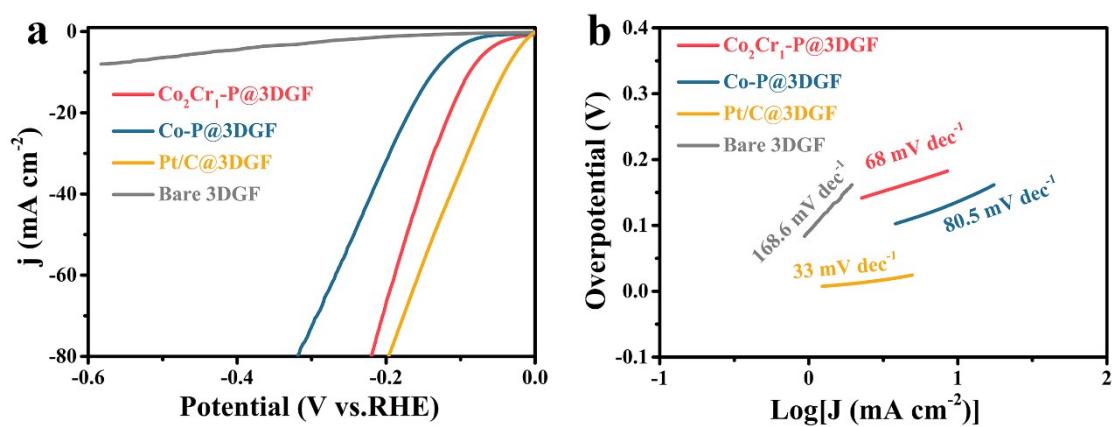


Fig. S10. (a) Polarization curves and (b) corresponding Tafel curves of $\text{Co}_2\text{Cr}_1\text{-P@3DGF}$, Co-P@3DGF , Pt/C@3DGF and bare 3DGF in 0.5 M H_2SO_4 .

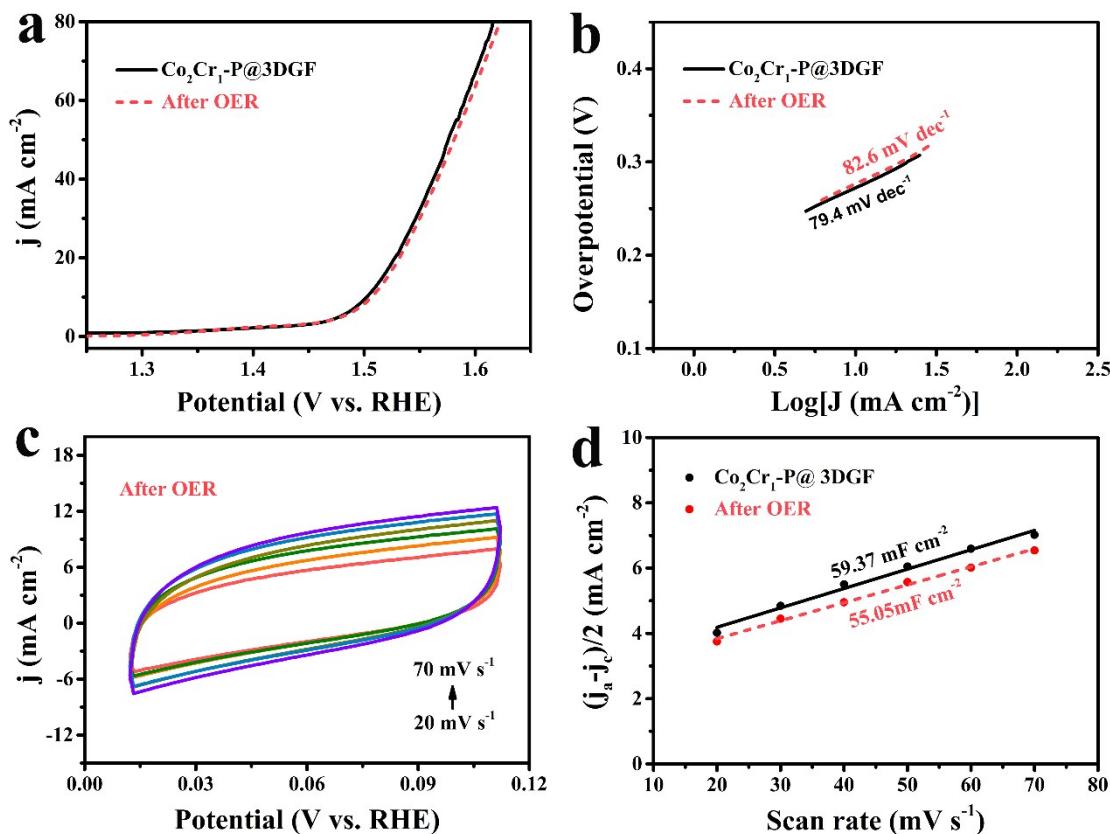


Fig. S11. (a) The polarization, (b) Tafel curves and (c) CV curves of $\text{Co}_2\text{Cr}_1\text{-P@3DGF}$ after 50 h stability tests for OER reaction in 1.0 M KOH. (d) Double layer capacitances of $\text{Co}_2\text{Cr}_1\text{-P@3DGF}$ before and after OER reaction.

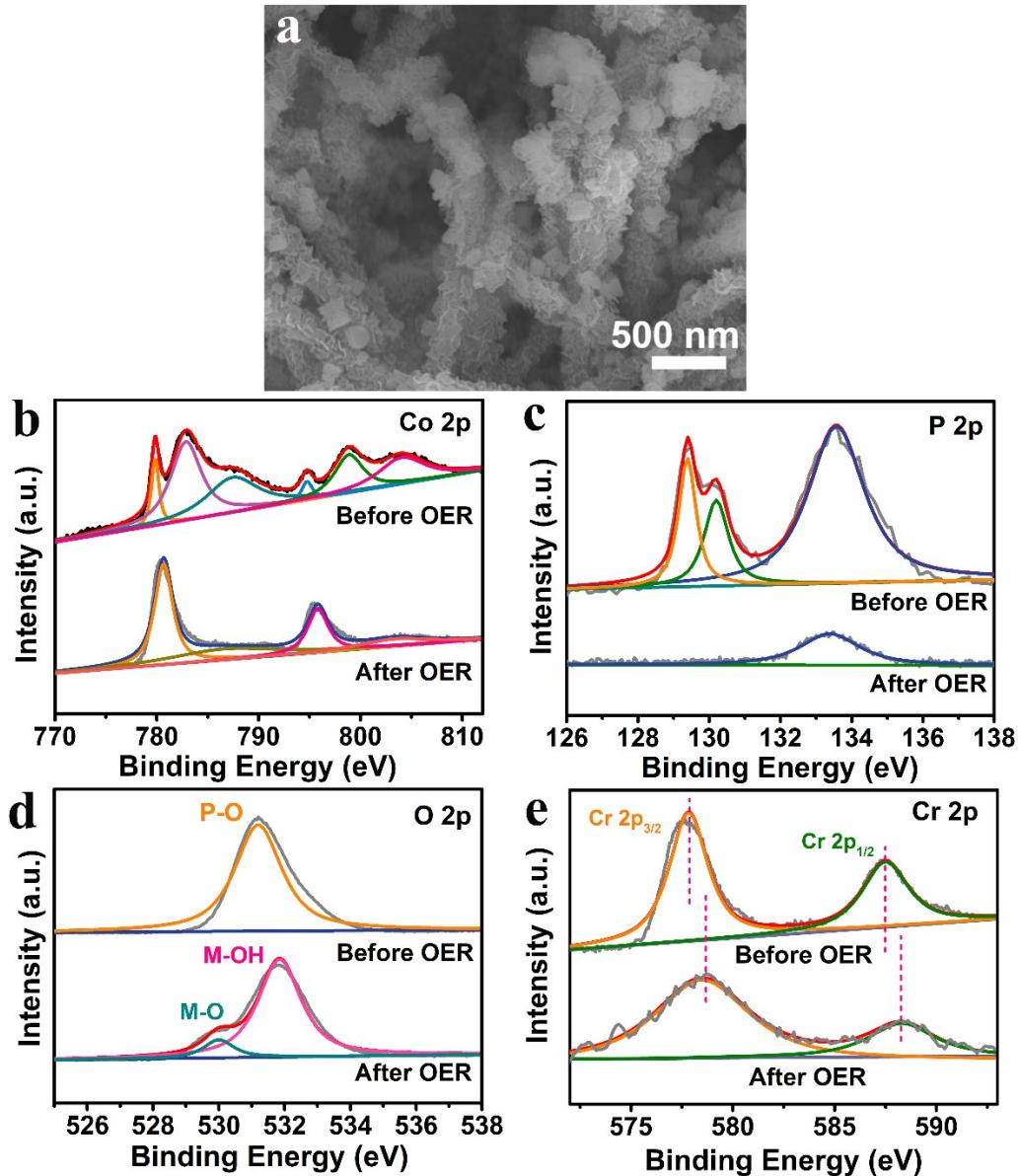


Fig. S12. (a) SEM images of $\text{Co}_2\text{Cr}_1\text{-P}@\text{3DGF}$ after the stability test of OER. High-resolution XPS spectra of $\text{Co}_2\text{Cr}_1\text{-P}@\text{3DGF}$ for (b) Co 2p, (c) P 2p, (d) O 1s, (e) Cr 2p before and after OER test.

Table S1. Estimated chemical formula of CoCr-P with different Co/Cr feeding ratios.

| Co/Cr feeding ratio | EDS analysis [at%] | | | Estimated chemical formula |
|---------------------|--------------------|------|-------|--|
| | Co | Cr | P | |
| 1:1 | 50.75 | 7.53 | 41.71 | Co _{0.87} Cr _{0.13} -P |
| 2:1 | 50.91 | 5.77 | 43.32 | Co _{0.89} Cr _{0.11} -P |
| 3:1 | 45.21 | 4.62 | 50.17 | Co _{0.91} Cr _{0.09} -P |
| 4:1 | 46.10 | 2.65 | 51.25 | Co _{0.95} Cr _{0.05} -P |

Table S2. Comparison of HER performances of $\text{Co}_2\text{Cr}_1\text{-P}@\text{3DGF}$ with recently reported catalysts in 1.0 M KOH.

| Catalysts | j (mA cm ⁻²) | Overpotential (mV) | Tafel slope (mV dec ⁻¹) | Ref. |
|---|-----------------------------|-----------------------|--|------------------|
| $\text{Co}_2\text{Cr}_1\text{-P}@\text{3DGF}$ | 10 | 118 | 71.2 | This work |
| Er-doped CoP NMs | 10 | 66 | 61 | S1 |
| Hollow Mo-CoP arrays | 10 | 40 | 65 | S2 |
| $\text{Co}_{5.47}\text{N NP}@\text{N-PC}$ | 10 | 149 | 86 | S3 |
| $\text{Co}_4\text{Ni}_1\text{P NTs}$ | 10 | 129 | 52 | S4 |
| CoP/C | 10 | 160 | 20 | S5 |
| $\text{Cu}_{0.075}\text{Co}_{0.0925}\text{P/CP}$ | 10 | 47 | 47.2 | S6 |
| (Ni,Co)Se ₂ -GA | 10 | 127 | 79 | S7 |
| CoP-400 | 10 | 151 | 72 | S8 |
| S-CoP | 10 | 109 | 79 | S9 |
| $\text{Co}_3\text{S}_4@\text{MoS}_2$ | 10 | 136 | 74 | S10 |

Table S3. Comparison of HER performances of Co₂Cr₁-P@3DGF with recently reported catalysts in 0.5 M H₂SO₄.

| Catalysts | j (mA cm ⁻²) | Overpotential (mV) | Tafel slope (mV dec ⁻¹) | Ref. |
|---|-----------------------------|-----------------------|--|------------------|
| Co₂Cr₁-P@3DGF | 10 | 88 | 68 | This work |
| Er-doped CoP NMs | 10 | 52 | 32 | S1 |
| Cu _{0.075} Co _{0.0925} P/CP | 10 | 70 | 55.1 | S6 |
| Urchin-like CoP | 10 | 105 | 46 | S11 |
| CoP-400 | 10 | 113 | 67 | S8 |
| CoP ₃ /Ni ₂ P | 10 | 115 | 49 | S12 |
| W-CoP NAs/CC | 10 | 89 | 58 | S13 |
| CoMoP-5 | 10 | 95 | 61.1 | S14 |
| CoP@CC | 10 | 131 | 64 | S15 |
| CoP/NCNHP | 10 | 140 | 53 | S16 |
| HNDCM-Co/CoP | 10 | 138 | 64 | S17 |

Table S4. Comparison of OER performances of Co₂Cr₁-P@3DGF with recently reported catalysts in 1.0 M KOH.

| Catalysts | j (mA cm ⁻²) | Overpotential (mV) | Tafel slope (mV dec ⁻¹) | Ref. |
|---|-----------------------------|-----------------------|--|------------------|
| Co₂Cr₁-P@3DGF | 10 | 270 | 79.4 | This work |
| Er-doped CoP NMs | 10 | 256 | 70 | S1 |
| Hollow Mo-CoP nanoarrays | 10 | 305 | 56 | S2 |
| Co _{5.47} N NP@N-PC | 10 | 248 | 72 | S3 |
| Co ₄ Ni ₁ P NTs | 10 | 245 | 87 | S4 |
| CoP/C | 10 | 430 | 115 | S5 |
| Cu _{0.075} Co _{0.0925} P/CP | 10 | 221 | 70.4 | S6 |
| (Ni,Co)Se ₂ -GA | 10 | 250 | 70 | S7 |
| CoCr-LDH | 10 | 340 | 81 | S18 |
| Co@Co ₉ S ₈ nanochains | 10 | 285 | 86.5 | S19 |
| S-CoP | 10 | 270 | 82 | S9 |

Table S5. Comparison of overall water splitting performances of Co₂Cr₁-P@3DGF with recently reported catalysts in 1.0 M KOH.

| Catalysts | Cell voltage (V) at $j = 10 \text{ mA cm}^{-2}$ | Ref. |
|--|--|------------------|
| Co₂Cr₁-P@3DGF | 1.56 | This work |
| Er-doped CoP NMs | 1.58 | S1 |
| Hollow Mo-CoP nanoarrays | 1.56 | S2 |
| Co _{5.47} N NP@N-PC | 1.62 | S3 |
| Co ₄ Ni ₁ P NTs | 1.59 | S4 |
| Cu _{0.075} Co _{0.0925} P/CP | 1.55 | S6 |
| (Ni,Co)Se ₂ -GA | 1.6 | S7 |
| Co ₃ S ₄ @MoS ₂ | 1.58 | S10 |
| CoP@CC | 1.68 | S15 |
| CoP/NCNHP | 1.64 | S16 |
| CoP-Co ₂ P@PC/PG | 1.567 | S20 |

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