Electronic Supplementary Information

Multi-channel V doped CoP hollow nanofibers for high-performance hydrogen

evolution reaction electrocatalyst

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Fig. S1 (a) low magnification and (b) high magnification SEM images for precursor fiber of MC-V-CoP.



Fig. S2 XRD patterns of V doped Co₃O₄



Fig. S3 (a) low magnification and (b) high magnification SEM images of MC-V-Co₃O₄ nanofiber, (c) low magnification and (d) high magnification TEM images of MC-V-Co₃O₄ nanofiber, (e) element mapping of MC-V-Co₃O₄ nanofiber.



Fig. S4 (a) low magnification and (b) high magnification SEM images of precursor nanofibers for NMC-V-CoP.



Fig. S5 (a) low magnification and (b) high magnification SEM images of NMC-V-CoP nanofiber, (c) low magnification and (d) high magnification TEM images of MC-V-CoP nanofiber, (e) element mapping of MC-V-CoP nanofiber.



Fig. S6 (a) N_2 adsorption-desorption curves and (b) corresponding pore size distribution of MC-V-Co₃O₄, MC-V-CoP and NMC-V-CoP.



Fig. S7 EPR spectrum of MC-CoP and MC-V-CoP



Fig. S8 LSV polarization curves of MC-V-CoP in alkaline medium with different loading weight at the scan rate of 5 mV s^{-1} .



Fig. S9 LSV polarization curves of MC-V-Co₃O₄ and MC-V-CoP in alkaline medium at the scan rate of 5 mV s⁻¹.



Fig. S10 CV curves of NMC-V-CoP, MC-CoP and MC-V-CoP in alkaline medium with different scan rates.



Fig. S11 (a) LSV polarization curves, (b) overpotential at different current densities, and (c) EIS Nyquist plots of MC-CoP with different V doping amount.



Fig. S12 (a) SEM and TEM image of MC-V-CoP nanofiber fabricated by the weight ratio of PAN to PS as 2:1.



Fig. S13 (a) SEM and TEM image of MC-V-CoP nanofiber fabricated by the weight ratio of PAN to PS as 2:3.



Fig. S14 (a) LSV polarization curves and (b) EIS Nyquist plots of MC-V-CoP nanofiber fabricated by different addition ratio of PA N and PS.



Fig. S15 CV curves of NMC-V-CoP, MC-CoP and MC-V-CoP in neutral medium with different scan rates.



Fig. S16 EIS Nyquist plots of MC-V-CoP nanofiber in neutral medium.



Fig. S17 (a) SEM image, (b) TEM image and (c) element mapping of MC-V-CoP nanofiber after cycling stability test in alkaline medium.



Fig. S18 (a) SEM image, (b) TEM image and (c) element mapping of MC-V-CoP nanofiber after cycling stability test in neutral medium.



Fig. S19 High-resolution XPS spectrum of MC-V-CoP after long-term test in (I) alkaline and (II) neutral medium, (a) Co 2p, (b) P 2p, (c) V 2p.

| Sample | Specific surface area | Pore volume | Mean pore size |
|-------------------------------------|-----------------------|---------------|----------------|
| | $(m^2 g^{-1})$ | $(cc g^{-1})$ | (nm) |
| MC-V-Co ₃ O ₄ | 101 | 0.371 | 14.846 |
| MC-V-CoP | 39.9 | 0.255 | 2.976 |
| NMC-V-CoP | 38.52 | 0.115 | 3.322 |

 Table S1 The comparison of specific surface, pore volume and mean pore size of

 different electrocatalysts

| Electrocatalyst | Loading | Current density | Overpotential | Reference |
|---|----------------|-----------------------|---------------|-----------|
| | $(mg cm^{-2})$ | (mA cm ²) | (mV) | |
| MC-V-CoP/GCE | 1 | 10 | 65 | This work |
| | | 100 | 132 | |
| | | 200 | 161 | |
| | | 300 | 189 | |
| NiCoP nanocone arrays/NF | 8 | 10 | 104 | 1 |
| | | 100 | 197 | |
| NiCoP/CC | 2 | 10 | 62 | 2 |
| Nicol/ee | | 100 | 158 | |
| $\frac{Co_{0.9}S_{0.58}P_{0.42}}{/GCE}$ | | 10 | 139 | 3 |
| | | 10 | 80 | 4 |
| COP/NPC/IF | | 200 | 162 | |
| $\begin{array}{c} (Co_{1-x}Ni_x)(S_{1-y}P_y)_2 \\ /G/GCE \end{array}$ | 3 | 10 | 117 | 5 |
| Zn _{0.08} Co _{0.92} P/TM | 1.52 | 10 | 67 | 6 |
| NiFe LDH @NiCoP/NF | 2 | 10 | 120 | 7 |
| CoP@a-CoO/CC | 1.5 | 10 | 132 | 8 |
| Ni-Co-P HNB/NF | 2 | 10 | 107 | 9 |
| CoP/Ni ₅ P ₄ /CoP | | 10 | 71 | |
| /NF | | 100 | 140 | 10 |
| Fe-CoP UNSs/NF | 1.4 | 10 | 67 | 11 |
| | | 100 | 148 | |
| | 2 | 10 | 40 | 12 |
| Mo-CoP/CC | | 100 | 130 | |
| | 1 | 10 | 121 | 13 |
| $C-Co_xP/GCE$ | | 50 | 173 | |
| W-CoP NAs/CC | 10 | 10 | 94 | 14 |
| NiCoP-CoP | 1.5 | 10 | 73 | |
| nanowires/NF | | 100 | 183 | 15 |
| N-NiCoP/NCF | 2.08 | 10 | 78 | 16 |
| MoP/CC | 2.5 | 10 | 187 | 17 |
| $(Fe_xNi_{1-x})_2P/NF$ | 1.0 | 10 | 90 | 18 |
| CoP/Graphene/CP | 2.5 | 10 | 83 | 19 |
| Ni _x P/NF | | 10 | 71 | 20 |

Table S2 Comparison of HER activity of MC-V-CoP nanofiber with other reportedphosphide-based HER electrocatalysts in 1.0 M KOH electrolyte.

Note: GCE glass carbon electrode, NF: Ni foam, CC: carbon cloth, TF: Ti foil, TM: Ti mesh, NCF: Ni-Co foam. CP: carbon paper

| Electrocatalyst | Loading (mg cm ⁻²) | Current density (mA cm ⁻²) | Overpotential (mV) | Reference |
|------------------------------------|-----------------------------------|---|-----------------------|-----------|
| | | 10 | 106 | |
| MC-V-CoP | 1.0 | 100 | 243 | This work |
| | | 300 | 540 | |
| W-CoP NAs/CC | 10 | 10 | 102 | 14 |
| FLNPC@MoPNC /MoP-C/CC | 2.42 | 10 | 106 | 21 |
| MoP NA/CC | 2.5 | 10 | 187 | 17 |
| CoP NPs@NPC | 1.4 | 10 | 423 | 22 |
| Ni ₂ S ₃ /NF | 1.6 | 10 | 170 | 23 |
| FeP/CC | 1.5 | 10 | 202 | 24 |
| CoO/CoSe ₂ | 2 | 10 | 337 | 25 |

 Table S3 Comparison of HER activity of MC-V-CoP nanofiber with other reported

 phosphide-based HER electrocatalysts in 1.0 M PBS electrolyte.

Note: GCE glass carbon electrode, NF: Ni foam, CC: carbon cloth, TM: Ti mesh,

Reference

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