Electronic Supplementary Information

CoP nanostructures with different morphologies: synthesis, characterization and study of their electrocatalytic performace toward hydrogen evolution reaction

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Fig. S1 (a) TEM and (b) HRTEM images taken from one single Co_3O_4 nanowire. (c) EDX spectrum of Co_3O_4 NWs. (d) Nitrogen adsorption/desorption isotherm plot and Barrett-Joyner-Halenda (BJH) poresize distribution curve (inset) of nanoporous Co_3O_4 NWs.

Table S1 Comparison of HER performance in acidic electrolytes for CoP nanostructures developed in this study with other non-noble-metal HER electrocatalysts (*a* catalysts directly grown on current collectors).

| Catalyst | Tafel slope | Current density | η at the | Exchange current | Ref. |
|--|-------------|-----------------|------------------------|-----------------------|------|
| | (mV/dec) | (j, mA/cm²) | corresponding <i>j</i> | density (mA/cm²) | |
| | | | (mV) | | |
| double-gyroid MoS ₂ /FTO ^a | 50 | 2 | 190 | 6.9×10 ⁻⁴ | 6c |
| metallic MoS ₂ nanosheets | 54 | 10 | 195 | - | 6d |
| defect-rich MoS ₂ | 50 | 13 | 200 | 8.91×10 ⁻³ | 6e |
| MoS ₂ /graphene/Ni foam ^a | 42.8 | 10 | 141 | - | 6f |
| | | 100 | 263 | | |
| MoO ₃ -MoS ₂ /FTO ^a | 50-60 | 10 | 310 | 8.2×10 ⁻⁵ | 6ј |
| bulk Mo ₂ C | 56 | 1 | ~150 | 1.3×10-3 | 61 |
| bulk MoB | 55 | 1 | ~150 | 1.4×10 ⁻³ | 61 |
| NiMoN _x /C | 35.9 | 2 | 170 | 0.24 | 6р |
| Co _{0.6} Mo _{1.4} N ₂ | - | 10 | 200 | 0.23 | 60 |
| Ni ₂ P hollow nanoparticles | 46 | 10 | 116 | 0.033 | 10a |
| | | 100 | 180 | | |
| Ni ₂ P nanoparticles | 87 | 20 | 140 | - | 10b |
| FeP nanosheets | 67 | 10 | ~240 | - | 10c |
| interconnected network of | 54 | 10 | 125 | 0.086 | 10d |
| MoP nanoparticles | | | | | |
| bulk MoP | 54 | 30 | 180 | 0.034 | 10e |
| Cu ₃ P NWs/CF ^a | 54 | 10 | 122 | 0.13 | 10f |
| CoP hollow nanoparticles | 50 | 20 | 85 | 0.14 | 11 |
| CoP/CNT | 54 | 2 | 70 | 0.13 | 12a |
| | | 10 | 122 | | |

| | 51 | 10 | (7 | 0.200 | 101 |
|--------------------------------------|------|----|------|----------------------------|-----------|
| CoP/CC ^a | 51 | 10 | 6 / | 0.288 | 126 |
| | | | | | |
| np-CoP NWs/Ti ^a | 65 | 20 | 95 | - | 12c |
| - | | | | | |
| CoSe ₂ nanobelts | 50 | 10 | ~120 | 8.4×10-3 | 20 |
| - | | | | | |
| CoSe ₂ NP/CP ^a | 42.1 | 10 | 137 | $(4.9\pm1.4)\times10^{-3}$ | 21 |
| - | | | | · · · · | |
| Co-NRCNTs | 69 | 1 | 140 | 0.01 | 22 |
| | | | | | |
| | _ | 10 | 260 | _ | |
| | | | | | |
| CoP NWs | 54 | 2 | 65 | 0.15 | This work |
| | | - | 00 | 0.10 | |
| | _ | 10 | 110 | - | |
| | | 10 | 110 | | |
| | - | 20 | 1/12 | _ | |
| | | 20 | 142 | | |
| CoPNSs | 61 | 10 | 164 | 0.054 | This work |
| | 01 | 10 | 104 | 0.034 | THIS WOLK |
| CoD NDs | 07 | 10 | 221 | 0.022 | This work |
| COP INFS | 0 / | 10 | 221 | 0.032 | THIS WOLK |



Fig. S2 Calculated exchange current density for CoP NWs in $0.5 \text{ M H}_2\text{SO}_4$ by applying extrapolation method to the Tafel plot.



Fig. S3 (a) XRD pattern, (b) TEM image, (c) HRTEM image, (d) EDX spectrum, and (e) nitrogen adsorption/desorption isotherm plot of CoP NSs.



Fig. S4 (a) XRD pattern of CoP NPs. (b) TEM and HRTEM (inset) images of CoP NPs. (c) EDX spectrum and (d) nitrogen adsorption/desorption isotherm plot of CoP NPs.