

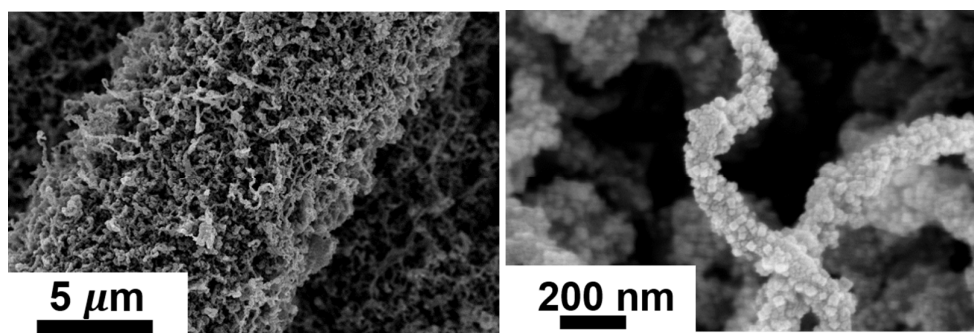
## **Supporting Information**

Toward High-performance and Low-cost Hydrogen  
Evolution Reaction Electrocatalysts: Nanostructuring  
Cobalt Phosphide (CoP) Particles on Carbon Fiber Paper

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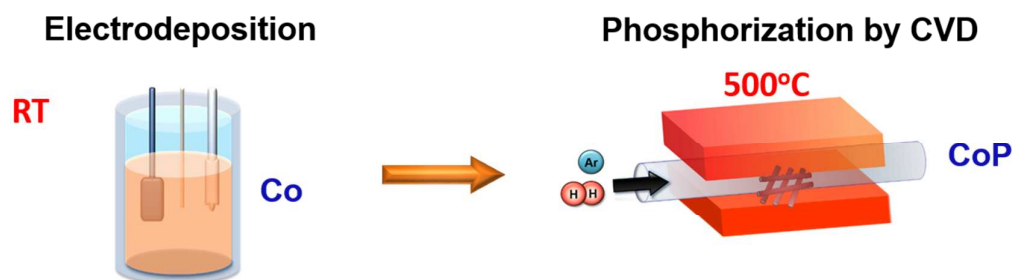
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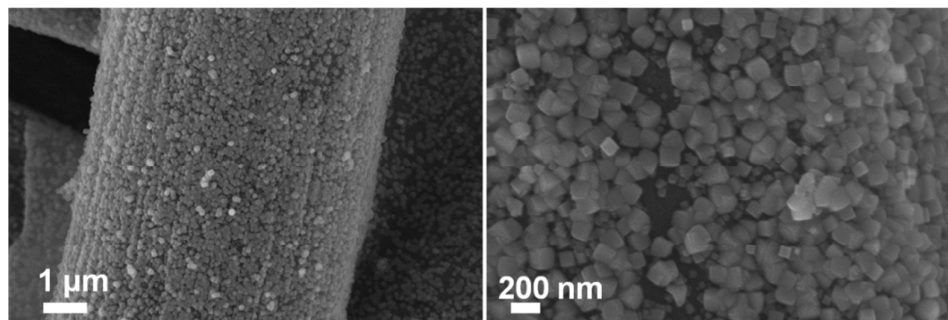
**Figure S1.** The conditions of growing crystalline  $\text{Co}_3\text{O}_4$  nanocubes with size 30-60 nm are the same as growing  $\text{Co}_3\text{O}_4/\text{CFP}$  (150-200 nm) except with a shorter hydrothermal time (4 hrs).



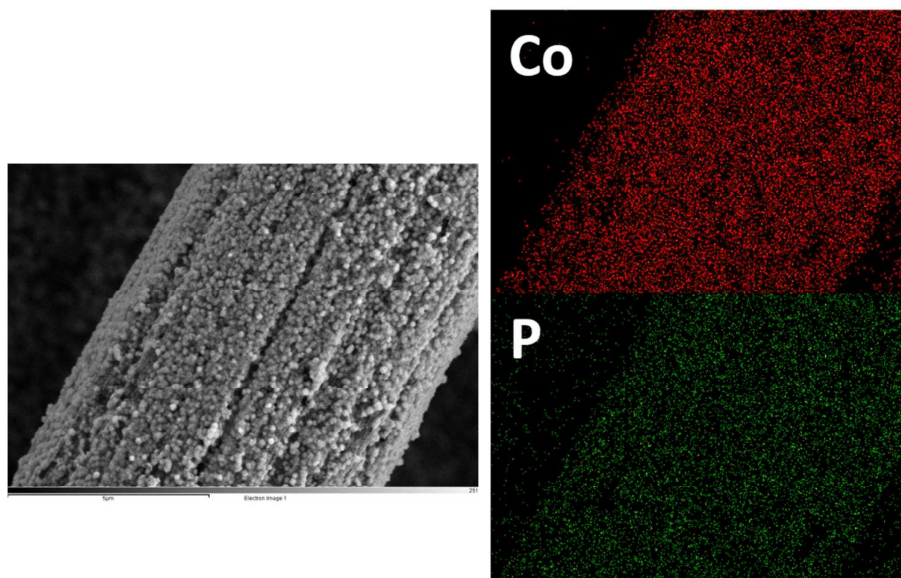
**Figure S2:** The photo shows a HER electrode (1.5 cm x 6 cm) with CoP loaded on carbon fiber paper, suggesting large-scale fabrication is possible.



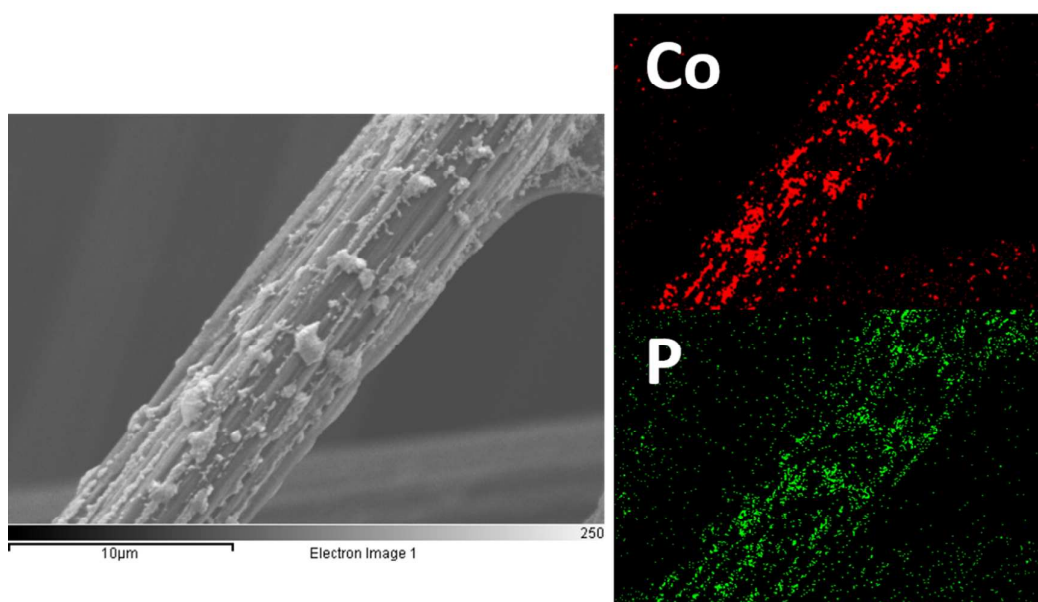
**Figure S3.** The schematic diagram of fabricating CoP by using electrodeposition followed by CVD phosphorization.



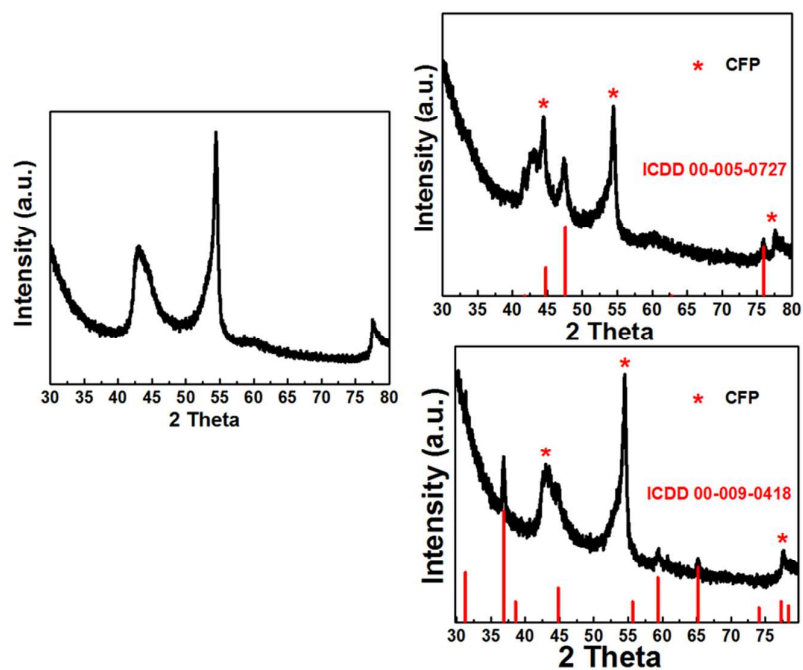
**Figure S4:** As-synthesized cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) by a hydrothermal method. The size of cubic Co<sub>3</sub>O<sub>4</sub> particles is between 150 nm to 200 nm.



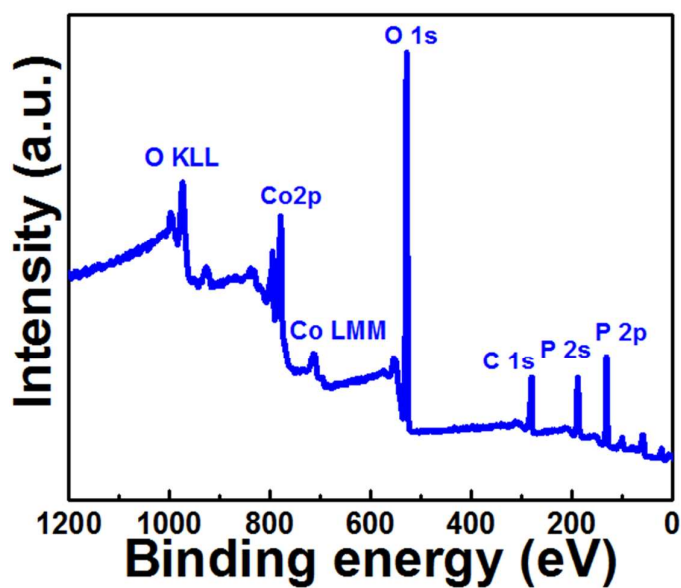
**Figure S5:** EDX element mapping of CoP/CFP-H. It was found that cobalt and phosphorus are evenly distributed.



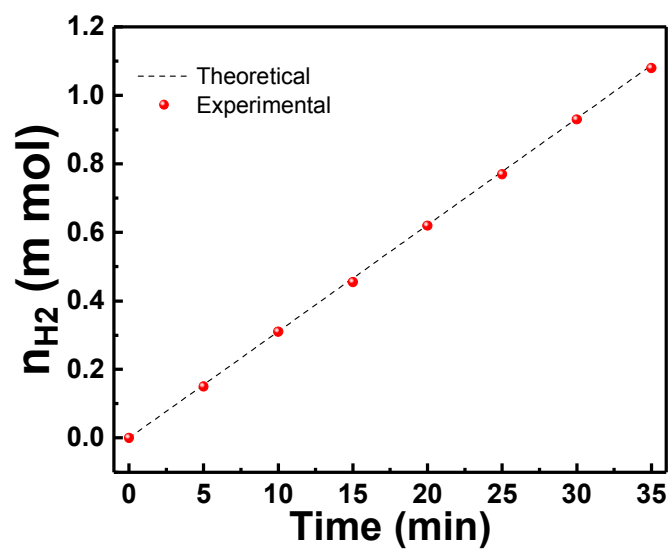
**Figure S6:** EDX element mapping of CoP/CFP-E. It was found that cobalt and phosphorus elements are evenly distributed.



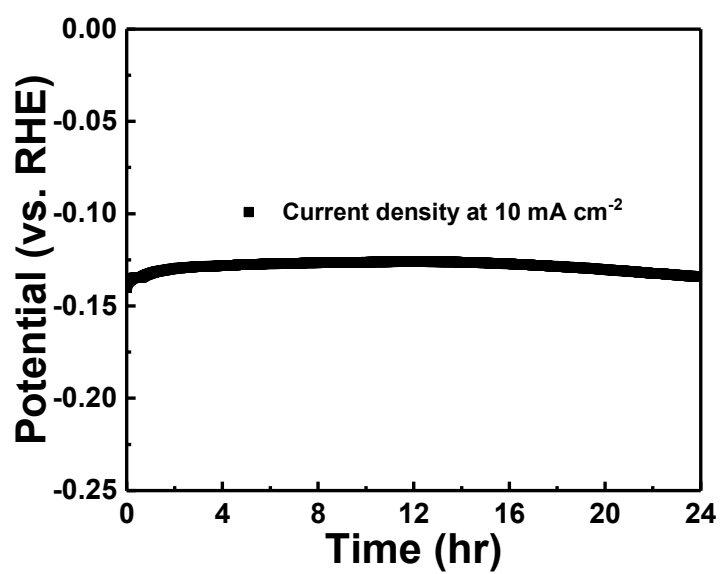
**Figure S7:** XRD of carbon fiber paper,  $\text{Co}_3\text{O}_4/\text{CFP}$  prepared through hydrothermal, and  $\text{Co}/\text{CFP}$  prepared through electrodeposition.



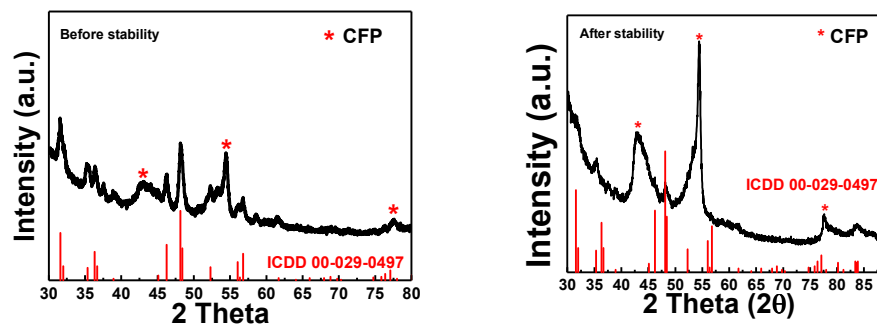
**Figure S8:** Survey scan of  $\text{CoP}/\text{CFP-H}$  shows the presence of Co, P, C and O elements.



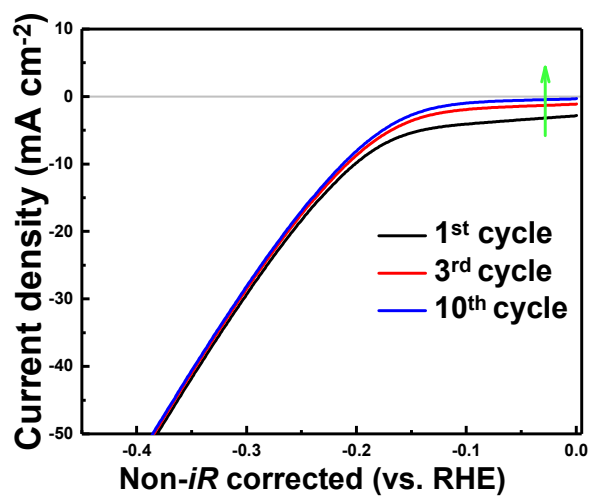
**Figure S9:** The Faradaic efficiency of CoP/CFP-H at cathode current density of  $-100 \text{ mA cm}^{-2}$ .



**Figure S10:** The durability test of CoP/CFP-H in chronopotentiometry mode for 24 hours.



**Figure S11.** The typical XRD of CoP/CFP-H after and stability test for 24 hrs.



**Figure S12:** LSV of CoP/CFP-H after adding 10 mM NaSCN.

Electrocatalysts	Overpotential (mV)			Tafel slope (mV dec <sup>-1</sup> )	Synthesis method	Ref.
	$\eta_{10}$	$\eta_{20}$	$\eta_{100}$	<i>b</i>		
CoP/CFP-H (0.3 mg cm <sup>-2</sup> )	128	144	191	49.7	Hydrothermal (IPA) followed by CVD phosphorization	This work
Metallic MoS2 nanosheets (Loading is not given)	187	-	-	43	Chemically exfoliation via lithium intercalation	(1)
MoO <sub>3</sub> -MoS <sub>2</sub> /FTO (Loading is not given)	310	-	-	50-60	Hot-wire CVD	(2)
CoSe <sub>2</sub> /CFP (Loading is not given)	131	150	181	40	Drop casting (DMF) followed by CVD selenization	(3)
FeP/Graphene (0.28 mg cm <sup>-2</sup> )	123	-	-	50	Solvothermal (DMF) followed by CVD phosphorization	(4)
CoP on RGO (0.29 mg cm <sup>-2</sup> )	> 200	-	-	104 ~ 149 (5 samples)	Hydrothermal (NH <sub>3</sub> ) followed by CVD phosphorization	(5)
In situ CoP-CNTs coupling (Not given)	139	-	-	52	Self-assembly of Co <sub>3</sub> O <sub>4</sub> assisted by MIN solvent & ZIF 67 followed by CVD phosphorization	(6)
CoP nanocrystal on CNT (0.285 mg cm <sup>-2</sup> )	122	-	-	54	Hydrothermal (NH <sub>4</sub> OH) followed by CVD phosphorization	(7)
Co <sub>2</sub> P/Ti (1.0 mg cm <sup>-2</sup> )	95	109	-	45	Reflux condenser (1-octadecene, oleyamine, and nonanoic acid)	(8)
Self-supported CoP nanowire (0.92 mg cm <sup>-2</sup> )	67	100	204	51	Hydrothermal ( NH <sub>4</sub> F, urea) followed by CVD phosphorization	(9)

**Table S1:** This table lists out the performances of some non-noble catalysts and their synthesis methods.



## References

1. Lukowski MA, Daniel AS, Meng F, Forticaux A, Li L, Jin S. Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS<sub>2</sub> nanosheets. *J Am Chem Soc.* 2013;135(28):10274-7.
2. Chen Z, Cummins D, Reinecke BN, Clark E, Sunkara MK, Jaramillo TF. Core-shell MoO<sub>3</sub>-MoS<sub>2</sub> nanowires for hydrogen evolution: a functional design for electrocatalytic materials. *Nano Lett.* 2011;11(10):4168-75.
3. Kong D, Wang H, Lu Z, Cui Y. CoSe<sub>2</sub> nanoparticles grown on carbon fiber paper: an efficient and stable electrocatalyst for hydrogen evolution reaction. *J Am Chem Soc.* 2014;136(13):4897-900.
4. Zhang Z, Lu B, Hao J, Yang W, Tang J. FeP nanoparticles grown on graphene sheets as highly active non-precious-metal electrocatalysts for hydrogen evolution reaction. *Chem Commun (Camb).* 2014;50(78):11554-7.
5. Ma L, Shen X, Zhou H, Zhu G, Ji Z, Chen K. CoP nanoparticles deposited on reduced graphene oxide sheets as an active electrocatalyst for the hydrogen evolution reaction. *Journal of Materials Chemistry A.* 2015;3(10):5337-43.
6. Wu C, Yang Y, Dong D, Zhang Y, Li J. In Situ Coupling of CoP Polyhedrons and Carbon Nanotubes as Highly Efficient Hydrogen Evolution Reaction Electrocatalyst. *Small.* 2017;13(15).
7. Liu Q, Tian J, Cui W, Jiang P, Cheng N, Asiri AM, et al. Carbon nanotubes decorated with CoP nanocrystals: a highly active non-noble-metal nanohybrid electrocatalyst for hydrogen evolution. *Angew Chem Int Ed Engl.* 2014;53(26):6710-4.
8. Callejas JF, Read CG, Popczun EJ, McEnaney JM, Schaak RE. Nanostructured Co<sub>2</sub>P Electrocatalyst for the Hydrogen Evolution Reaction and Direct Comparison with Morphologically Equivalent CoP. *Chemistry of Materials.* 2015;27(10):3769-74.
9. Tian J, Liu Q, Asiri AM, Sun X. Self-supported nanoporous cobalt phosphide nanowire arrays: an efficient 3D hydrogen-evolving cathode over the wide range of pH 0-14. *J Am Chem Soc.* 2014;136(21):7587-90.