

Electronic Supplementary Information

Hierarchically scaffolded CoP/CoP₂ nanoparticles: controllable synthesis and their application as a well-matched bi-functional electrocatalyst for overall water splitting

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Figure S1

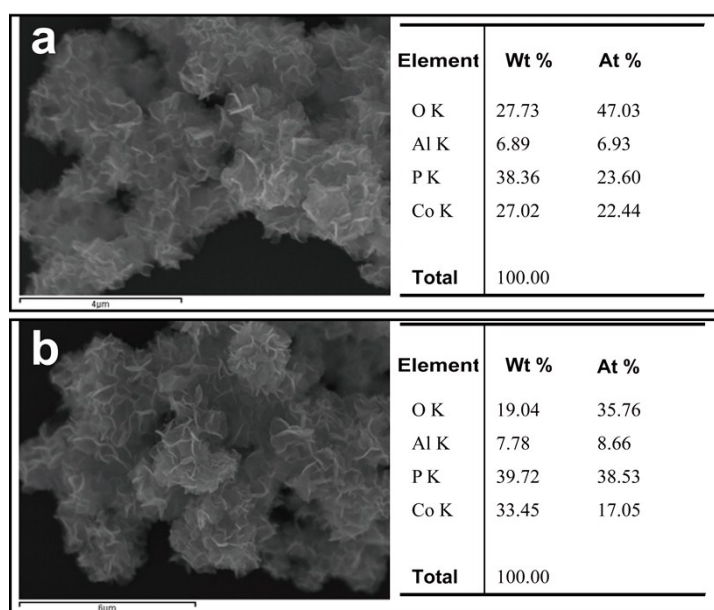


Fig. S1 SEM/EDX images of (a) f-CoP/Al₂O₃ electrocatalyst and (b) f-CoP/CoP₂/Al₂O₃ electrocatalyst.

Figure S2

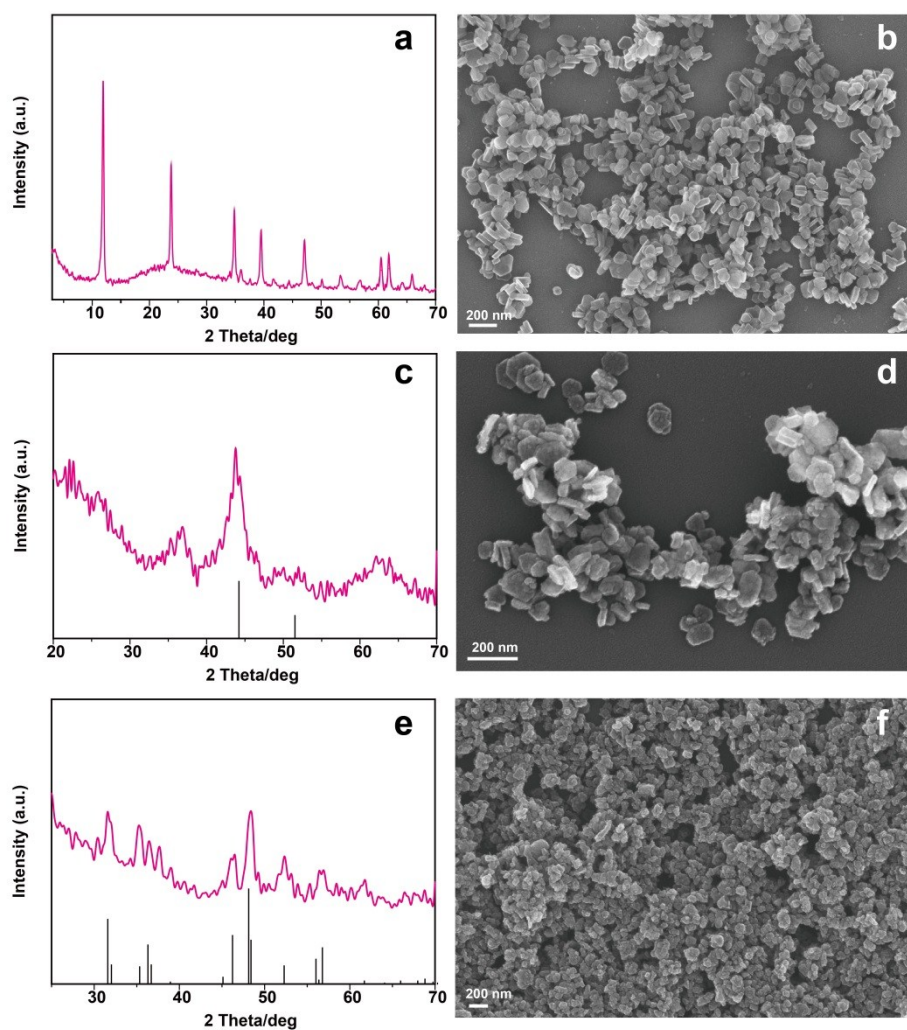


Fig. S2 (a) XRD pattern and (b) SEM images of p-CoAl-LDH precursor, (c) XRD pattern and (d) SEM images of p-Co/Al₂O₃ nanoparticles formed after reduction of p-CoAl-LDH precursor, (e) XRD pattern and (f) SEM images of p-CoP/Al₂O₃ composite formed after short-duration phosphorization of p-Co/Al₂O₃.

Figure S3

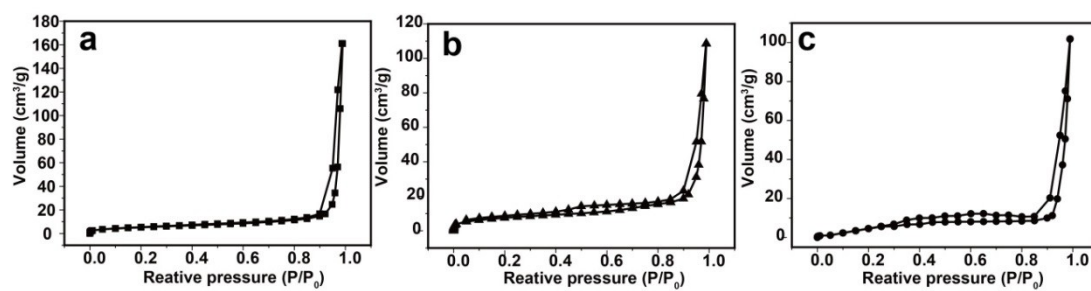


Fig. S3 N_2 adsorption/desorption isotherm of (a) p-CoP/ Al_2O_3 , (b) f-CoP/ Al_2O_3 , and (c) f-CoP/ CoP_2 / Al_2O_3 composites.

Figure S4

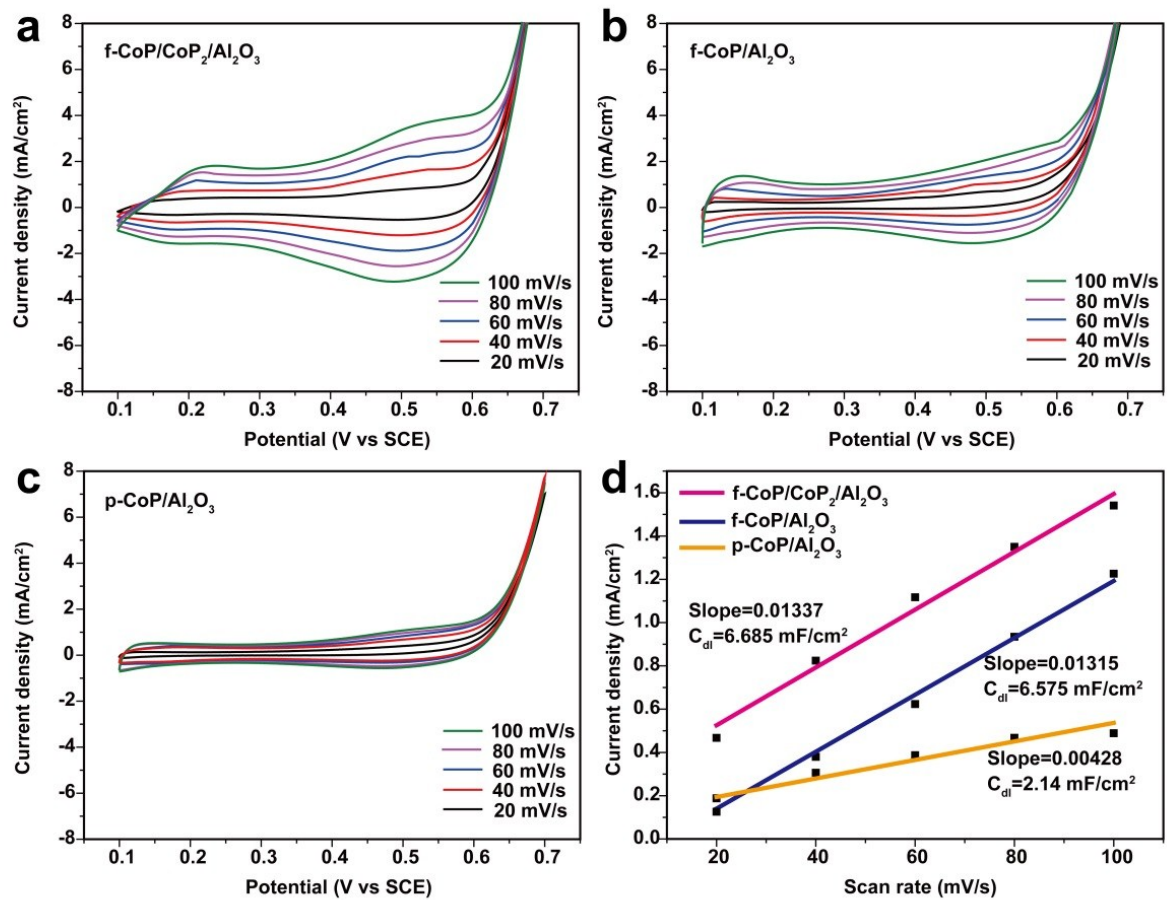


Fig. S4 Cyclic voltammograms (CVs) for (a) f-CoP/CoP₂/Al₂O₃, (b) f-CoP/Al₂O₃, (c) p-CoP/Al₂O₃ measured at different scan rates from 20 to 100 mV/s and (d) corresponding plots of the current density at 0.2 V vs SCE at the scan rate.

Figure S5

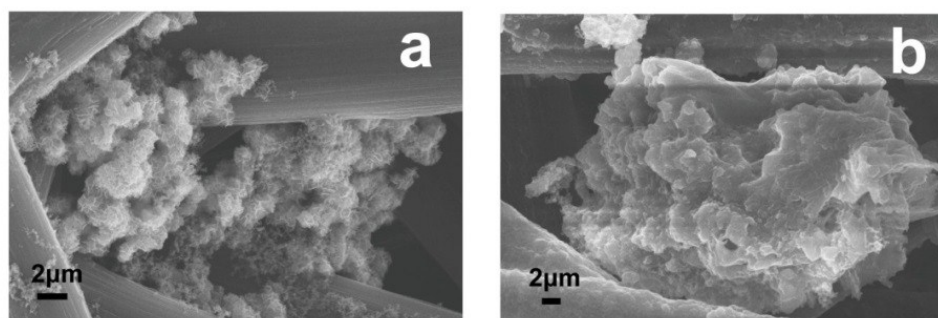


Fig. S5 The SEM images of f-CoP/CoP₂/Al₂O₃ electrode which is adhesion in carbon paper (a) before electrochemical testing, (b) after electrochemical testing for 24h.

Table S1

Comparison of OER performance in alkaline electrolytes for f-CoP/CoP₂/Al₂O₃ composite and some reported high-efficient non-noble metal phosphides based OER electrocatalysts.

Catalyst	Loading mass (mg cm ⁻²)	Electrolyte	Over-potential at 10 mA cm ⁻² (mV)	Ref.
NiCoFe-LDHs/CFC	0.4	1.0 M KOH	234	[1]
Co NPs	0.2	1.0 M KOH	390	[2]
NiCo ₂ O ₄	0.069	1.0 M KOH	419.3	[3]
Co ₃ O ₄	0.136	1.0 M KOH	410	[4]
NiCo-LDH	0.17	1.0 M KOH	370	[5]
Sandwich-like CoP/C	0.36	1.0 M KOH	330	[6]
CoP film	~	1.0 M KOH	345	[7]
CoP nanorod	0.71	1.0 M KOH	320	[8]
p-CoP/Al ₂ O ₃	0.2	1.0 M KOH	357	This work
f-CoP/Al ₂ O ₃	0.2	1.0 M KOH	320	This work
f-CoP/CoP ₂ /Al ₂ O ₃	0.2	1.0 M KOH	300	This work

Reference:

- [1] A. Wang, H. Xu, G. Li, *ACS Energy Lett.*, 2016, **1**, 445.
- [2] L. Wu, Q. Li, C. H. Wu, H. Zhu, *J. Am. Chem. Soc.*, 2015, **137**, 7071.
- [3] J. Wang, T. Qiu, X. Chen, Y. Lu, W. Yang, *J. Power Sources*, 2014, **268**, 341.
- [4] Y. Wang, T. Zhou, K. Jiang, P. Da, Z. Peng, J. Tang, B. Kong, W. B. Cai, Z. Yang, G. Zheng, *Adv. Energy Mater.*, 2014, **4**, 1400696.
- [5] H. Liang, F. Meng, M. Cabán-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang, S. Jin, *Nano Lett.*, 2015, **15**, 1421.
- [6] Y. Bai, H. Zhang, Y. Feng, L. Fang, Y. Wang, *J. Mater. Chem. A*, 2016, **4**, 9072.
- [7] N. Jiang, B. You, M. Sheng, Y. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 6251.
- [8] J. Chang, Y. Xiao, M. Xiao, J. Ge, C. Liu, W. Xing, *ACS Catal.*, 2015, **5**, 6874.

Table S2

Comparison of HER performance in alkaline electrolytes for f-CoP/CoP₂/Al₂O₃ composite and some reported high-efficient non-noble metal phosphides based HER electrocatalysts.

Catalyst	Loading mass (mg cm ⁻²)	Electrolyte	Over-potential at 10 mA cm ⁻² (mV)	Ref.
NiCoFe-LDHs/CFC	0.4	1.0 M KOH	200	[1]
CoP/CC	0.92	1.0 M KOH	209	[2]
FeP NAs/CC	1.5	1.0 M KOH	218	[3]
Fe ₂ P/NGr	1.71	1.0 M KOH	380	[4]
Amorphous MoS ₂ /FTO	~	1.0 M KOH	540	[5]
Ni wire	0.1	1.0 M NaOH	350	[6]
Ni-Mo alloy/Ti foil	1.0	2.0 M KOH	80	[6]
Co-NRCNTs	0.28	1.0 M KOH	370	[7]
CP@Ni-P		1.0 M KOH	117	[8]
p-CoP/Al ₂ O ₃	0.2	1.0 M KOH	181	This work
f-CoP/Al ₂ O ₃	0.2	1.0 M KOH	170	This work
f-CoP/CoP ₂ /Al ₂ O ₃	0.2	1.0 M KOH	138	This work

Reference:

- [1] A. Wang, H. Xu, G. Li, *ACS Energy Lett.*, 2016, **1**, 445.
- [2] J. Tian, Q. Liu, A. M. Asiri, X. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587.
- [3] Y. Liang, Q. Liu, A. M. Asiri, X. Sun, Y. Luo, *ACS Catal.*, 2014, **4**, 4065.
- [4] Z. Huang, C. Lv, Z. Chen, Z. Chen, F. Tian, C. Zhang, *Nano Energy*, 2015, **12**, 666.
- [5] D. Merki, S. Fierro, H. Vrubel, X. Hu, *Chem. Sci.*, 2011, **2**, 1262.
- [6] J. R. McKone, B. F. Sadtler, C. A. Werlang, N. S. Lewis, H. B. Gray, *ACS Catal.*, 2013, **3**, 166.
- [7] X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova, T. Asefa, *Angew. Chem. Int. Ed.*, 2014, **53**, 4372.
- [8] X. Wang, W. Li, D. Xiong, D. Y. Petrovykh, L. Liu, *Adv. Funct. Mater.*, 2016, **26**, 4067.