Supporting Information

Phosphorus-bridged ternary metal alloy encapsulated in few-layered nitrogen-doped graphene for highly efficient electrocatalytic hydrogen evolution

Liping Huang,[a] Wenyao Li*,[a,c] Xudun Shen,[a] Chunyan Sun,[a] Jin Yang,[a] Xue-rong Shi*,[a] and Min Zeng*,[b]

[a.] School of Materials Engineering, Shanghai University of Engineering Science, Shanghai 201620, China.

[b.] Department of Micro/Nano Electronics, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai, 200240, PR China.

[c.] Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, London, WC1E 7JE, UK.

* Corresponding authors

E-mails: Wenyao.li@ucl.ac.uk (Wenyao Li); shixuer05@mails.ucas.ac.cn (Xue-Rong Shi); minzeng@sjtu.edu.cn (Min Zeng)

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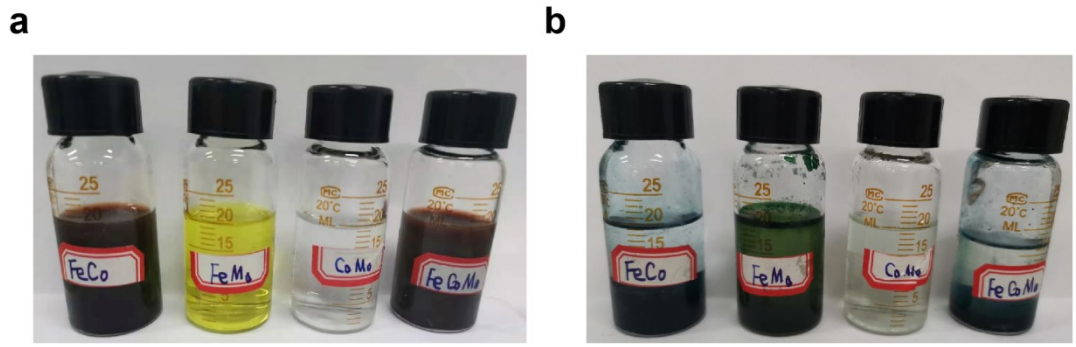

Figure S1 Phenomenon of the materials before reaction (a) and after the reaction completed (b).

The left picture shows the state when all the reaction materials are added, and the mixed solution is uniform, the right picture shows the phenomenon of the reaction after 20 h at 80 °C. From the picture, we can find that the bottles labeled FeCo, FeMo, FeCoMo generate precipitations, while the CoMo has no reaction. Thus, in subsequent experiments, CoMo was not used as a reference control.

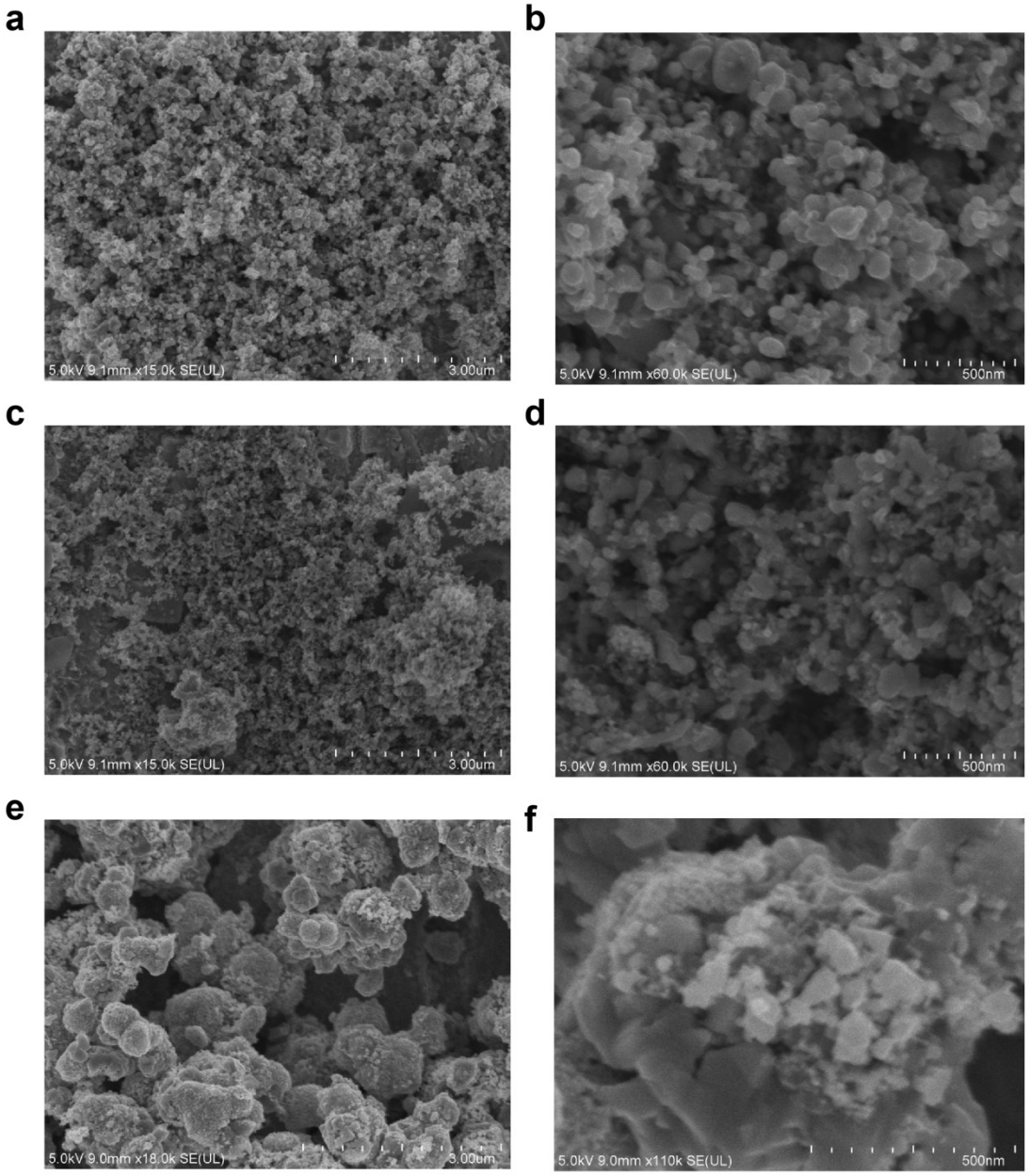

Figure S2 (a-b) SEM images of FeCo@NC. (c-d) SEM images of FeMo@NC. (e-f) SEM images of FeCoMo@NC.

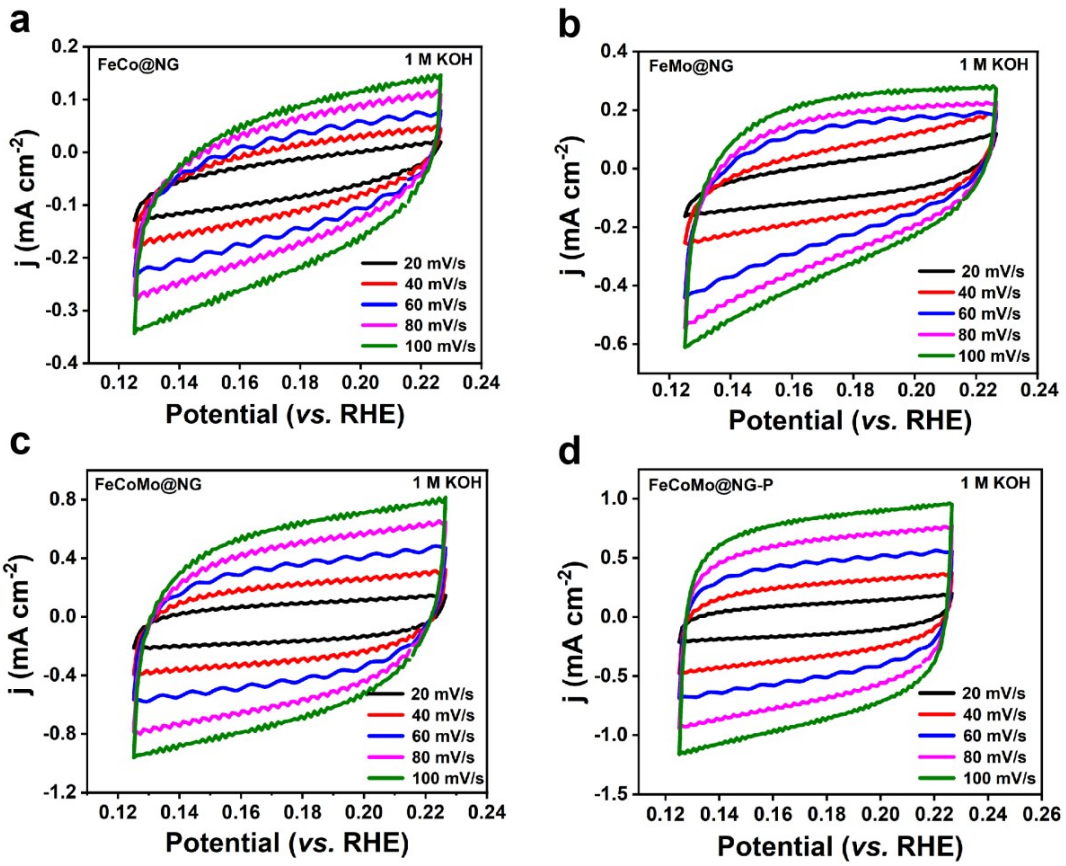

Figure S3 Cyclic voltammograms of FeCo@NG, FeMo@NG, FeCoMo@NG, FeCoMo@NG-P within the range of 0.13 to 0.23 V *vs* RHE with scan rate from 20 to 100 mV s^{-1} in 1 M KOH.

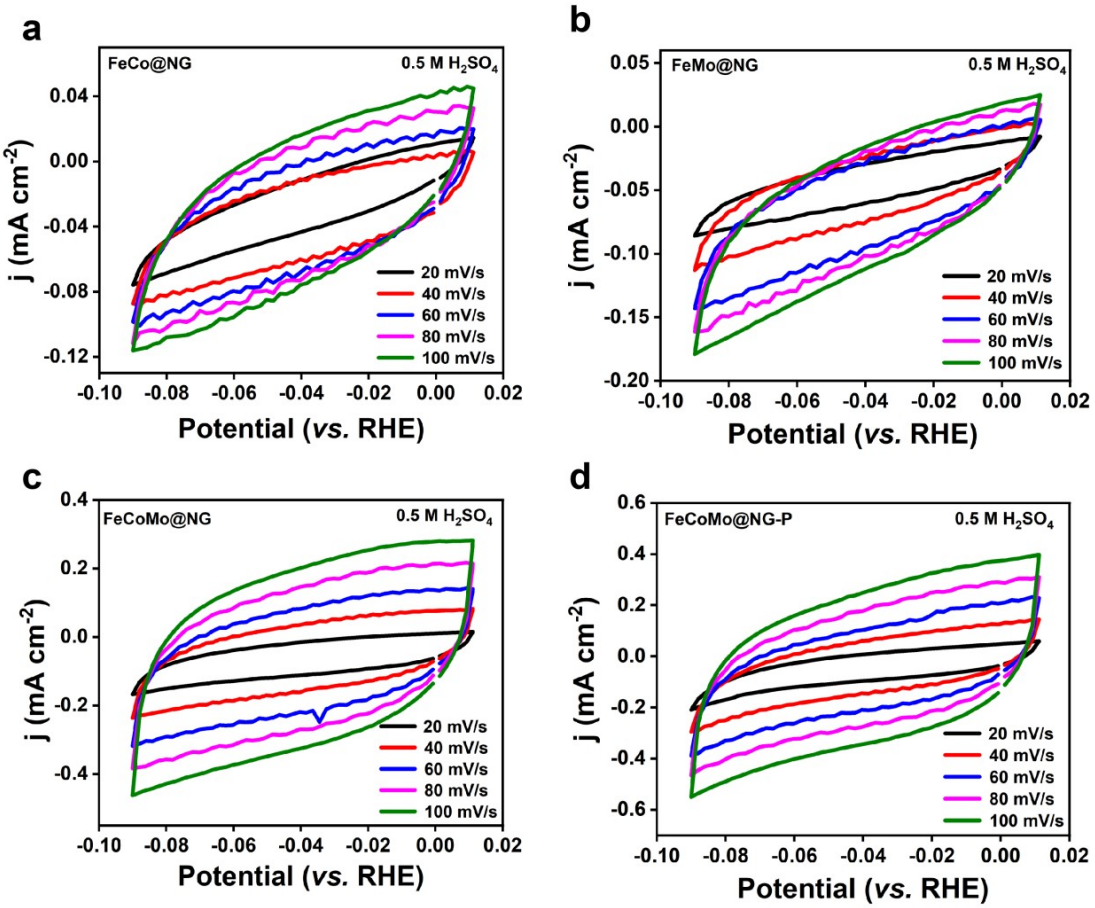

Figure S4 Cyclic voltammograms of FeCo@NG, FeMo@NG, FeCoMo@NG, FeCoMo@NG-P within the range of 0.13 to 0.23 V *vs* RHE with scan rate from 20 to 100 mV s^{-1} in 0.5 M H_2SO_4.

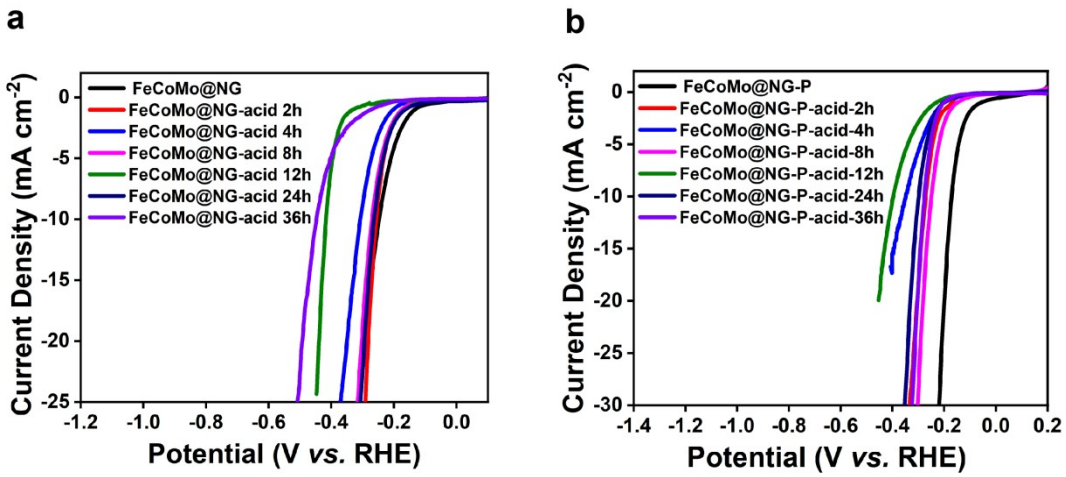

Figure S5 HER polarization curves for FeCoMo@NC and FeCoMo@NC-P samples after soaking in 0.5 M H_2SO_4 for several hours.

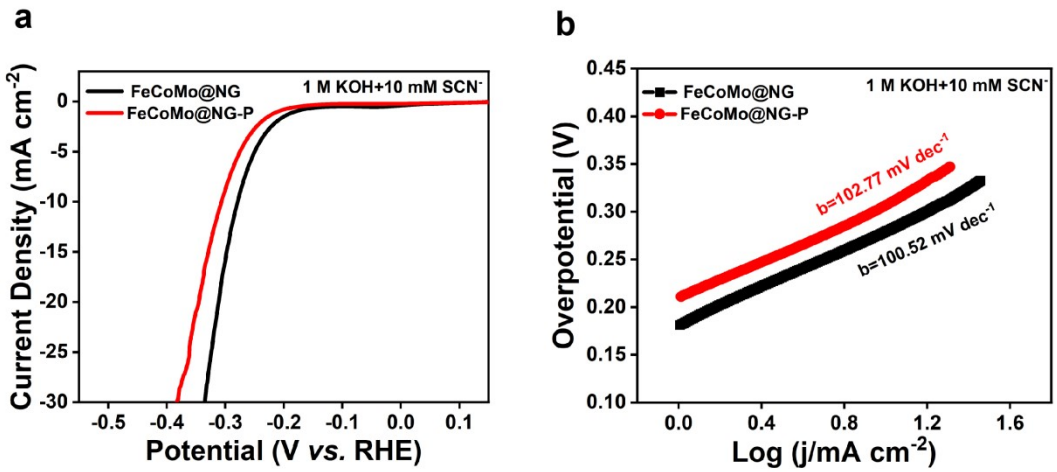

Figure S6 (a) HER polarization curves for FeCoMo@NC and FeCoMo@NC-P samples in 1 M KOH+10 mM SCN^- mixed electrolyte. (b) The corresponding Tafel slope from (a).

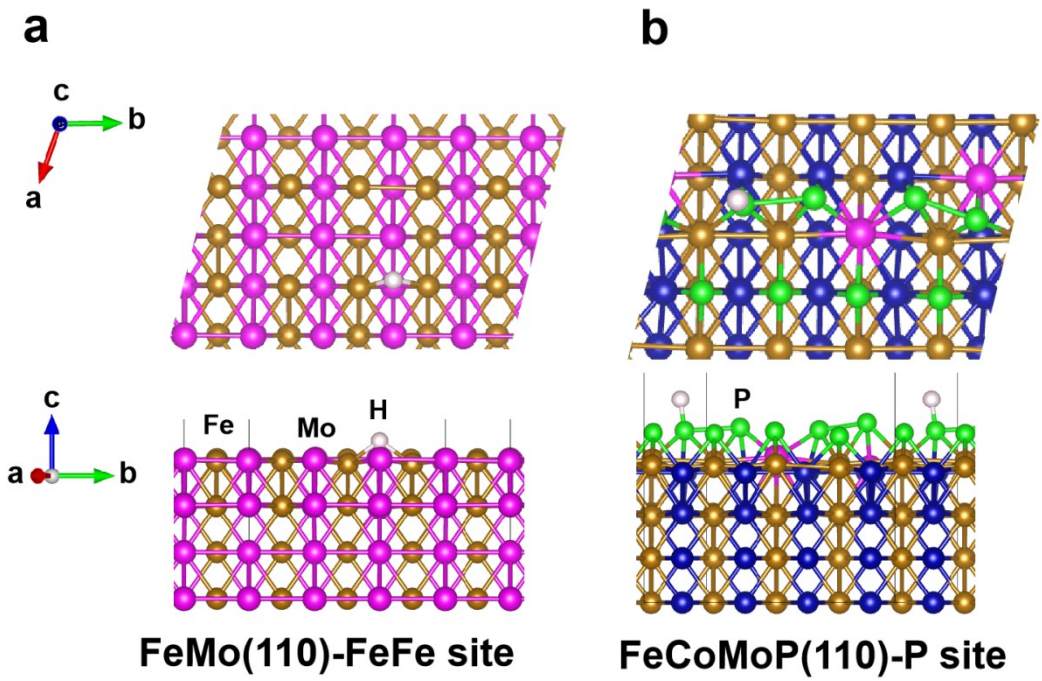

Figure S7 (a) Top and side view of the most stable H adsorption configuration on FeMo(110), and (b) FeCoMoP(110)-P site.

Table S1 Chemical compositions of FeCoMo@NC-P by XPS measurement.

Sample	C (atom %)	N (atom %)	Fe (atom %)	Co (atom %)	Mo (atom %)	P (atom %)
FeCoMo@NC-P	79.91	4.74	2.56	2.88	0.94	8.96

Table S2 Comparison of HER performance of FeCoMo@NG-P with reported electrocatalysts in alkaline solution.

Electrocatalyst	Electrolyte	Mass loading (mg cm^{-2})	Overpotential @10 mA cm^{-2}	Tafel slops (mV dec^{-1})	*Ref.*
FeCoMo@NG-P	1.0 M KOH	0.189	170 mV	93.57	This work
CoFe-Se-P	0.1 M KOH	0.14	183.1 mV	181	1
Ni-Fe-Pt NCs	1.0 M KOH	0.7	463 mV	81	2
Ni-Fe-P	1.0 M KOH	0.42	182 mV	85	3
Co@Co-N/rGO	1.0 M KOH	0.5	180 mV	43	4
V-doped CoP	1.0 M KOH	0.2	340 mV	86.1	5
FeCo/Co_2P@NPCF	1.0 M KOH	0.28	260 mV	120	6
ONPPGC/OCC	1.0 M KOH	0.1	446 mV	154	7
Fe@N-C	1.0 M KOH	0.97	330 mV	158	8
Co@N-C	1.0 M KOH		210 mV	108	

Table S3 Comparison of HER performance of FeCoMo@NG-P with reported electrocatalysts in 0.5 M H_2SO_4.

Electrocatalyst	Electrolyte	Mass loading (mg cm^{-2})	Overpotential @10 mA cm^{-2}	Tafel slops (mV dec^{-1})	Ref.
FeCoMo@NG-P	0.5 M H_2SO_4	0.189	196 mV	63.17	This work
NSC/MPA-5	0.5 M H_2SO_4	0.25	331 mV	99	9
S-600	0.5 M H_2SO_4	0.285	262 mV	74	10
FeCo@NCNTs-NH	0.1 M H_2SO_4	0.32	276 mV	74	11
CoNi@NC	0.1 M H_2SO_4	0.32	224 mV	104	12
Fe-CoP/HPFs	0.5 M H_2SO_4	0.796	198 mV	68	13
Co-NRCNT	0.5 M H_2SO_4	0.28	260 mV	69	14
C_3N_4@NG	0.5 M H_2SO_4	0.1	240 mV	51.5	15
Ni-Sn@C NPs	0.5 M H_2SO_4	0.1	~350 mV	35	16

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