Supporting Information for

Mn doped CoP nanoparticle clusters: an efficient electrocatalyst for hydrogen evolution reaction

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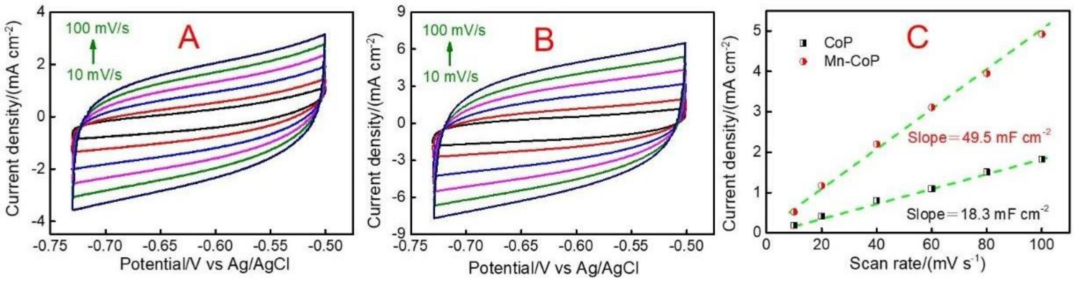

Fig. S1 CVs of Mn-CoP and CoP catalysts (A, B) between the potential region of -0.5 V to -0.73 V (Ag/AgCl) with scan rates of 10, 20, 40, 60, 80 and 100 mV/s in a 1 M KOH solution. The anodic charging currents measured at -0.6 V vs Ag/AgCl plotted as a function of scan rate (C). The determined double-layer capacitance of the system is taken as the average of the absolute value of the slope of the linear fits to the data

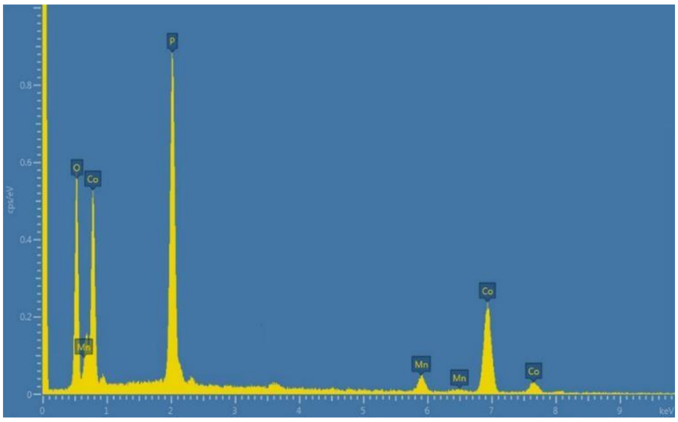

Fig. S2 EDX spectra of Mn-CoP materials

All the spectra peaks of Mn, Co, P elements were revealed obviously. A strong peak of O element was due to that some phosphide species on the material surface were oxidized to phosphates in the air.

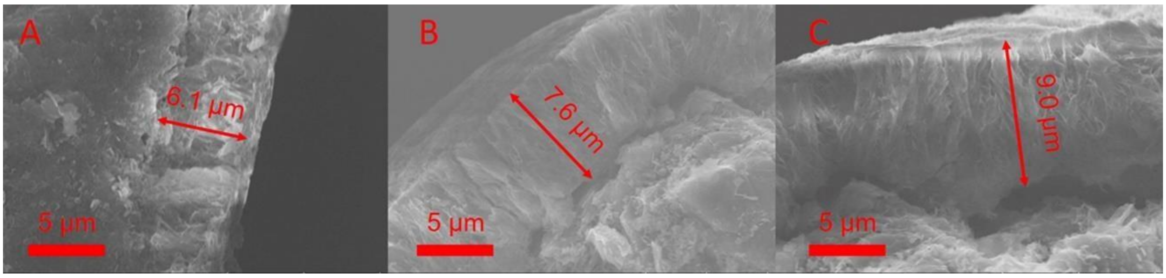

Fig. S3 SEM images of Mn-CoP catalysts prepared at the pulse cycles of 400, 600, and 800 times.

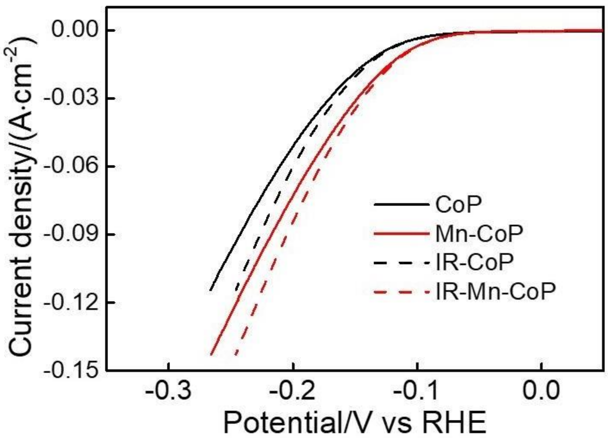

Fig. S4 Original and IR-corrected polarization curves of CoP and Mn-CoP catalysts

The influence of material type of counter electrode on the HER activity was presented in Fig. S1. It is found that there is only a slight difference in catalytic activity for Pt wire and carbon rod counter electrodes.

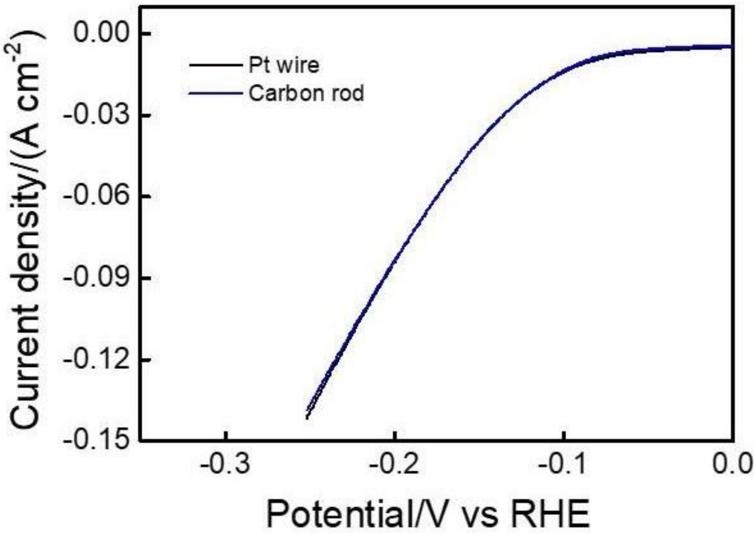

Fig. S5 Polarization curves of Mn-CoP measured in the 1 M KOH solution where Pt wire or carbon rod was used as the counter electrode.

Table S1. Summary of HER performance of representative catalysts*.

Catalyst	Substrate	10 (mV)	Tafel slope (mV/dec)	Electrolyte	Citation Information
$Ni_{12}P_5$-Ni_2P	Ni foam	120	79.1	0.5 M H_2SO_4	Angew. Chem. Int. Ed. 2015, 54, 8188 –8192
Mn-Ni_2P	Nickel foam	<103	135	1 M NaOH	Chem. Commun, 2017, 53(80): 11048-11051.
Ni_2P	Ti foil	117	46	0.50 M H_2SO_4	J. Am. Chem. Soc. 2013, 135, 9267-9270.
CoP	Carbon cloth	67	51	0.50 M H_2SO_4	J. Am. Chem. Soc. 2014, 136, 7587-7590.
CoP/CNTs	GCE	139	52	0.50 M H_2SO_4	Small, 2017, 13, 1602873
CoP/CNTs	GCE	122	54	0.50 M H_2SO_4	Angew. Chem. Int. Ed. 2014, 53, 6710-6714.
Ni-Mo nanopowder	Ti foil	79		1 M NaOH	ACS Catal. 2013, 3, 166-169.
Bulk Mo_2C	Carbon paste	208	56	0.50 M H_2SO_4	Angew. Chem. Int. Ed. 2012, 51, 12703-12706.
Bulk MoB	Carbon paste	212	55	0.50 M H_2SO_4	
Mo_2N–MoC	GCE	157	68	1 M NaOH	Adv. Mater. 2018, 30, 1704156
		154	55	0.50 M H_2SO_4	
Mo_2C/CNTs	Carbon paper	149	55.2	0.1 M $HClO_4$	Energ. Environ. Sci. 2013, 6, 943-951.
Mo_1Soy	Carbon paper	177	66.4	0.1 M $HClO_4$	Energ. Environ. Sci. 2013, 6, 1818-1826.
Mo_1Soy-RGO	Carbon paper	109	62.7	0.1 M $HClO_4$	
Mo_2C/C	Carbon paper	311	87.6	0.1 M $HClO_4$	
$Co_{0.6}Mo_{1.4}N_2$	GCE	202		0.1M $HClO_4$	J. Am. Chem. Soc. 2013, 135, 19186-19192

MoS_3(33%)/MWCNT-NC	Silver electrode	206	40	1 M H_2SO_4	Appl. Catal. B-Environ. 2013, 134-135, 75-82.
Core-shell MoO_3-MoS_2	FTO	254	50-60	0.5 M H_2SO_4	Nano. Lett. 2011, 11, 4168-4175.
Defect-rich MoS_2 nanosheets	GCE	190	50	0.5 M H_2SO_4	Adv. Mater. 2013, 25, 5807-5813.
MoS_2	Carbon cloth	191	64	0.5 M H_2SO_4	Adv. Mater. 2017, 29, 1703863
MoS_2@Au	Au electrode	226	69	0.5 M H_2SO_4	Energ. Environ. Sci. 2013, 6, 625-633.
amorphous MoS_3	GCE	211	40	1 M H_2SO_4	Chem. Sci. 2011, 2, 1262-1267.
MoS_2/RGO hybrid	GCE	154	41	0.5M H_2SO_4	J. Am. Chem. Soc. 2011, 133, 7296-7299.
MoS_2/MGF	GCE	146	42	0.5 M H_2SO_4	Adv. Funct. Mater. 2013, 23, 5326-5333.
MoS_2/CNTs	Glass carbon	184	44.6	0.5 M H_2SO_4	Nanoscale 2013, 5, 7768-7771.
Cu_2MoS_4	GCE	321	95	pH 0 H_2SO_4	Energ. Environ. Sci. 2012, 5, 8912-8916.
WS_2/RGO	GCE	265	58	0.5M H_2SO_4	Angew. Chem. Int. Ed. 2013, 52, 13751-13754
WS nanosheets	GCE	233	55	0.5 M H_2SO_4	Nat. Mater. 2013, 12, 850-855.
WS_2 nanosheets	GCE	151	72	1 M H_2SO_4	Appl. Catal. B-Environ. 2012, 125, 59-66.
Cobalt-sulfide	FTO	165	93	1.0MpH7PBS	J. Am. Chem. Soc. 2013, 135, 17699-17702
$NiWS_x$	FTO	373	96	pH 7 PBS	Energ. Environ. Sci. 2013, 6, 2452-2459.
$CoWS_x$	FTO	271	78	pH 7 PBS	

$CoMoS_x$	FTO	241	85	pH 7 PBS	
FeS_2	GCE	192.6	62.5	0.5 M H_2SO_4	Energ. Environ. Sci. 2013, 6, 3553-3558
$FeSe_2$	GCE		65.3	0.5 M H_2SO_4	
$Fe_{0.43}Co_{0.57}S_2$	GCE	264	55.9	0.5 M H_2SO_4	
CoS_2	GCE	232	44.6	0.5 M H_2SO_4	
$CoSe_2$	GCE	231	42.4	0.5 M H_2SO_4	
$Co_{0.56}Ni_{0.44}Se_2$	GCE	250	49.7	0.5 M H_2SO_4	
$Co_{0.32}Ni_{0.68}S_2$	GCE		66.8	0.5 M H_2SO_4	
NiS_2	GCE		41.6	0.5 M H_2SO_4	
$NiSe_2$	GCE	250	56.9	0.5 M H_2SO_4	

*Notes

CNT: carbon nanotube; RGO: reduced graphene oxide; NC: nanocomposite;

MGF: mesoporous graphene foams; FTO: fluorine-doped tin oxide;

GCE: glassy carbon electrode