Electronic Supplementary Material (ESI)

CoMn phosphide encapsulated in nitrogen-doped graphene for electrocatalytic hydrogen evolution over a broad pH range

I. Material preparation

Raw materials

Potassium hexacyanocobaltate, Manganese acetate ($Mn(CH_3COO)_2 \cdot H_2O$), Anhydrous ethanol were purchased from Shanghai Chemical Reagent Co. Ltd. The Pt was purchased from Pharmaceutical Group Co. Ltd. All prepared solutions are deionized water (18.2 Ω•cm^{-2} resistivity). All chemicals were of analytical grade and used as received without further purification.

Synthesis of CoMn@NG and CoMn-P@NG

10 mL of 25 mM manganese acetate solution was used as solution A, and 1.5 g PVP was added. After stirring, 10 mL 25 mM cobalt potassium cyanide was added to solution A with a dropper, and leave to set at room temperature for 24 h to obtain a solid precipitate. After washing with distilled water and ethanol for several times, freeze-drying was used to produce off-white PB-CoMn colloids. PB-CoMn was then annealed in Ar gas at 600 °C for 1 h with a heating rate of 10 °C min^{-1}, and the product was obtained. In order to obtain CoMn-P@NG, sodium hypophosphate and CoMn@NG were placed at both ends of the same crucible, and the part containing sodium hypophosphate was placed in the upper part of the gas in a tubular heating furnace. The part containing sodium hypophosphate was calcinated at 400 °C for 2 h in an argon atmosphere, and the heating rate was 5 °C min^{-1}.

Electrochemical measurements

1 mg CoMn-P@NG or CoMn@NG powder, 0.5 mg Ketjen black mix with 220 μL absolute ethanol and 60 μL deionized water, and add 10 μL Naftion solution. And then the electrocatalyst ink is prepared through ultrasonic dispersion in ice-water bath for 45 minutes. Drop 10 μL catalyst ink on the glass carbon electrode with a diameter of 4 mm with a load of 0.27 mg cm^{-2}. 20 wt % Pt/C was prepared in the same manner. Drop 10 μL ink on the glass carbon electrode as a reference. Carbon rod was used as a counter electrode and a saturated Ag/AgCl electrode was used as a reference electrode in the three-electrode test system. Fast activation CV cycles were performed in 1 M KOH and 0.5 M H_2SO_4 solution at the scan rate of 100 mV s^{-1}. After the CV curves were stabilized, the test scanning rate of LSV was set to 2 mV s^{-1}, and hydrogen evolution reaction tests were performed for 20 wt% Pt/C, CoMn@NG and CoMn-P@NG.

Physical characterization

SEM images were taken from Zeiss scanning electron microscope. TEM and scanning transmission electron microscopy (STEM) were carried on an FEI Tecnai F20 transmission electron microscope at an accelerating voltage of 200 kV. XRD was performed on a PANalytical X-ray diffractometer. XPS spectra were collected on SSI S-Probe XPS Spectrometer. Raman spectrum of powder samples was recorded on Lab RAM HR Raman microscope with a laser excitation wavelength of 514 nm.

Supplementary Experimental Figures

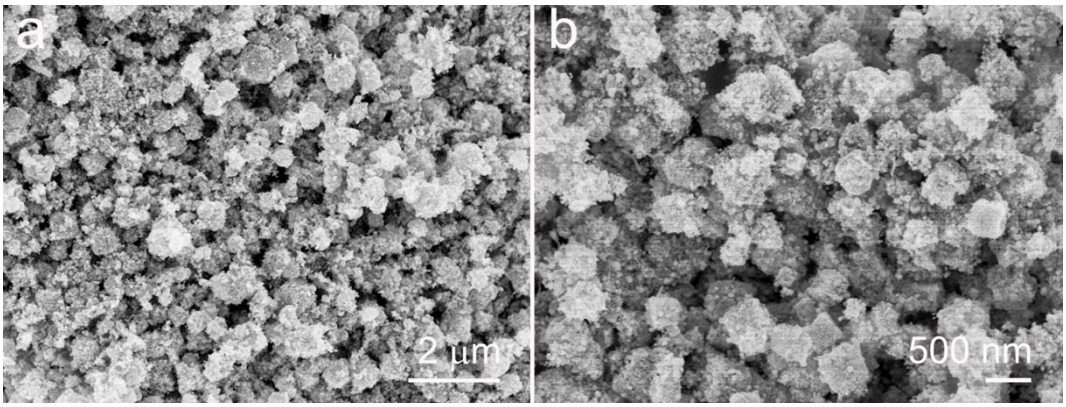

Figure S1 SEM image of CoMn@NG at (a) low magnification (b) high magnification.

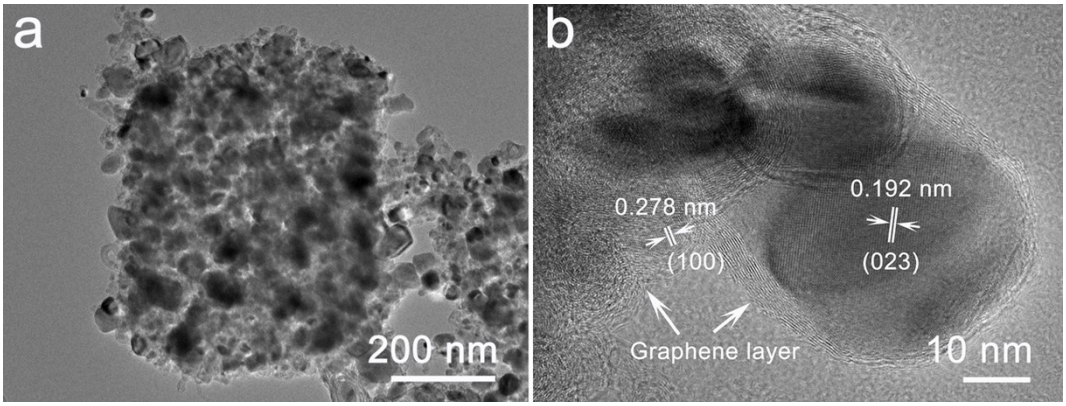

Figure S2 (a) TEM image of CoMn@NG. (b) HRTEM image of CoMn@NG. In the CoMn@NG structure, there are two lattices spacing of 0.16 nm and 0.278 nm inside the core, corresponding to the (100) plane of CoO (JCPDS No. 89-2803) and (023) plane of $Co_2Mn_3O_8$ (JCPDS No. 30-0446), and the outer layer is the graphene layer.

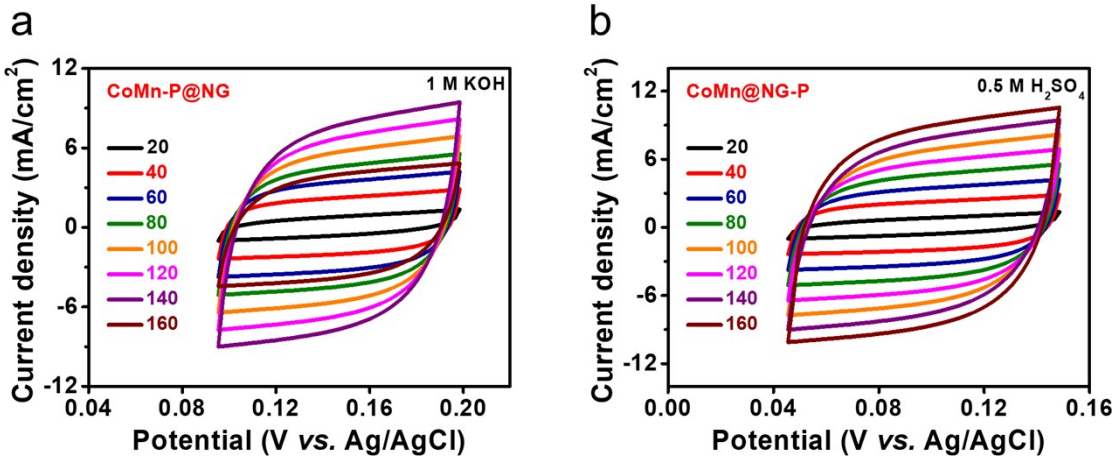

Figure S3 ECSA of CoMn-P@NG in (a) 1 M KOH (b) 0.5 M H_2SO_4.

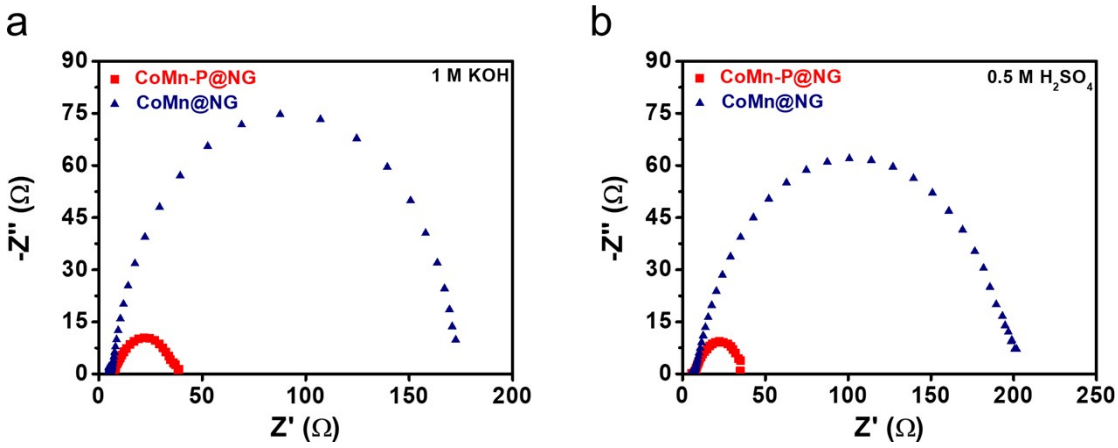

Figure S4 EIS curves of CoMn@NG, CoMn-P@NG and Pt/C in (a) 1 M KOH (b) 0.5 M H_2SO_4.

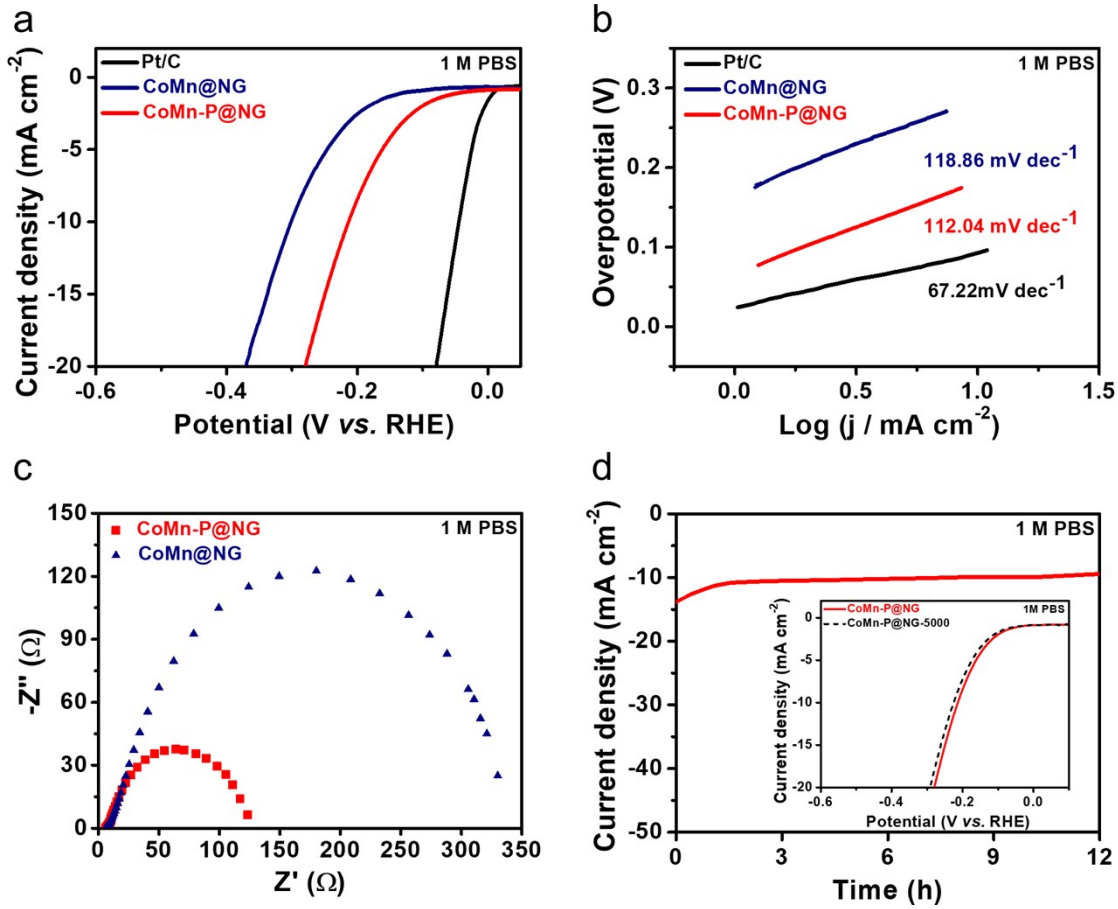

Figure S5 (a) LSV curves of CoMn-P@NG, CoMn@NG and Pt/C catalysts after normalizing the currents to the geometric area in 1 M PBS solution. (b) Tafel plots of CoMn-P@NG, CoMn@NG and Pt/C catalysts calculated from the LSV curves. (c) EIS curves of CoMn-P@NG and CoMn@NG in 1 M PBS. (d) HER stability measurement of CoMn-P@NG in 1 M PBS solution at a current density of 10 mA cm^{-2} for 12 h. Inserted LSV curves show the initial and after 5000 ADT CV cycles.

Table S1 HER properties comparison of the similar electrocatalysts in KOH and H_2SO_4 electrolyte

Catalysts	Electrolyte	Overpotential at 10 mA cm^{-2}	Tafel (mV dec^{-1})	Ref.
CoMn-P@NG	1M KOH	164 mV	111	This work
CoMn-P@NG	0.5M H_2SO_4	140 mV	65	This work
CoMn@NG	1M KOH	263 mV	113	This work
CoMn@NG	0.5M H_2SO_4	211 mV	133	This work
Fe_2P/CoP	0.1M KOH	109 mV	64	s1
FeCo@NG/NCNT	1M KOH	332 mV	110	s2
CoSx@Cu_2MoS_4-MoS_2/NSG	0.1M KOH	118 mV	41	s3
CoFe-Se-P	0.5M H_2SO_4	119 mV	62	s4
Co@CN	1M KOH	96 mV	79	s5
(Fe-Co)Se_2F	1M KOH	90 mV	58.7	s6
$CoSe_2$	1M KOH	124 mV	96.3	s6
$FeSe_2$	1M KOH	158 mV	98.6	s6
Mo-ZnCoP-3	1M KOH	162 mV	61.1	s7
$Zn_{0.975}Co_{0.025}S/CoS_2$	1M KOH	152 mV	108	s8

Supplementary References

[s1] Du Y. X., Chen J., Li L., et al. Core-shell FeCo prussian blue analogue/$Ni(OH)_2$ derived porous ternary transition metal phosphides connected by graphene for effectively electrocatalytic water splitting. *ACS. Sustain. Chem. Eng.*, 2019, 7(15):13523-13531.

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[s3] Nguyen D. C., Tran D. T., Doan T. L. L., Kim D. H., Kim N. H., Lee J. H. Rational Design of Core@shell Structured CoSx@Cu_2MoS_4 Hybridized MoS_2/N,S-codoped graphene as advanced electrocatalyst for water splitting and Zn-Air battery. *Adv. Energy Mater.*, 2020, 10(8):1614-1628.

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