MOFs-derived Mn doped porous CoP nanosheets as efficient and stable bifunctional electrocatalysts for water splitting

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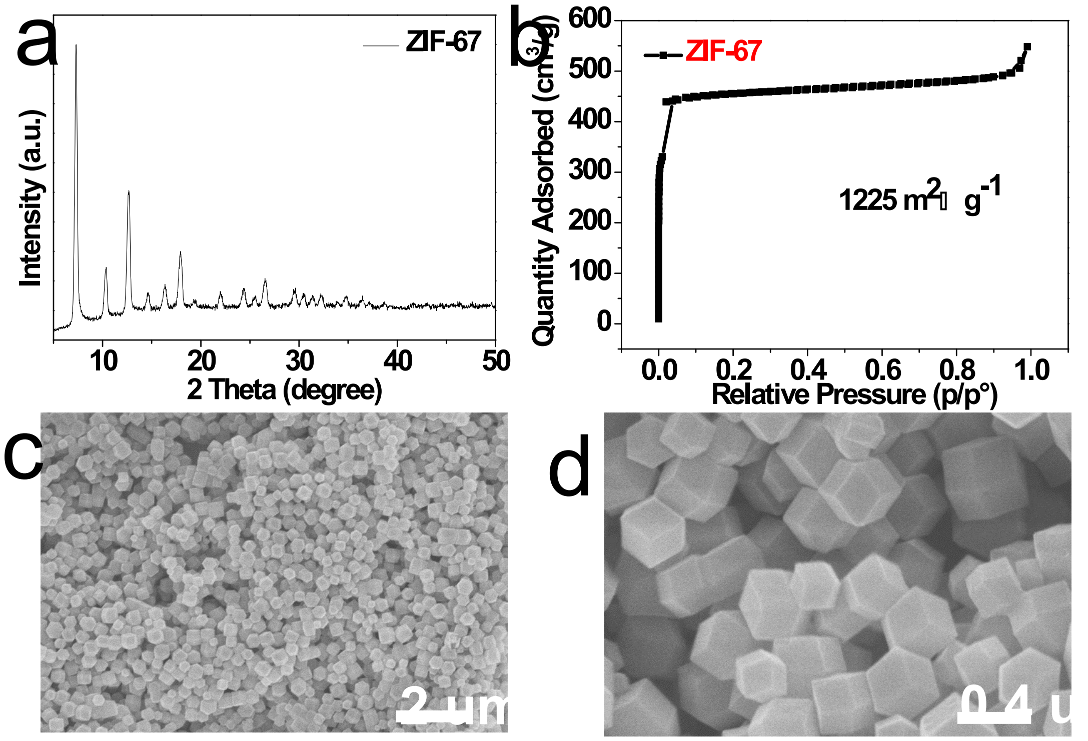

Figure S1. (a) XRD patterns of the as-synthesized ZIF-67; (b) N_2 adsorption-desorption isotherm of ZIF-67; (c and d) the SEM images of precursor ZIF-67

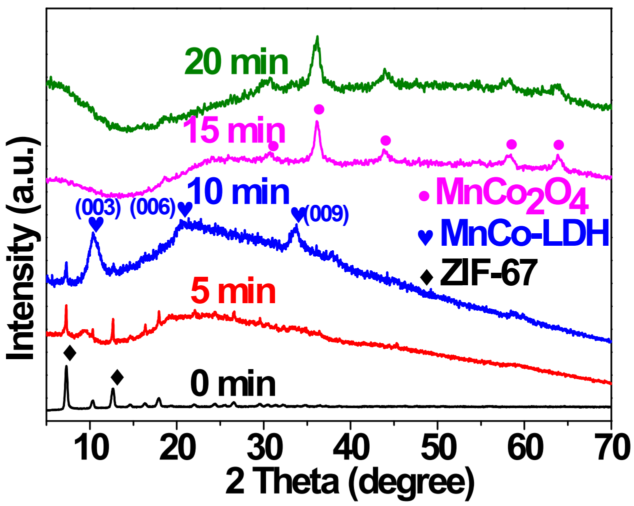

Figure S2. (a) XRD patterns of different etching time.

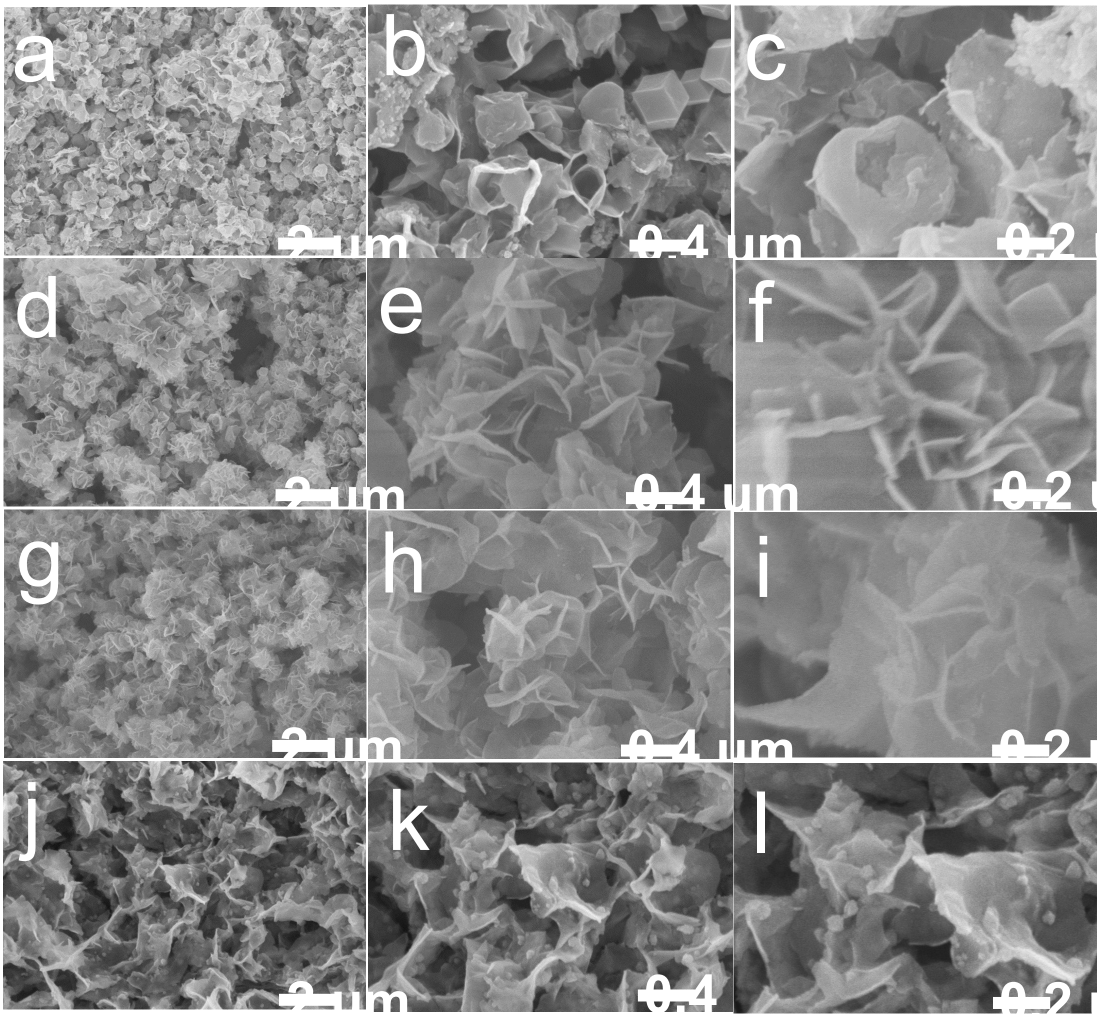

Figure S3 the SEM images of (a, b, c) obtained materials after etching 5 min; (d, e, f) etching 10 min; (g, h, i) etching 15 min; (j, k, l) etching 20 min;

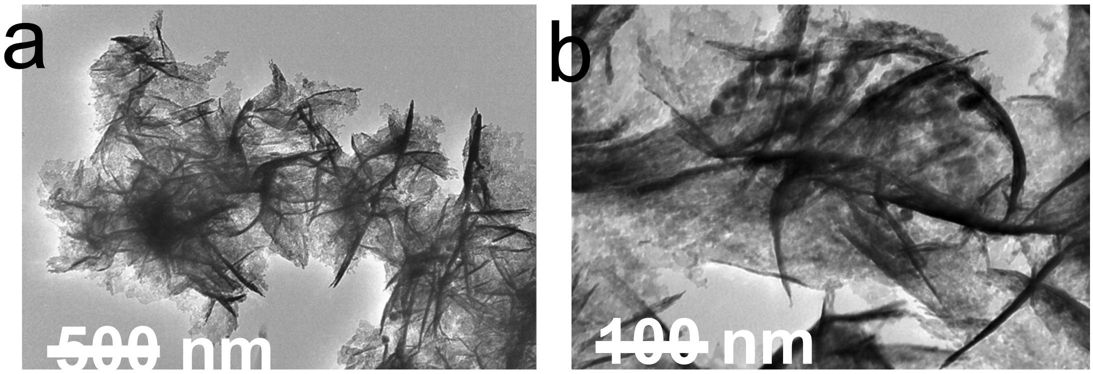

Figure S4 TEM images of $MnCo_2O_4$ nanopsheets

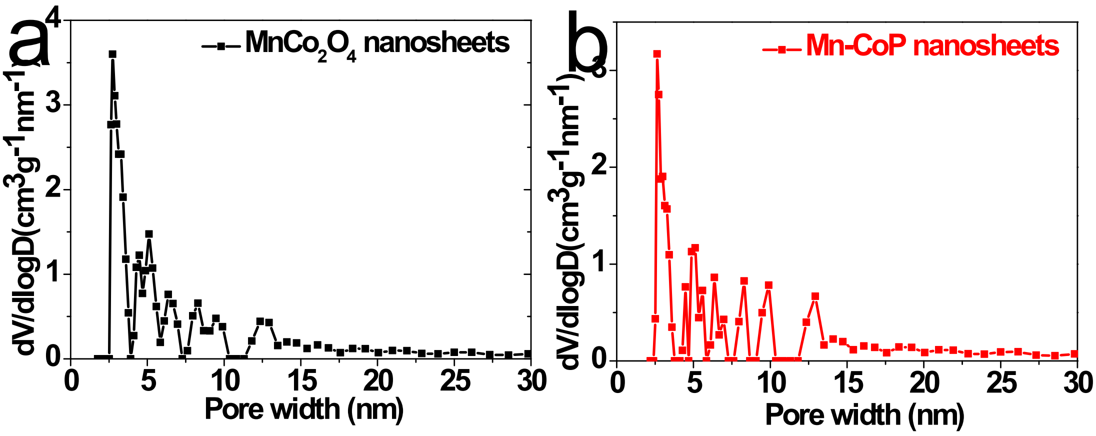

Figure S5 the pore size distributions of $MnCo_2O_4$ and Mn-CoP nanosheets calculated by using NLDFT method.

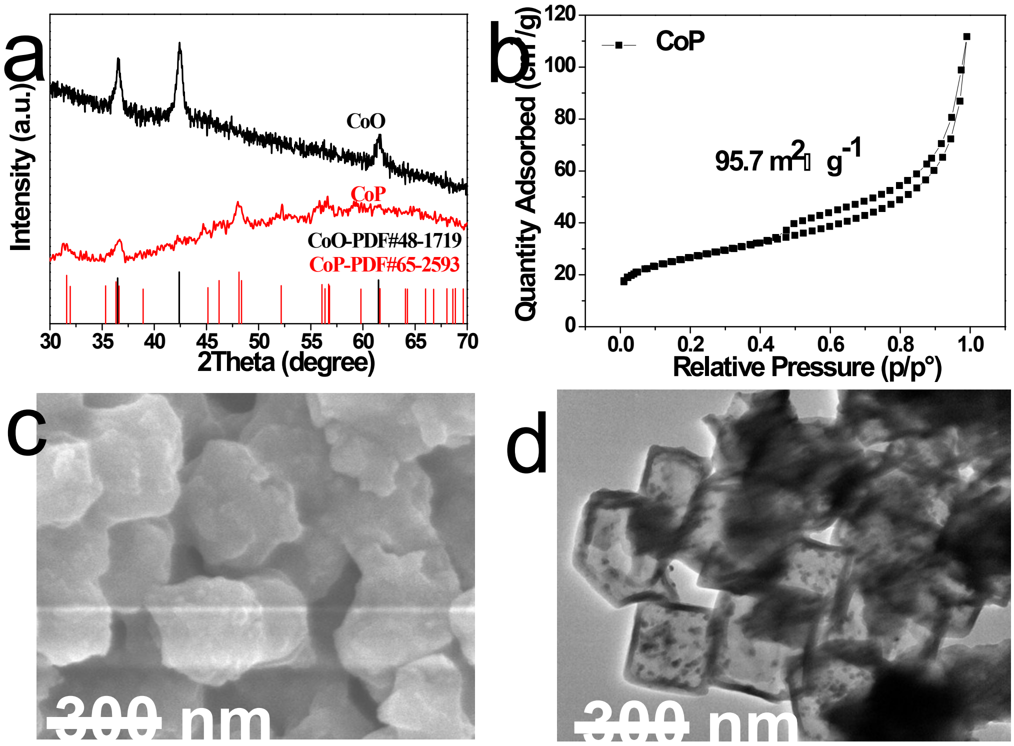

Figure S6 (a) The XRD of CoO and CoP nanoparticles; (b) N_2 sorption of hollow CoP; (c-d) SEM and TEM of hollow CoP nanoparticles

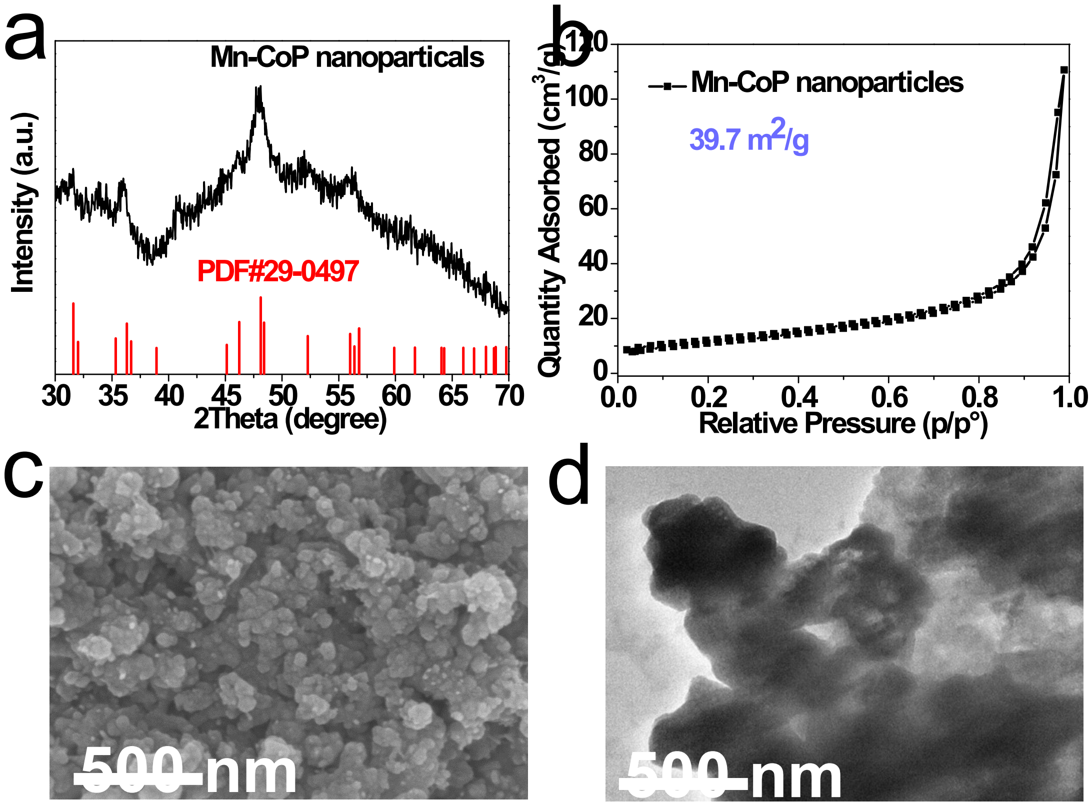

Figure S7 (a) The XRD of Mn-CoP nanoparticles; (b) N_2 sorption of Mn-CoP nanoparticles; (c-d) SEM of Mn-CoP nanoparticles

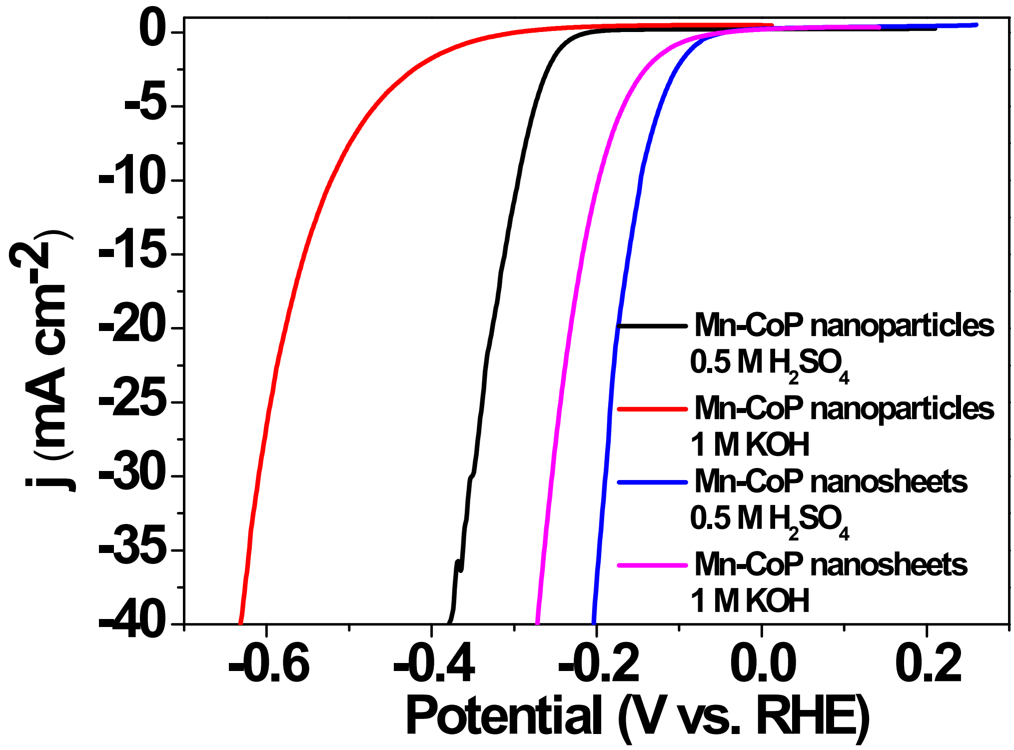

Figure S8 the HER performance of Mn-CoP nanoparticles and Mn-CoP nanosheets in 0.5 M H_2SO_4 and 1 M KOH

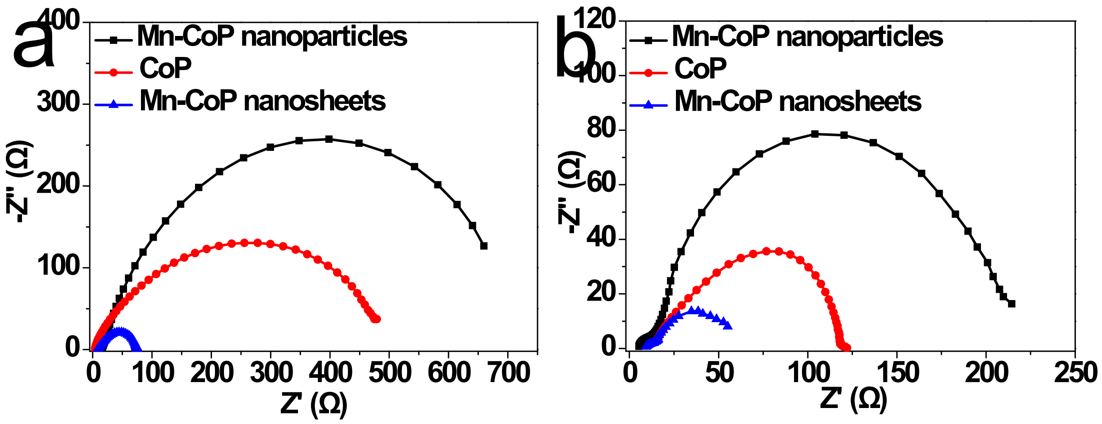

Figure S9 Nyquist plots of the as-synthesized Mn-CoP nanosheets, hollow CoP and Mn-CoP nanoparticles catalysts in (a) 0.5 M H_2SO_4 with an overpotential of 165 mV vs. RHE and (b) 1 M KOH with an overpotential of 200 mV vs. RHE for HER.

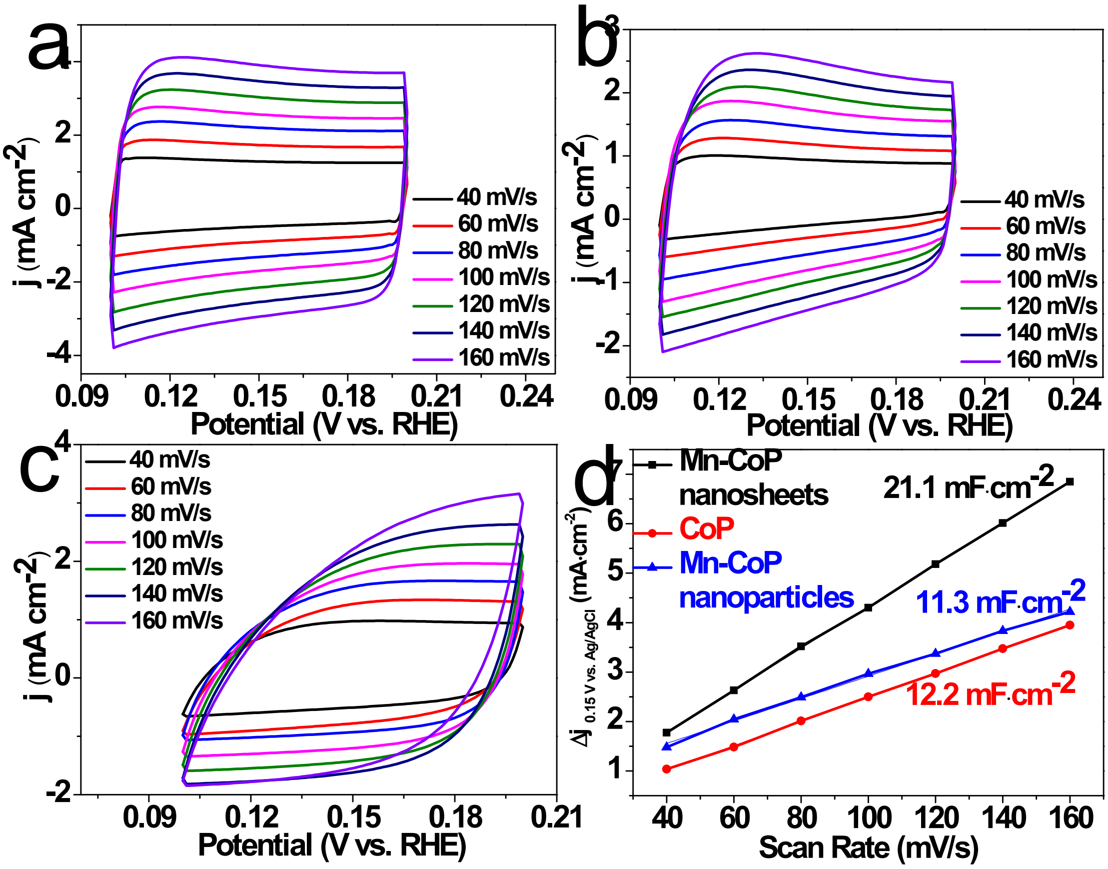

Figure S10 Voltammograms of the (a) Mn-CoP nanosheets; (b) hollow CoP, (c) Mn-CoP nanoparticles at various scan rates (40-160 mV s^{-1}); (d) Current difference (Δj) plotted against the scan rate.

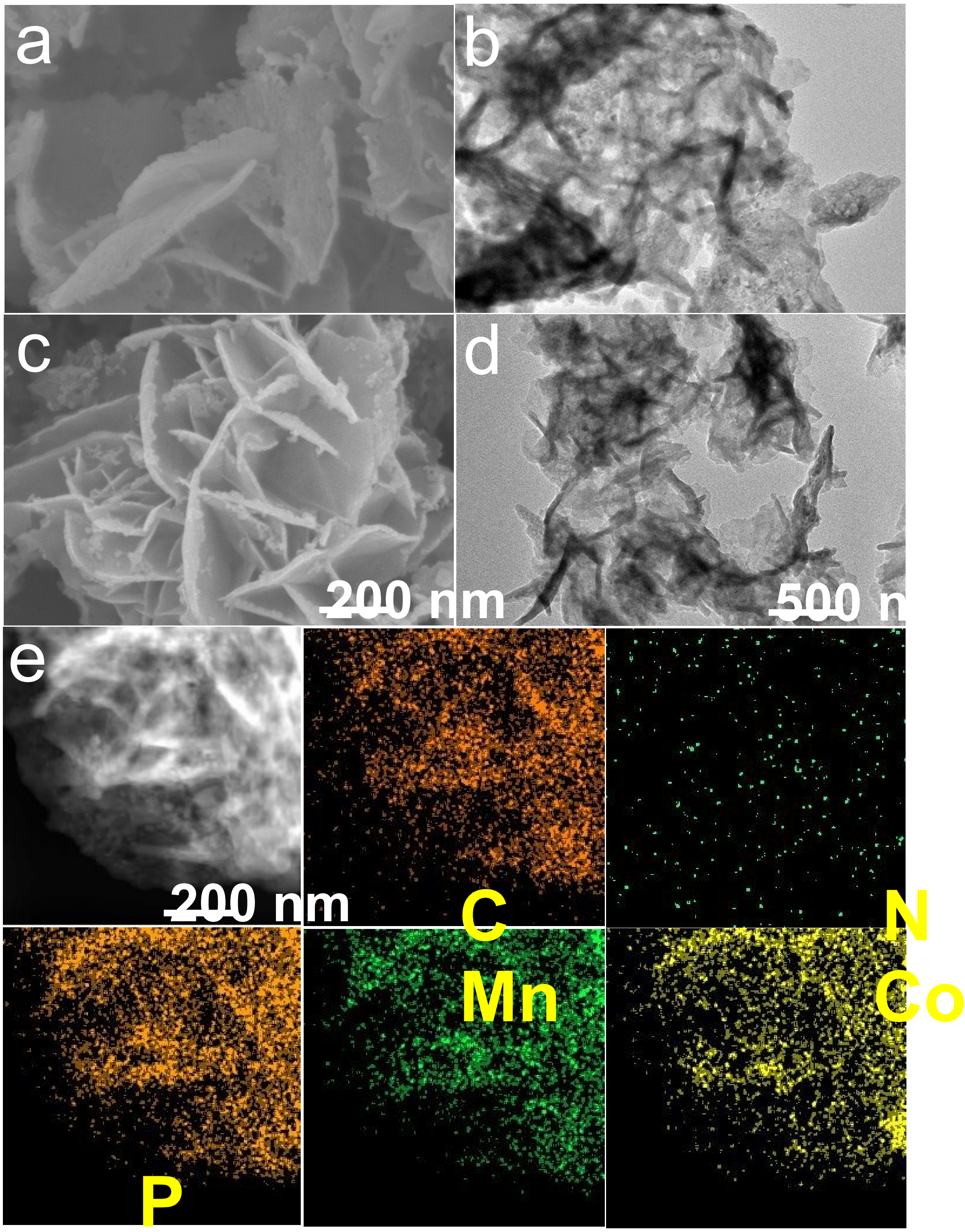

Figure S11 the SEM and TEM image of the Mn-CoP nanosheets catalyst after long term test in (a and b) 0.5 M H_2SO_4 and (c and d) 1 M KOH for HER. (e) HAADF-STEM elemental mapping of the Mn-CoP nanosheets catalyst after long term test 0.5 M H_2SO_4 solution .

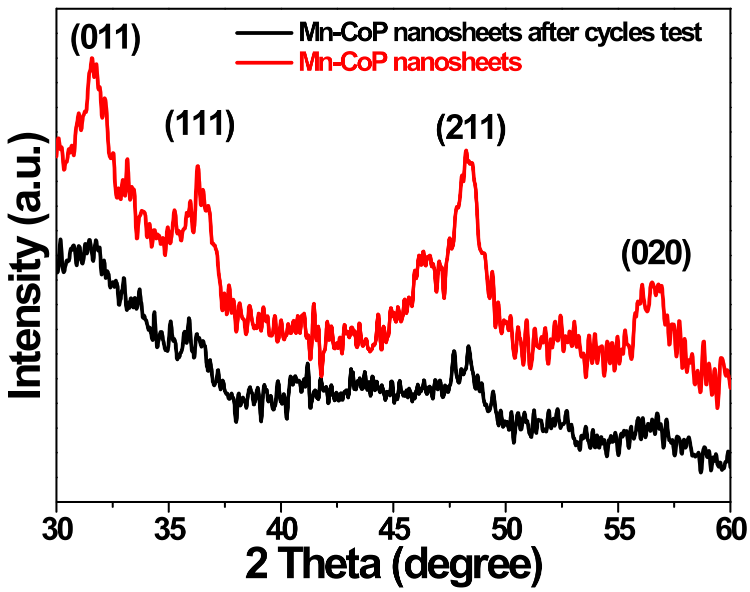

Figure S12 the XRD of Mn-CoP nanosheets before and after cycles tests

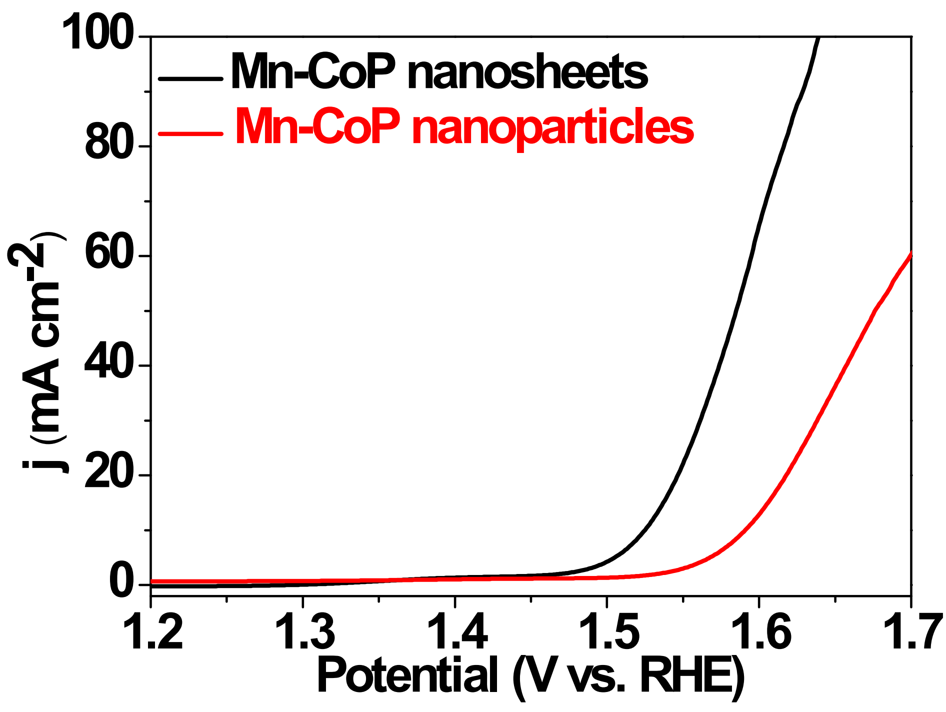

Figure S13 the LSV curves of the Mn-CoP nanosheets and Mn-CoP nanoparticles catalyst in 1 M KOH for OER.

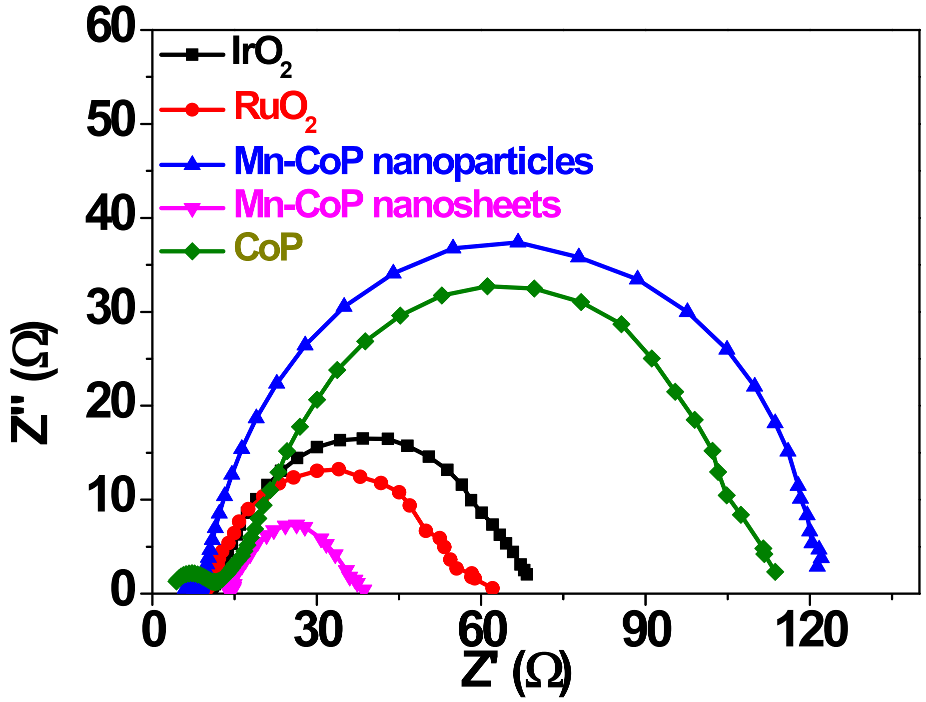

Figure S14 Nyquist plots of the as-synthesized catalysts in 1 M KOH with an overpotential of 320 mV vs. RHE for OER.

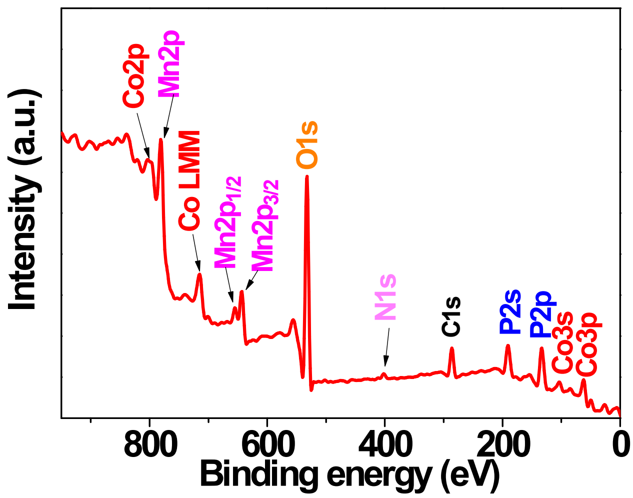

Figure S15 XPS survey spectrum for Mn-CoP nanosheets

Tabls S1 Summary of various non-noble metal catalysts for HER in 0.5 M H_2SO_4.

Catalyst	Overpotential @ j=10 / mV	Tafel slope ($mV\cdot dec^{-1}$)	Reference
Cu_3P NW/CF	143	67	*Angew. Chem. Int. Ed.*, 2014, **53**, 9577
$Ni_{0.62}Co_{0.38}P$	166	72	*Adv. Funct. Mater.*, 2016, **26**, 7644.
$MoS_{2(1-x)}P_x$	150	57	*Adv. Mater.*, 2016, **28**, 1427.
CoPx NPs@NC	191	51	*Chem. Mater.*2015, **27**, 7636
Mo_2C@PC	177	96	*Angew. Chem. Int. Ed.* 2016, **55**, 12854
$Mn_{0.05}Co_{0.95}Se_2$	195	36	*J. Am. Chem. Soc*. 2016, **138**, 5087.
CoP hollow polyhedron	159	59	*ACS Appl. Mater. Interfaces* 2016, **8**, 2158
CoNi@NC	142	104	*Angew. Chem., Int. Ed.* 2015, **54**, 2100
CoP@C	170	61	*J. Power Source* 2015, **286**, 464
CoP/RGO-0.36	250	104.8	*J. Mater. Chem. A* 2015, **3**, 5337
Mn-CoP nanosheets	148	61	This work

Table S2. Summary of various Co-based non-noble metal catalysts for HER in 1 M KOH.

Catalyst	Overpotential @ j=10 / mV	Tafel slope ($mV \cdot dec^{-1}$)	Reference
CoP/CC	209	129	*J. Am. Chem. Soc.*, 2014,**136**, 7587.
NiCoP/rGO	209	124.1	*Adv. Funct.Mater.*, 2016, **26**, 6785.
MoB	225	59	*Angew. Chem. Int. Ed.* 2012, **51**, 12703.
Co/CoP	253	73.8	*Adv. Energy Mater.*, 2017,**7**,1602355.
FeP nanorod arrays	218	146	*ACS Catalysis*, 2014, **4**, 4065.
Co, N-codoped nanocarbons	240	85	*Nanoscale* 2015, **7**, 2306.
Ni_2P nanoparticles	225	100	*Phys. Chem. Chem. Phys.* 2014, **16** , 5917.
NiFe LDH/NF	210	58.9	*Science* 2014, **345**, 1593
Ni_3S_2/NF	223	123.3	*J. Am. Chem. Soc.* 2015, **137**, 14023
Co_2B-500/NG	230	92.4	*Adv. Energy Mater.* 2016, 1502313.
CoOx@CN	232	N/A	*J. Am. Chem. Soc.* **2015**, **137**, 2688.
CoP/CC	209	129	*J. Am. Chem. Soc.* **2014**, **136**, 7587.
Co-NRCNTs	370	N/A	*Angew. Chem. Int. Ed.* **2014**, *53*, 4372.
Ni_2P	205	N/A	*J. Am. Chem. Soc.* **2013**, 135, 9267.
FeP NAs/CC	218	146	*ACS Catal.* **2014**, 4,4065.
Co@N-CNTs	370	N/A	Angew. Chem., Int. Ed. 2014, **53**, 4372
Mn-CoP nanosheets	195	69	This work

Table S3. Summary of various Co-based non-noble metal catalysts for OER in 1 M KOH.

Catalyst	Overpotential @ j=10 / mV	Tafel slope ($mV\cdot dec^{-1}$)	Reference
CoP hollow polyhedron	400	57	*ACS Appl. Mater. Interfaces* 2016, **8**, 2158
Zn-doped $CoSe_2$/CFC	356	88	*ACS Appl. Mater. Interfaces* 2016, **8**, 26902
ZnxCo$_{3-x}$O$_4$ yolk-hell polyhedron	337	59.3	*ACS Appl. Mater. Interfaces* 2017, **9**, 31777
Co-P films	345	47	*Angew. Chem. Int. Ed.* 2015,**127,** 6349
Co-P/NC	319	52	*Chem. Mater.* 2015, **27**, 7636
NixCo$_{3-x}$O$_4$	370	59-64	*Adv. Mater.* **2010**, **22**, 1926.
Co_3O_4/N-rmGO	310	67	*Nat. Mater.* **2011**, **10**, 780
CoOx@CN	385	N/A	*J. Am. Chem. Soc.* **2015**, **137**, 2688.
CoCo LDH	393	59	*Nat. Commun.* **2014**, **5**, 4477
$MnCo_2O_x$	410	84	*J. Am. Chem. Soc.* **2014**, **136**, 16481.
Mn-CoP nanosheets	290	76	This work