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Electronic supplementary information

Metal–Organic Framework Derived Hollow CoS_2 Nanotube Arrays: an Efficient Bifunctional Electrocatalyst for Overall Water Splitting

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Material and methods

Material Synthesis

Preparation of Co-MOF arrays on carbon cloth: an aqueous solution contains 2-methylimidazole ($C_4H_6N_2$, 40 mL, 0.4 M) was quickly added into the aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (40 mL, 25 mM), after which a piece of acid-treated CC substrate (2*5*0.036 cm^3, the upper side and back side protected with by polytetrafluoroethylene tape) was immersed into the mixture solution. After reaction for 4 h, the sample was taken out, cleaned with deionized water and underwent another 4 h of growth in the same solution. Finally the sample was cleaned and vacuum dried overnight.

Preparation of CoS_2 NTA/CC: a piece of Co-MOF arrays on carbon cloth was immersed into an ethanol solution (80 mL) containing TAA (0.36 g). After reaction at 90 °C for 180 min, the sample was taken out, washed with ethanol, and dried at 60 °C. Then the sample was annealed in N_2 at 350 °C for 2h with a ramp rate of 2 °C min^{-1}. The mass loading of CoS_2 was measured to be ~1.2 mg cm^{-2}. Decreasing the reaction time to 60 min resulted in insufficient etching, while prolonging the reaction time to 300 min resulted in the collapse of the nanoarrays.

Preparation of Co_3O_4 NWA/CC: a piece of Co-MOF array on carbon cloth was annealed in N_2 at 500 °C for 2h with a ramp rate of 2 °C min^{-1}, and when the temperature dropped to 350 °C it was futher annealed in air for 2 h. The mass loading of Co_3O_4 was measured to ~0.6 mg cm^{-2}.

Preparation of Ir/C/CC and Pt/C/CC: commercial Pt/C (20 wt %, Alfa Aesar) or Ir/C (20 wt %, Premetek Co) was well-dispersed in diluted Nafion alcohol solution (0.5 mL of ethanol and 50 μL of Nafion) to form a homogeneous suspension. Then the suspension was drop casted onto CC with similar mass loading to that of the CoS_2 NTA. The samples were dried at room temperature before test.

Materials Characterization

Samples were characterized using Scanning Electron Microscopy (SEM, Zeiss, 5.0-20.0 kV), Transmission Electron Microscopy (TEM, JEOL-2100F), X-ray photoelectron spectroscopy (XPS, AXIS Ultra), and X-Ray Diffraction (XRD, Bruker D8 diffractometer). The mass of the electrode materials was also recorded by an AX/MX/UMX Balance (METTLER TOLEDO, maximum=5.1 g; delta= 0.001 mg). Scanning Transmission Electron Microscopy (STEM) and EDX studies were conducted using a JEOL ARM200F atomic resolution analytical electron microscope equipped with a cold field-emission gun and a new ASCOR 5th order aberration corrector.

Electrochemical Characterization

Electrochemical measurements were conducted using Solartron 1470E at room temperature. (a) The OER and HER catalytic activities were tested in a standard three-electrode system in 1 M KOH solution (PH=14), using a Pt plate (or a carbon plate) and SCE as the counter and reference electrode, respectively. Catalysts on carbon cloth were directly used as the working electrode. The polarization curves were measured at 5 mV s^{-1} and iR corrected, and all the measured potentials were referred to a reversible hydrogen electrode (RHE) using the following equation: E(RHE)=E(SCE)+0.0592*pH+0.241. EIS measurements were carried out by applying an AC voltage with 5 mV amplitude in a frequency range from 0.1 Hz to 100 kHz at open circuit potential. The electrochemical double-layer capacitance (C_{dl}) was determined from the CV curves measured in a potential range without redox process by: $C_{dl}=I/\nu$, where I is the charging current (mA cm^{-2}), and ν is the scan rate (mV s^{-1}). The electrochemical stability was tested under constant voltage. (b) The overall water splitting was carried out in a two-electrode system in 1 M KOH solution (PH=14). The polarization curve was recorded at a scan rate of 5 mV s^{-1}. The electrochemical stability was tested under constant voltage.

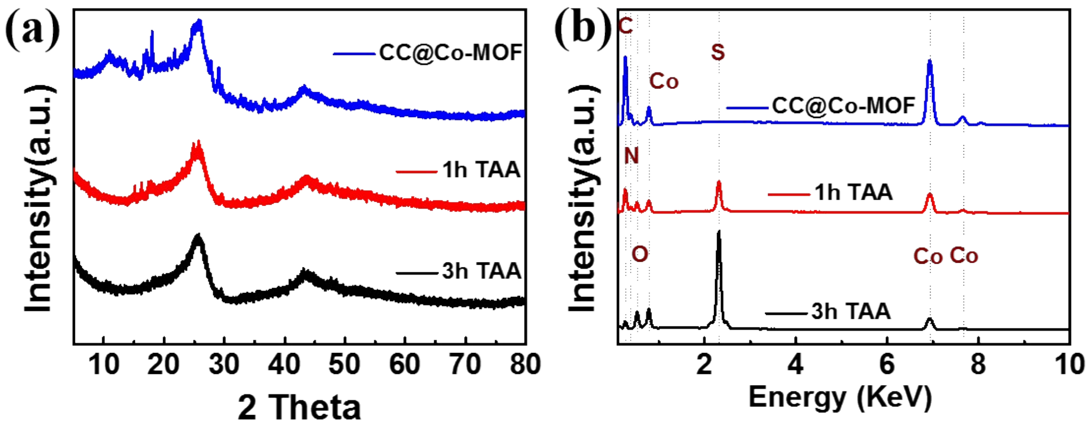

Fig. S1. (a) XRD and (b) EDX results of the wire-like Co-MOF arrays on carbon cloth with different reaction times with TAA.

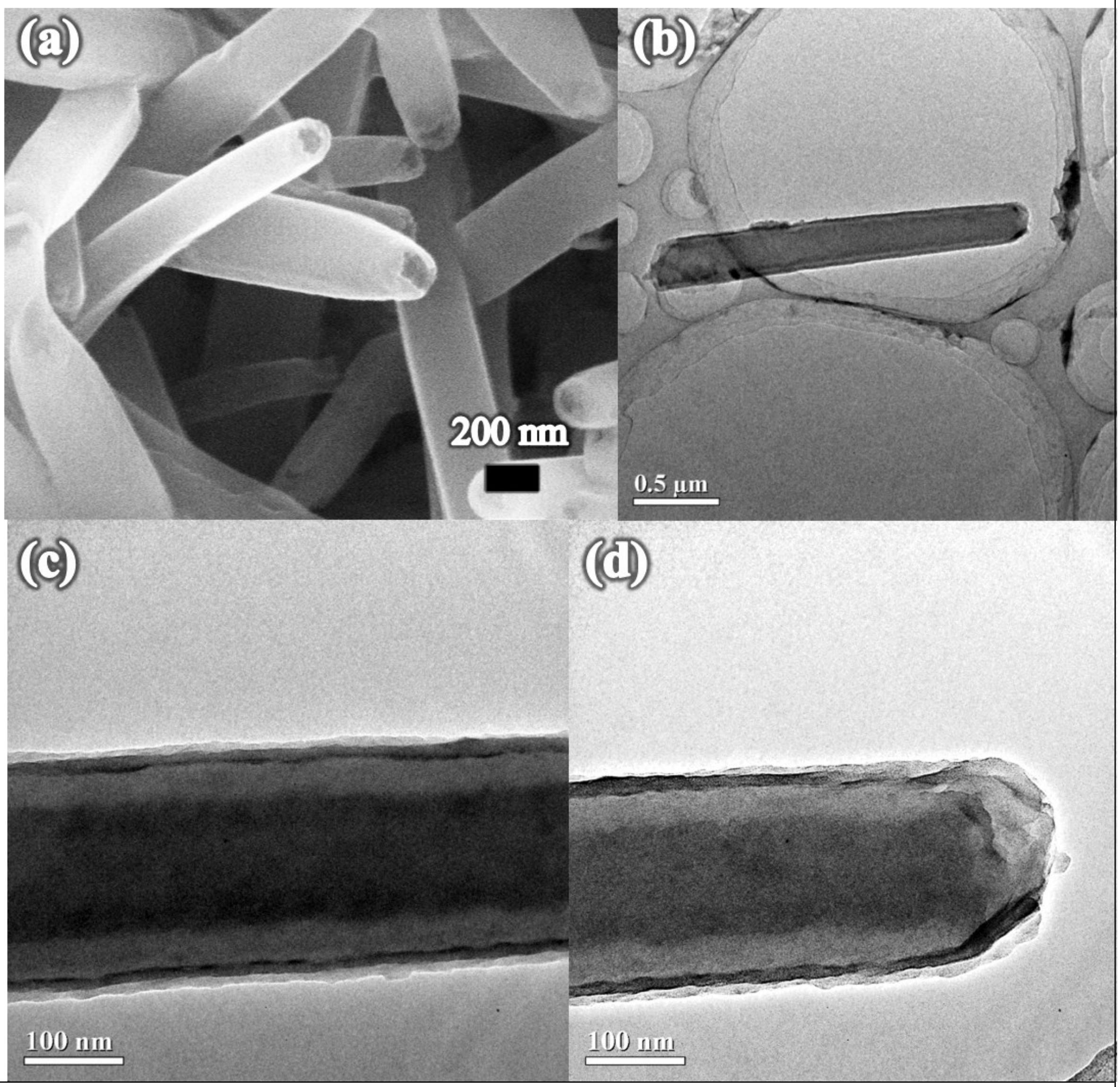

Fig. S2. (a) SEM and (b-d) TEM images of Co-MOF arrays on carbon cloth with 1 h reaction time with TAA, showing wire-in-tube structures.

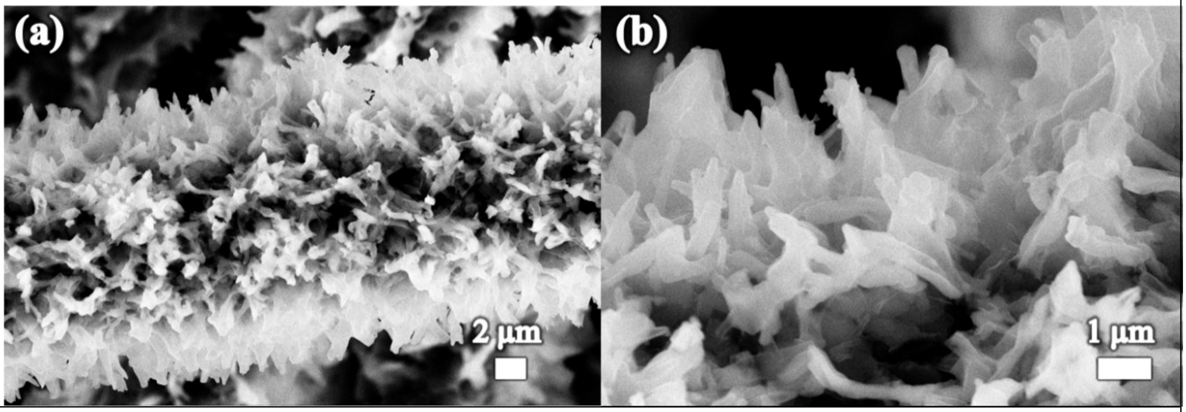

Fig. S3. SEM images of Co-MOF arrays on carbon cloth with 5 h reaction time with TAA, showing the structures has been collapsed.

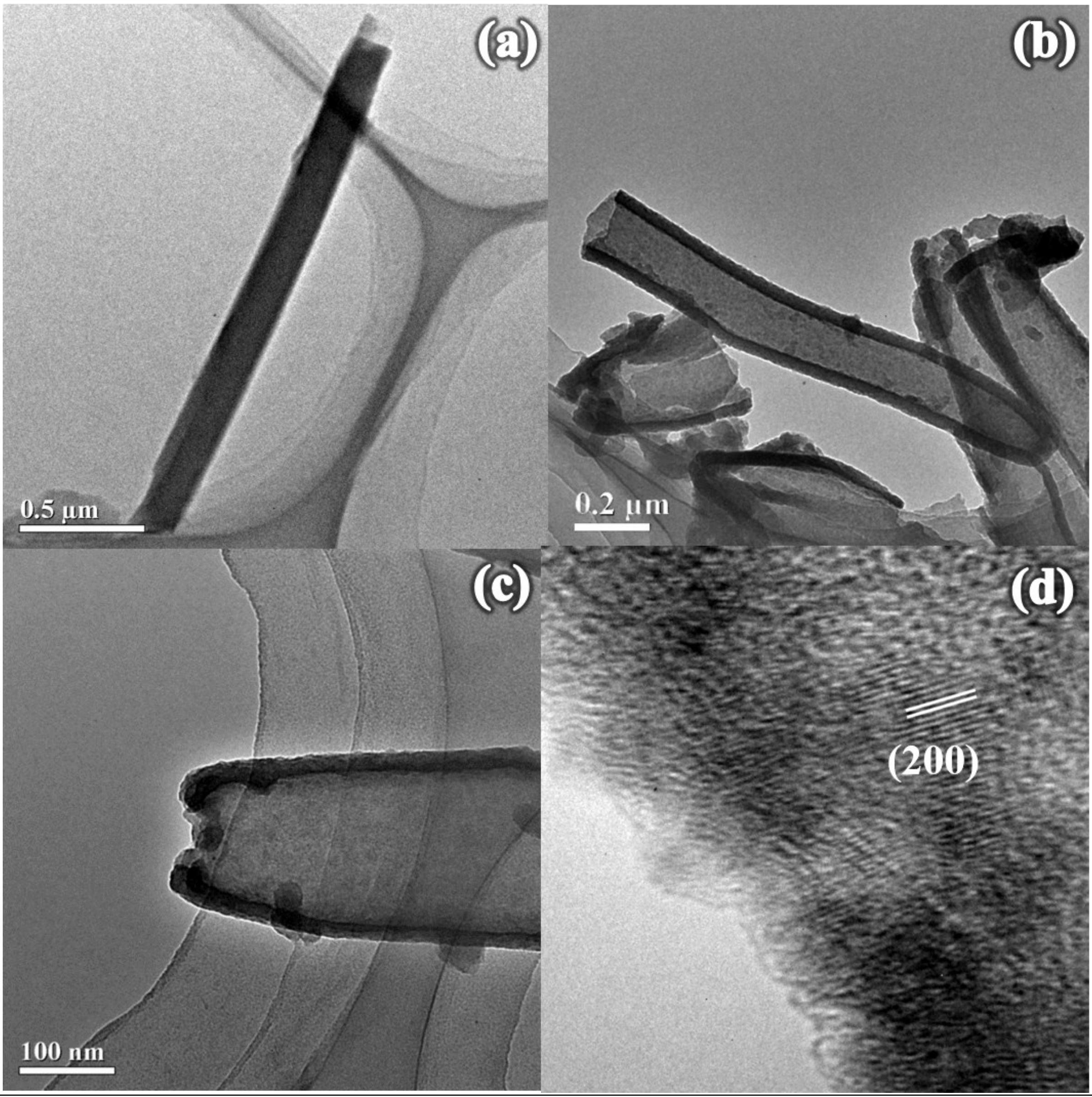

Fig. S4. TEM images of (a) wire-like Co-MOF, (b-c) Co-MOF arrays on carbon cloth with 3 h reaction time with TAA, (d) a typical part of a CoS_2 nanotube.

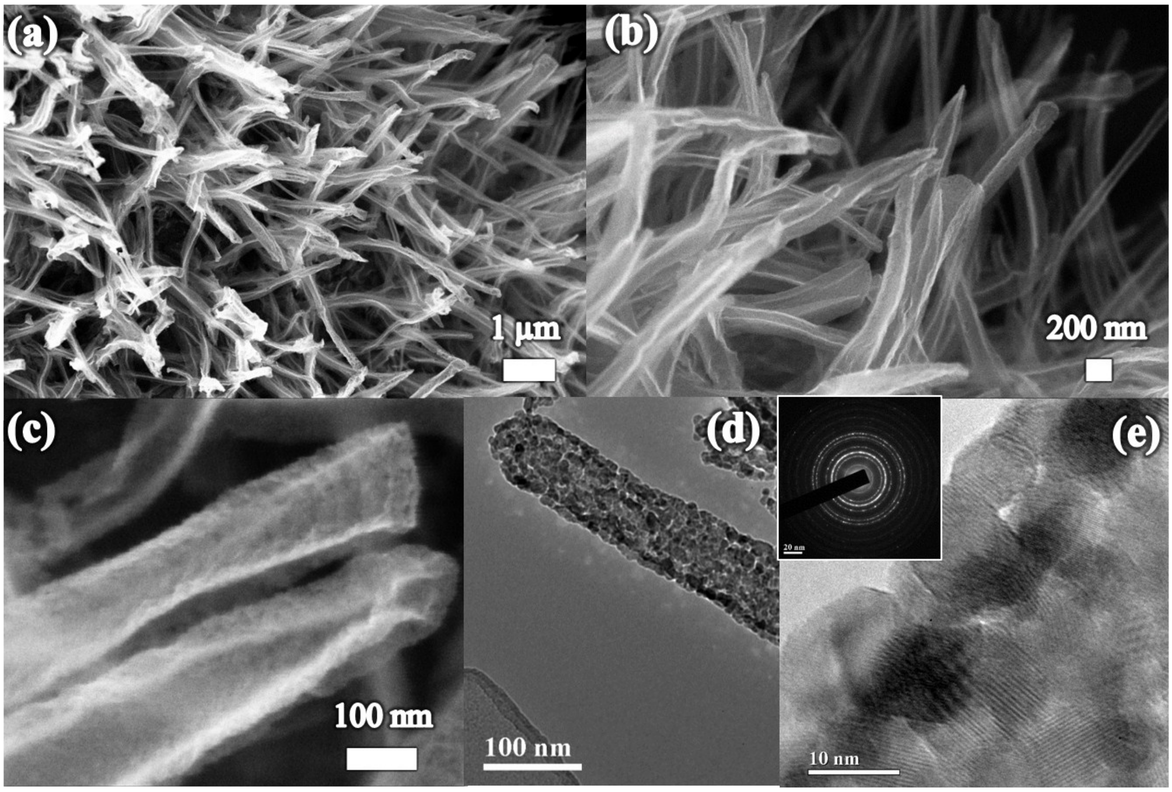

Fig. S5. (a-c) SEM and (d-e) TEM images of Co_3O_4 nanowires on carbon cloth.

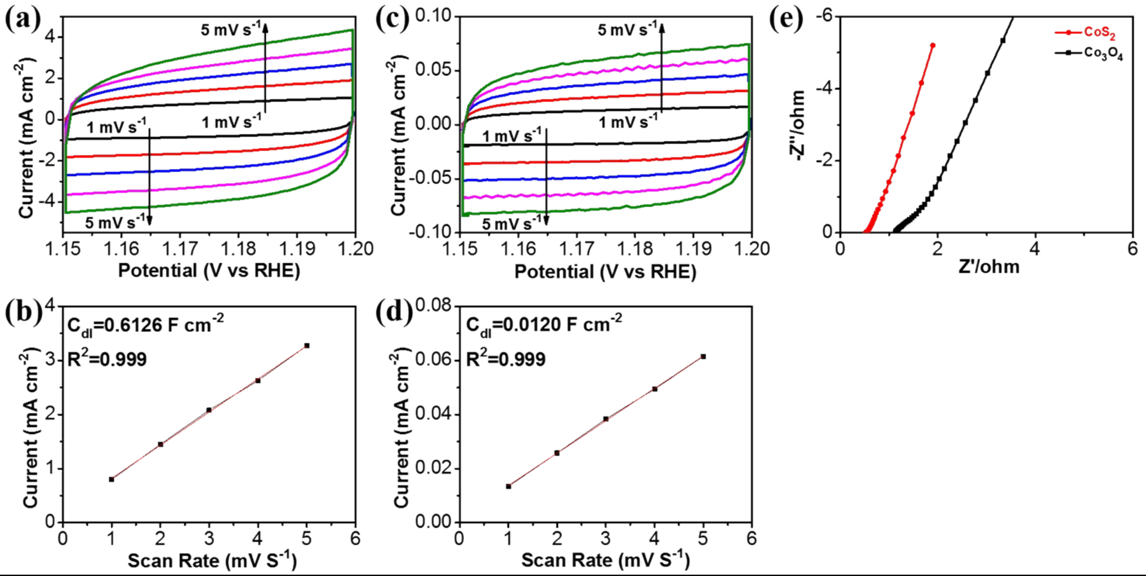

Fig. S6. (a) CV and (b) Plot of current density (@1.175 V vs RHE) vs scan rates of CoS_2 NTA/CC. (c) CV and (d) Plot of current density (@1.175 V vs RHE) vs scan rates of Co_3O_4 NWA/CC. (e) Nyquist plots of CoS_2 NTA and Co_3O_4 NWA.

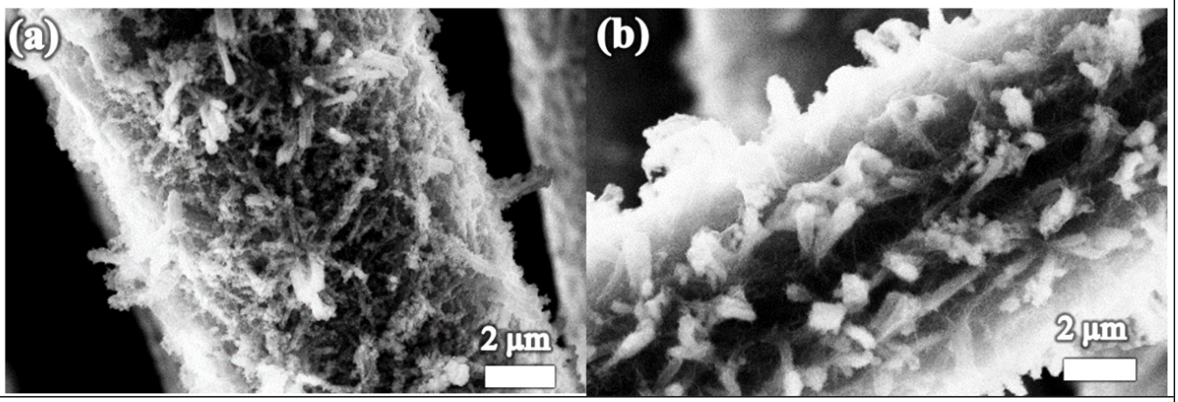

Fig. S7. SEM images of CoS_2 NTA/CC after 20 h of stability test in (a) OER, (b) HER.

Table S1. Summary of recent reported highly active **OER** catalysts in 1 M KOH or NaOH electrolyte.

Catalyst	Substrate	Mass loading (mg cm^{-2})	Current density (mA cm^{-2})	Potential (V vs. RHE)	Tafel Slope (mV dec^{-1})	Reference
CoS_2 NTA	Carbon cloth	1.2	10	1.506	81	Curent work
N-doped carbon nanotube frameworks	Glassy carbon (GC)/powder	0.2	10	1.60	93	[1]
CoP_x nanoparticles embedded in N-doped carbon	GC/powder	0.283	10	1.549	52	[2]
CoMnP nanoparticles	GC/powder	0.284	10	1.56	61	[3]
Cobalt-based borate nanosheets/ graphene	GC/powder	0.285	10	1.52	53	[4]
$Co_3O_4/NiCo_2O_4$ double-shelled nanocages	Ni foam/powder	1	10	1.57	88	[5]
$NiCo_2O_4$ Hollow Microcuboids	Ni foam/powder	1	10	1.52	53	[6]
Surface Oxidized CoP Nanorods	GC/powder	0.71	10	1.55	71	[7]
Co/CoP	GC/powder	0.22	10	1.57	79.5	[8]
NiCo LDH nanosheets	carbon paper	0.17	10	1.597	40	[9]
Co_3O_4-Carbon Nanowire Arrays	Cu foil	0.2	10	1.52	70	[10]
Hollow Co_3O_4 Microtube Arrays	Ni foam	N.A.	150	1.59	84	[11]
Carbon tubes/ cobalt-sulfide	Carbon paper	0.32 (Co-S)	10	1.536	72	[12]
Ni_8P_3	Ni foam	N.A.	30	1.5	73.2	[13]
MoS_2/Ni_3S_2	Ni foam	9.7	10	1.448	88	[14]
NiCoP	Ni foam	1.6	10	1.51	87	[15]
NiFe LDH	Ni foam	N.A.	10	1.47	N.A.	[16]
$Co_9S_8@MoS_2$/CNFs	GC/powder	0.212	10	1.66	61	[17]
NiCoP/C	GC/powder	0.05	10	1.56	96	[18]
Ni–Mo/Cu nanowires	Cu foam	2.17	20	1.51	66	[19]

Table S2. Summary of recent reported highly active **HER** catalysts in 1 M KOH electrolyte.

Catalyst	Substrate	Mass loading (mg cm^{-2})	Current density (mA cm^{-2})	Potential (V vs. RHE)	Tafel Slope (mV dec^{-1})	Reference
CoS_2 NTA	Carbon cloth	1.2	-10	-0.193	88	Curent work
CoP_x nanoparticles embedded in N-doped carbon	GC/powder	0.283	-10	-0.145	51	[2]
$NiCo_2O_4$ Hollow Microcuboids	Ni foam/powder	1	-10	-0.110	49.7	[6]
Co/CoP	GC/powder	0.22	-10	-0.253	73.8	[8]
Co_9S_8@MoS_2/C NFs	GC/powder	0.212	-10	-0.19	110	[17]
Carbon tubes/ cobalt-sulfide	Carbon paper	0.32(Co-S)	-10	-0.19	131	[12]
Hollow Co_3O_4 Microtube Arrays	Ni foam	N.A.	-20	-0.19	98	[11]
Ni_8P_3	Ni foam	N.A.	-10	-0.13	58.5	[13]
MoS_2/Ni_3S_2	Ni foam	9.7	-10	-0.11	83	[14]
NiCoP	Ni foam	1.6	-10	-0.032	37	[15]
$Ni_{1-x}Co_xSe_2$ mesoporous nanosheet	Ni foam	2.16	-10	-0.085	52	[20]
NiFe LDH	Ni foam	N.A.	-10	-0.21	N.A.	[16]
CoN_x/C	GC/powder	2	-10	-0.17	75	[21]
Cobalt embedded nitrogen-rich carbon nanotubes	GC/powder	0.28	-10	-0.37	N.A.	[22]
FeP nanorod arrays	Carbon cloth	1.5	-10	-0.218	146	[23]
CoP nanowire arrays	Carbon Cloth	0.92	-10	-0.209	129	[24]
Ni–Mo/Cu nanowires	Cu foam	2.17	-10	-0.115	107	[19]
Cu_3P	Ni foam	0.25	-10	-0.13	83	[25]

Table S3. Summary of recent reported representative of highly active **bifunctional** catalysts for overall water-splitting

Catalyst	Substrate	Mass loading (mg cm^{-2})	Current density (mA cm^{-2})	Voltage	Electrolyte	Reference
CoS_2 NTA	Carbon cloth	1.2	10	1.67	1 M KOH	Curent work
Surface Oxidized CoP Nanorods	titanium sheet/powder	5	10	1.587	1 M KOH	[7]
$NiCo_2O_4$ Hollow Microcuboids	Ni foam/powder	1	10	1.65	1 M NaOH	[6]
Hollow Co_3O_4 Microtube Arrays	Ni foam	N.A.	10	1.63	1 M KOH	[11]
Carbon tubes/ cobalt-sulfide	Carbon paper	0.32(Co-S)	10	1.743	1 M KOH	[12]
Ni_8P_3	Ni foam	N.A.	10	1.61	1 M KOH	[13]
MoS_2/Ni_3S_2	Ni foam	9.7	10	1.56	1 M KOH	[14]
NiCoP	Ni foam	1.6	10	1.58	1 M KOH	[15]
NiFe LDH	Ni foam	N.A.	10	1.7	1 M NaOH	[16]
Co/CoP	GC/powder	5	10	1.45	1 M KOH	[8]
Ni–Mo/Cu nanowires	Cu foam	2.17	10	1.61	1 M KOH	[19]

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