Electronic Supplementary Information

Aerosol-spray metal phosphide microspheres with bifunctional electrocatalytic properties for water splitting

Henglei Jia,[a] Ruibin Jiang,[b] Wenzheng Lu,[a] Qifeng Ruan,[a] Jianfang Wang*[a] and Jimmy C. Yu[c]

[a]Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong SAR, China
[b]Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China
[c]Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong SAR, China

Fig. S1 Photograph of the home-built setup for ultrasonic aerosol spray. The setup used for the preparation of mesoporous metal oxide microspheres is composed of three parts from right to left: a household ultrasonic humidifier, a tube furnace and a sample collection system. In the ultrasonic humidifier, the precursor solution is atomized by the ultrasonic wave to generate discrete droplets, which are then carried by N_2 into the tube furnace. In the tube furnace, the solvent evaporation-induced assembly process of the aerosol droplets takes place within 3–5 s, including solvent evaporation, the thermal decomposition of the inorganic metal salt and the self-assembly of the surfactant molecules with the decomposition product. The product is collected using a filter connected to a water pump, on the purpose of providing an extra driving force for the droplets.

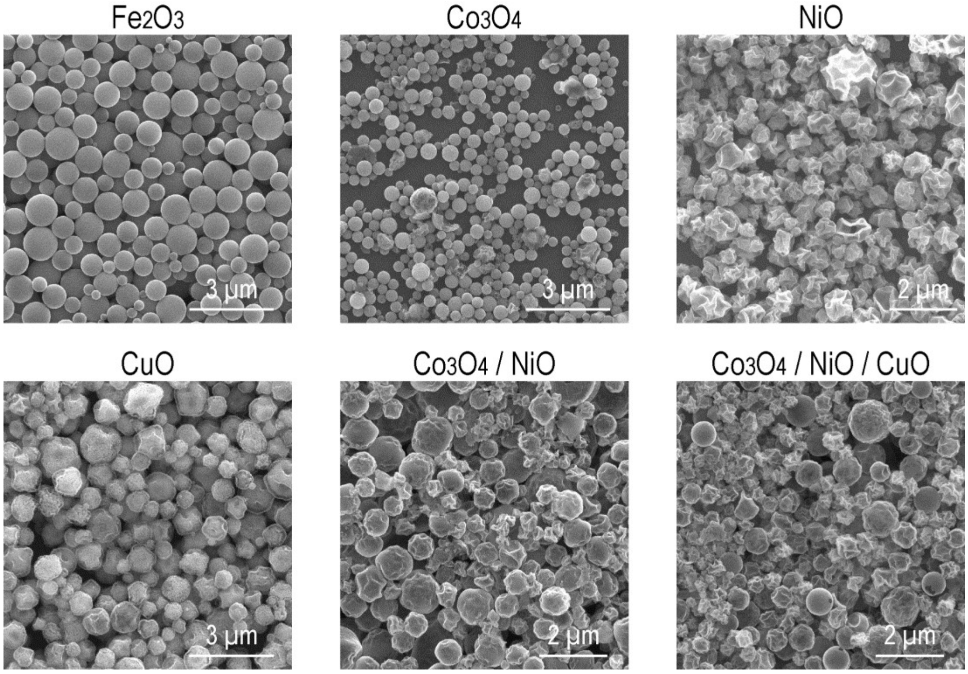

Fig. S2 SEM images of the oxide microsphere samples. The shown images are for the Fe_2O_3, Co_3O_4, NiO, CuO, Co_3O_4/NiO and Co_3O_4/NiO/CuO samples, respectively.

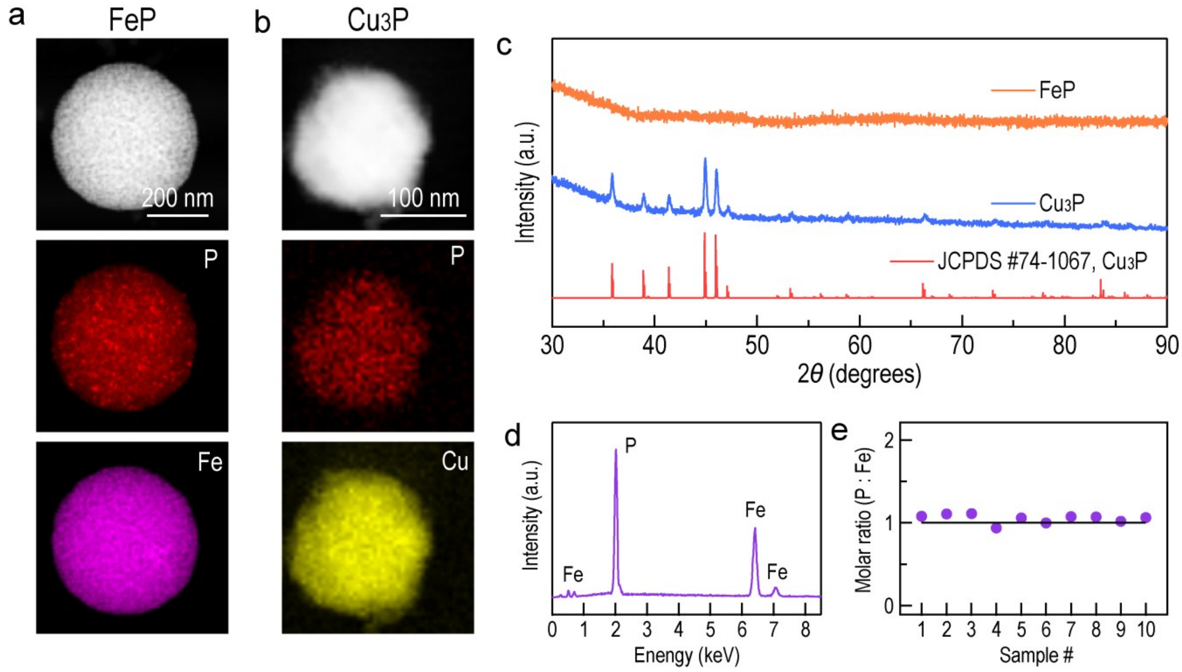

Fig. S3 FeP and Cu_3P microsphere samples. (a) HAADF-STEM image of a single FeP microsphere (top) and the corresponding elemental maps of P (middle) and Fe (bottom). (b) HAADF-STEM image of a single Cu_3P microsphere (top) and the corresponding elemental maps of P (middle) and Cu (bottom). The scale bars on the HAADF-STEM images also apply for the elemental maps. (c) XRD patterns of the FeP and Cu_3P samples, together with the standard diffraction pattern of Cu_3P. (d) EDX spectrum of the FeP sample. (e) Molar ratios of P to Fe taken from ten random FeP samples.

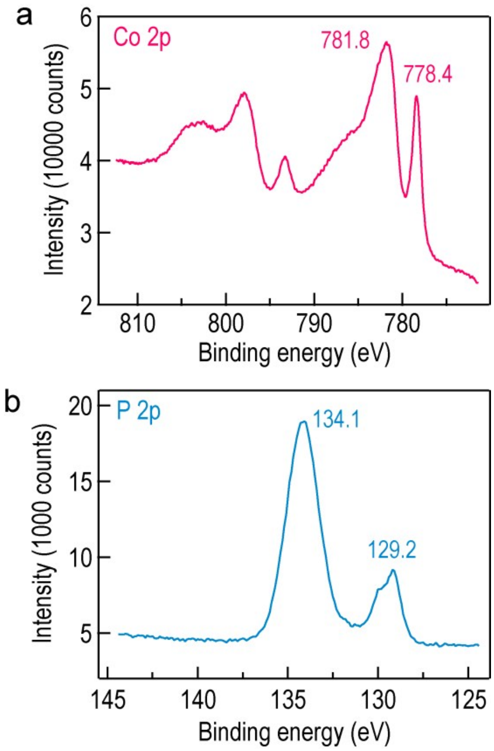

Fig. S4 XPS characterization of the CoP sample. (a) Co 2p spectrum. (b) P 2p spectrum.

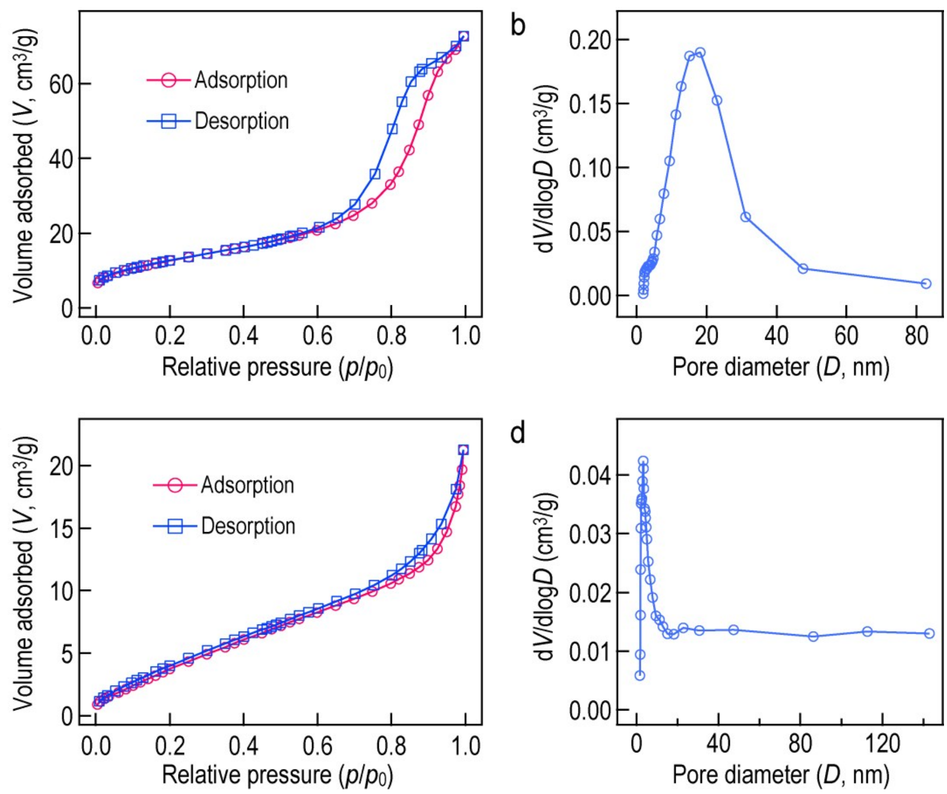

Fig. S5 Mesoporosity of the FeP and CoP microsphere samples. (a) N_2 adsorption-desorption isotherm of the FeP sample. (b) BJH pore size distribution of the FeP sample. (c) N_2

adsorption-desorption isotherm of the CoP sample. (d) BJH pore size distribution of the CoP sample.

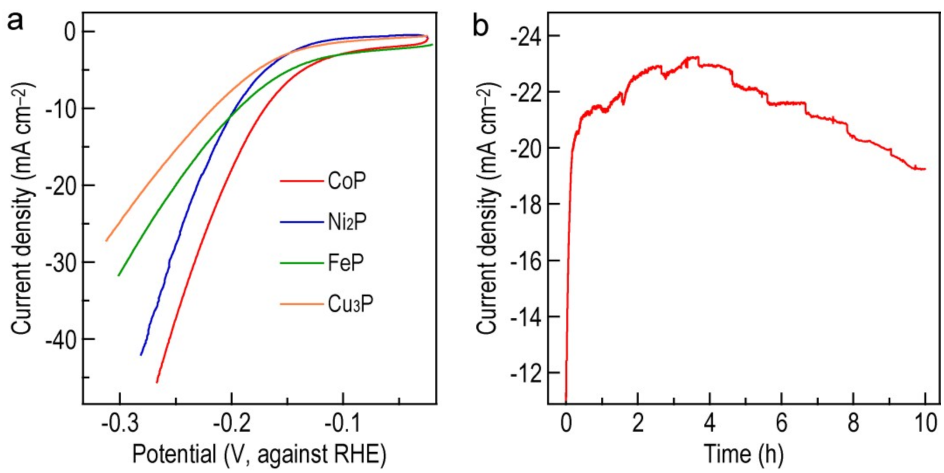

Fig. S6 HER performance in basic solutions. (a) HER polarization curves of the CoP, Ni_2P, FeP and Cu_3P samples in 1.0 M KOH solutions. (b) Time-dependent current density curve of the CoP sample at an overpotential of 206 mV for 10 h.

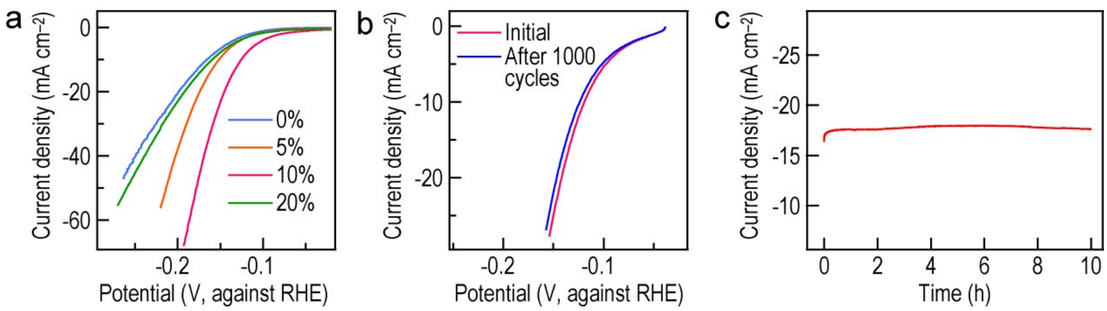

Fig. S7 HER performance in acidic solutions. (a) HER polarization curves of the CoP samples doped with Cr_2O_3 at different amounts in 0.5 M H_2SO_4 solution. (b) HER polarization curves of the 10% Cr-CoP sample before and after the 1000-cycle continuous cyclic voltammetry scanning in 0.5 M H_2SO_4 solution. (c) Time-dependent current density curve of the 10% Cr-CoP sample at a constant potential of 140 mV.

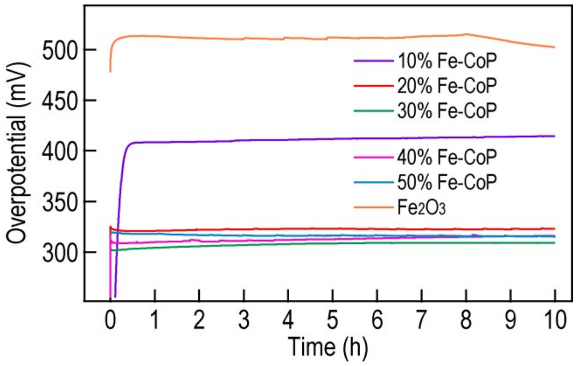

Fig. S8 Chronopotentiometry curves of the different Fe-CoP samples in 1.0 M KOH solution at a constant current density of 10 mA cm^{-2} for 10 h. The curve of the 10% Fe-CoP sample was measured for ~2 h and was extended to 10 h.

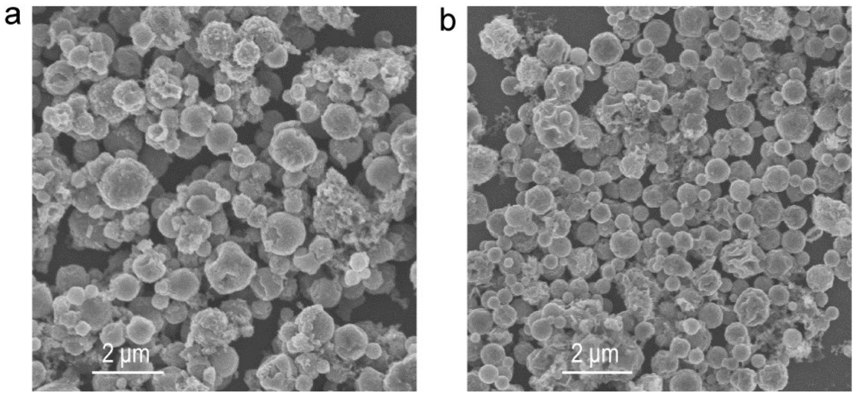

Fig. S9 SEM images of the doped CoP catalysts after 10-h overall water splitting measurement in 1 M KOH solution. (a) 10% Cr-CoP. (b) 30% Fe-CoP.

Table S1 Comparison of the HER catalytic activities among recently reported metal phosphide electrocatalysts in different shapes

Catalyst	η_{10} (mV)[a]	η_{20} (mV)[a]	Electrolyte	Mass loading (mg cm^{-2})	Supporting electrode	Reference
Self-supported Ni_5P_4–Ni_2P nanosheet array	120	140	0.5 M H_2SO_4	68.2	Ni foam	1
CoP nanowire arrays	67 209	100	0.5 M H_2SO_4 1 M KOH	0.92	carbon cloth	2
WP_2 submicroparticles	161		0.5 M H_2SO_4	0.5	glassy carbon	3
Bulk MoP	180 (η_{30})[a]		0.5 M H_2SO_4	0.86	glassy carbon	4
Cu_3P nanocubes	145 (onset overpotential)		0.5 M H_2SO_4	0.29	glassy carbon	5

MoP nanooctahedrons@porous carbon	153		0.5 M H_2SO_4	0.41	glassy carbon	6
Ni_5P_4 sheet	140 150		0.5 M H_2SO_4 1 M KOH	grown on Ni foam	Ni foam	7
Hierarchically porous urchin-like Ni_2P superstructures	98		1 M KOH	~77.6	Ni form	8
Ni_2P nanoparticles	220		1 M KOH	1.8	Ni foam	9
FeP nanowire arrays	55	72	0.5 M H_2SO_4	3.2	grown on Ti plate	10
Branched CoP nanostructures		117	0.5 M H_2SO_4	1	Ti foil	11
Co_2P nanorods	134	167 171	0.5 M H_2SO_4 1 M KOH	1	Ti foil	12
Ni_2P nanoparticles		130	0.5 M H_2SO_4	1	Ti foil	13
Ni_2P long nanowires		120	0.5 M H_2SO_4	0.3	glassy carbon	14
Janus Co/CoP	178 193	195 225	0.5 M H_2SO_4 1 M KOH	0.88	glassy carbon	15
CoP-based microspheres	125 121	145 154	0.5 M H_2SO_4 1 M KOH	0.4	ITO glass slide	This work

[a] η_{10}, η_{20} and η_{30} refer to the overpotentials at HER current densities of 10, 20 and 30 mA cm^{-2}, respectively.

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Table S2 Comparison of the OER catalytic activities among recently reported metal phosphide electrocatalysts in different shapes

Catalyst	η_{10} (mV)[a]	Electrolyte	Mass loading (mg cm^{-2})	Supporting electrode	Reference
NiCoP/C nanoboxes	330	1 M KOH	0.255	glassy carbon	1
Hierarchically porous urchin-like Ni_2P superstructures	200	1 M KOH	~77.6	Ni foam	2
Janus Co/CoP	283	1 M KOH	0.88	glassy carbon	3
Ni_5P_4 sheets	~320	1 M KOH	grown on Ni foam	Ni foam	4
Crystalline Cu_3P nanosheets	320	1 M KOH	1.2	Ni foam	5
Ni_2P nanoparticles	290	1 M KOH	0.14	glassy carbon	6
Fe-Co-P alloy hollow spheres	252	1 M KOH	0.2	glassy carbon	7
Co-P film	345	1 M KOH	2.71	Cu foil	8
NiCoP/reduced graphene oxide hybrids	270	1 M KOH	0.15	carbon fiber paper	9
CoP hollow polyhedrons	400	1 M KOH	0.102	glassy carbon	10
Flower-like $CoP/CoP_2/Al_2O_3$	300	1 M KOH	0.2	carbon paper	11
Co_2P	319	1 M KOH	grown on Co foil	Co foil	12
CoP nanorods	320	1 M KOH	0.71	glassy carbon	13
Ni-P porous nanoplates	300	1 M KOH	0.2	glassy carbon	14
$Ag@Co_xP$ core@shell nanostructures	310	1 M KOH	3.4	glassy carbon	15
CoP-based microspheres	302	1 M KOH	0.4	ITO glass slide	This work

[a]η_{10} = overpotential at an OER current density of 10 mA cm^{-2}.

[a] η_{10} refers to the overpotential at an OER current density of 10 mA cm^{-2}.

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Table S3 Comparison of the electrocatalytic activities towards overall water splitting among recently reported metal phosphides

Sample	Current density (mA cm^{-2})	Voltage (V)	Electrolyte	Mass loading (mg cm^{-2})	Supporting electrode	Reference
Three-dimensional hierarchically porous urchin-like Ni_2P microsphere superstructures	10 20 50 100	1.49 1.54 1.63 1.68	1 M KOH	77.6	Ni foam	1
MoP/CC and CoP/CC	40	1.6	1 M KOH		Carbon cloth	2
Ni_2P nanoparticles	10	1.63	1 M KOH	5	Ni foam	3
CoP film	100	1.744	1 M KOH	2.7	Copper foil	4
NiCoP	10 100 200	1.58 1.82 1.98	1 M KOH	1.6	Ni foam	5
Janus Co/CoP nanoparticles	10 20	1.45 1.66	1 M KOH	5	Ni foam	6
NiCoP/reduced graphene oxide hybrids	10	1.59	1 M KOH	0.15	Carbon fiber paper	7
Co_2P/Co foil	10	1.71	1 M KOH	grown on Co foil	Co foil	8

Flower-like $CoP/CoP_2/Al_2O_3$	20	1.69	1 M KOH	0.2	Carbon paper	9
CoP nanowires	10 100	1.56 1.78	1 M KOH	3	Co foam	10
CoP nanorod-based electrode	10	1.587	1 M KOH	5	Titanium felt sheet	11
Three-dimensional porous Ni/NiP	10	1.61	1 M KOH		Ni foam	12
CoP-based bifunctional electrocatalysts	50 100	1.47 1.67	1 M KOH	1	Ni foam	This work

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