Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information for

Boosting the hydrogen evolution performance of ruthenium clusters through synergistic coupling with cobalt phosphide

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Supplementary figures:

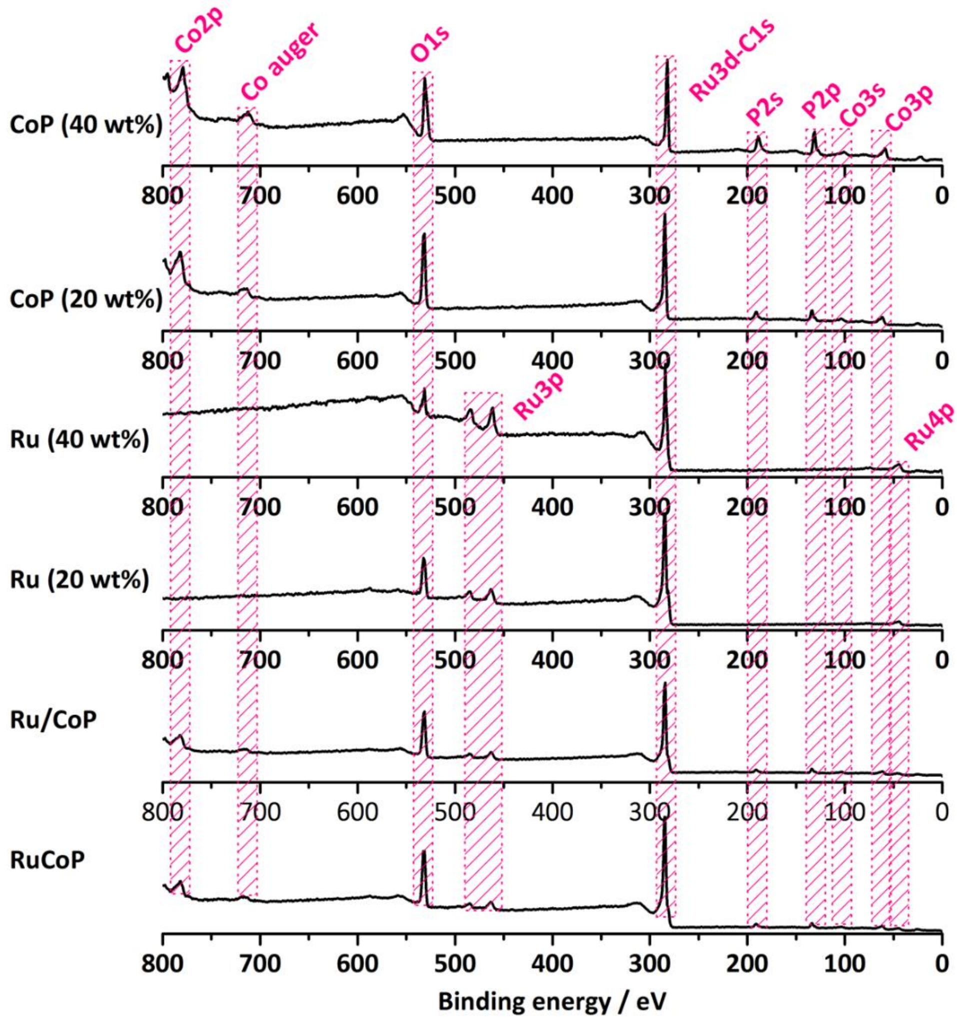

Fig. S1 XPS survey spectra of CoP-40, CoP-20, Ru-40, Ru-20, Ru/CoP and RuCoP catalysts.

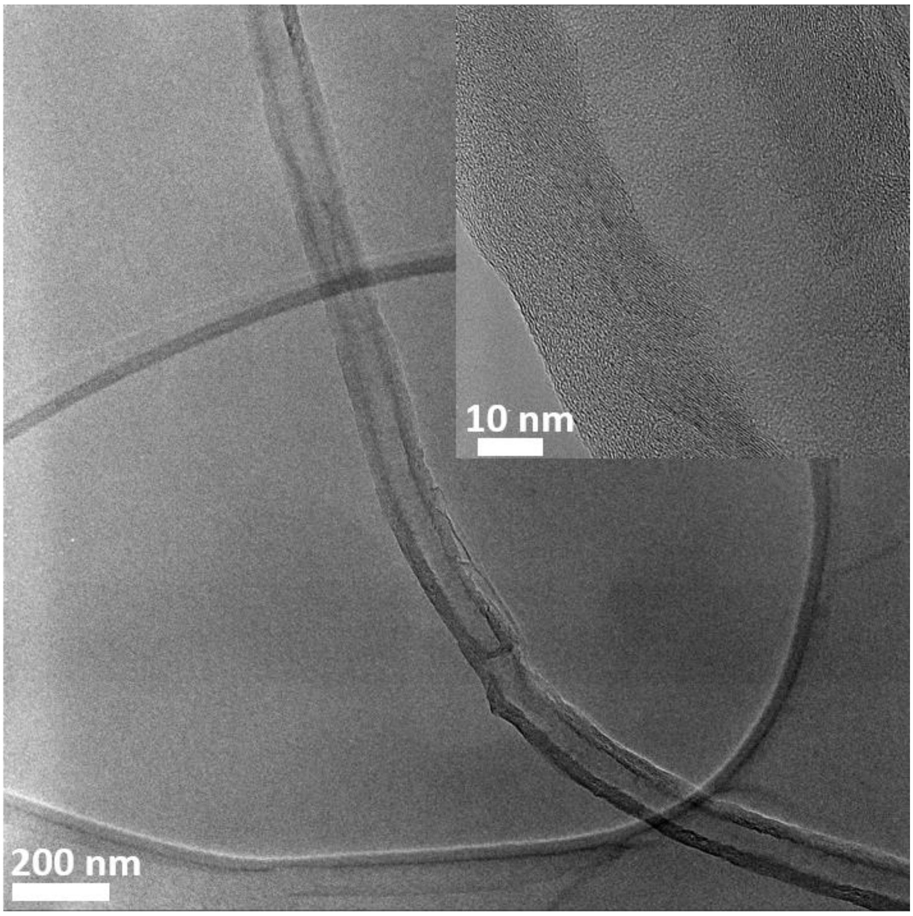

Fig. S2 TEM images of CNFs after pre-treatment in acid. Inset: HRTEM.

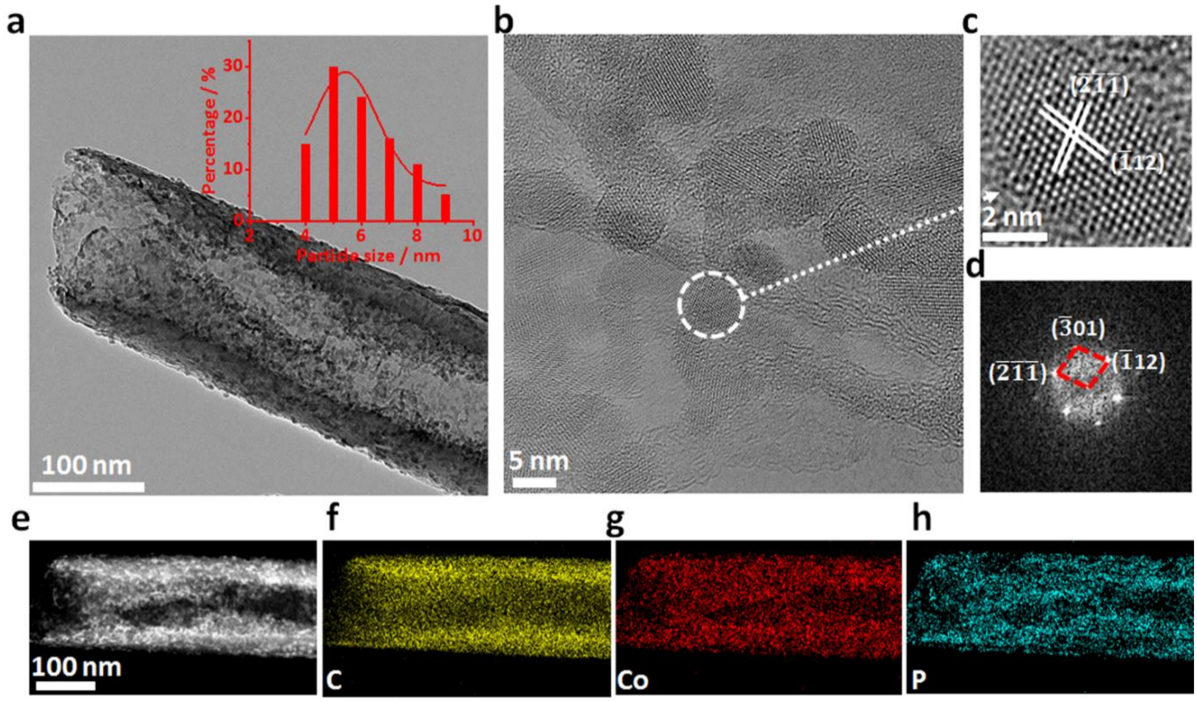

Fig. S3 Morphology and microstructure of CoP-40 catalysts. (a) Low-magnification TEM image. Inset: particle size distribution. (b) High-magnification TEM image. (c) HRTEM image (lattices indexed according to orthorhombic CoP, ICDD No. 00-029-0497). (d) FFT-ED pattern taken from a single CoP NP. (e) STEM-HAADF image. (f-h) Elemental maps of C, Co and P.

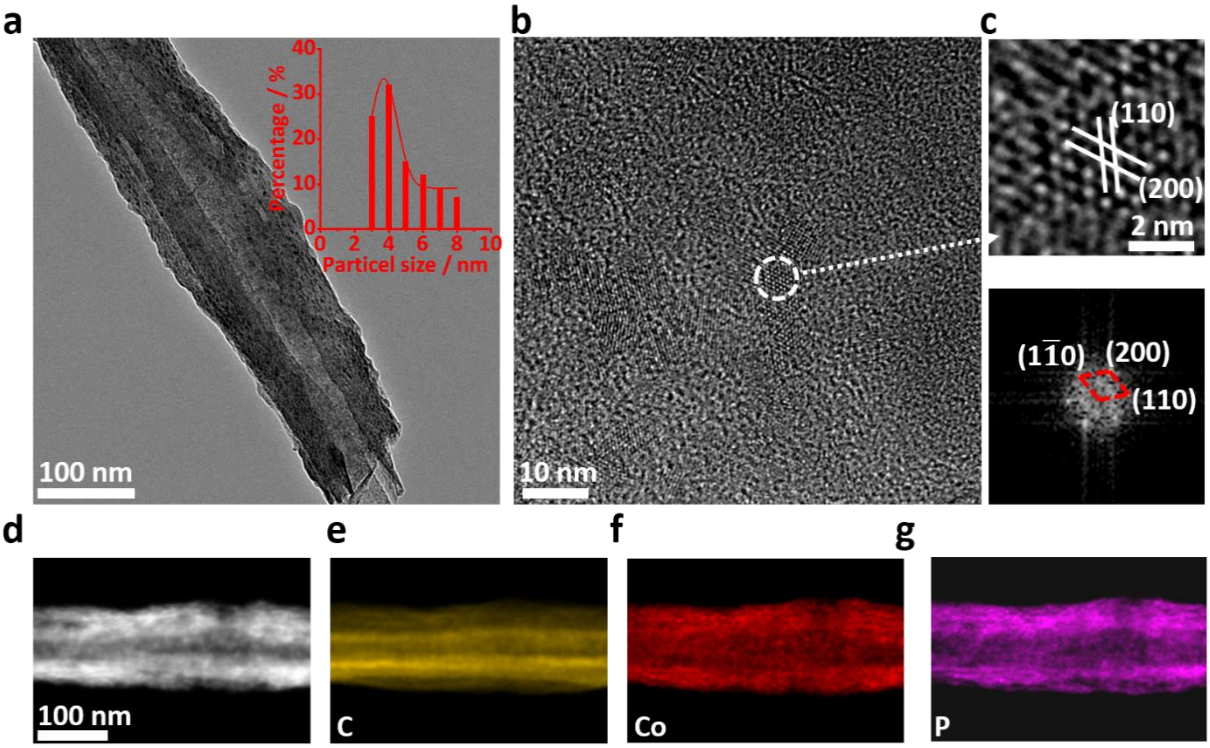

Fig. S4 Morphology and microstructure of CoP-20 catalysts. (a) TEM image. Inset: particle size distribution. (b) HRTEM image (lattices indexed according to orthorhombic CoP, ICDD No. 00-029-0497). (c) Zoomed view of a single CoP NP and the corresponding FFT-ED pattern. (d) STEM-HAADF image. (e-g) Elemental maps of C, Co and P.

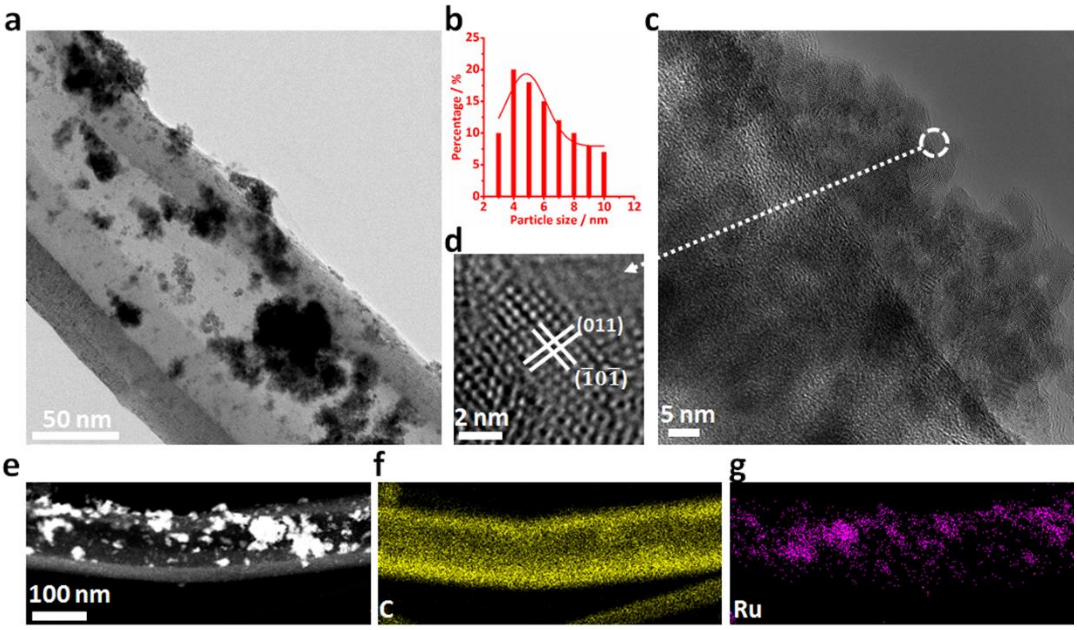

Fig. S5 Morphology and microstructure of Ru-40 catalysts. (a) TEM image. (b) particle size distribution. (c) High-magnification TEM image. (d) HRTEM image (lattices indexed according to hexagonal Ru, ICDD No. 01-089-4903). (e) STEM-HAADF image. (f, g) Elemental maps of C and Ru.

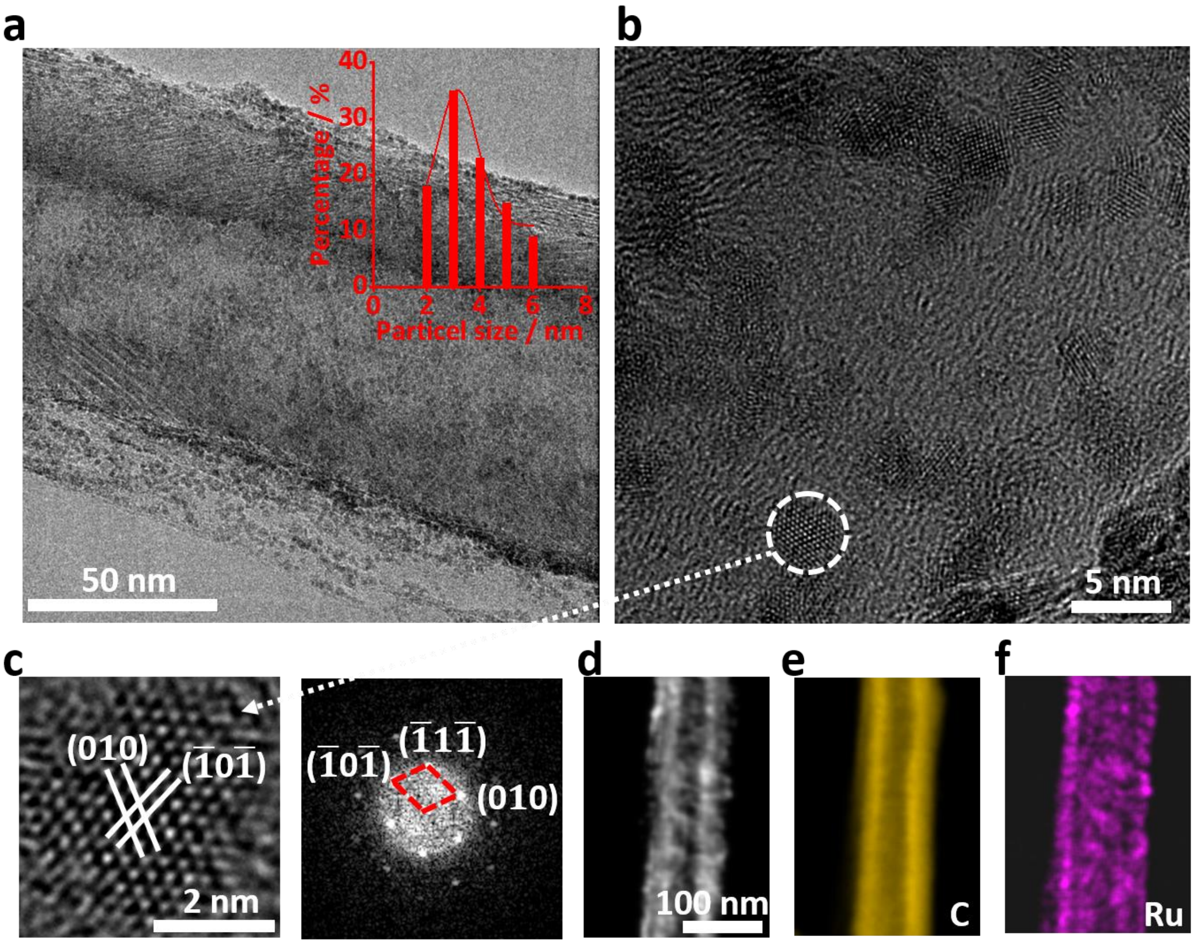

Fig. S6 Morphology and microstructure of Ru-20 catalysts. (a) TEM image. Inset: particle size distribution. (b) HRTEM image (lattices indexed according to hexagonal Ru, ICDD No. 01-089-4903). (c) Zoomed view of a single Ru NP and the corresponding FFT-ED pattern. (d) STEM-HAADF image. (e, f) Elemental maps of C and Ru.

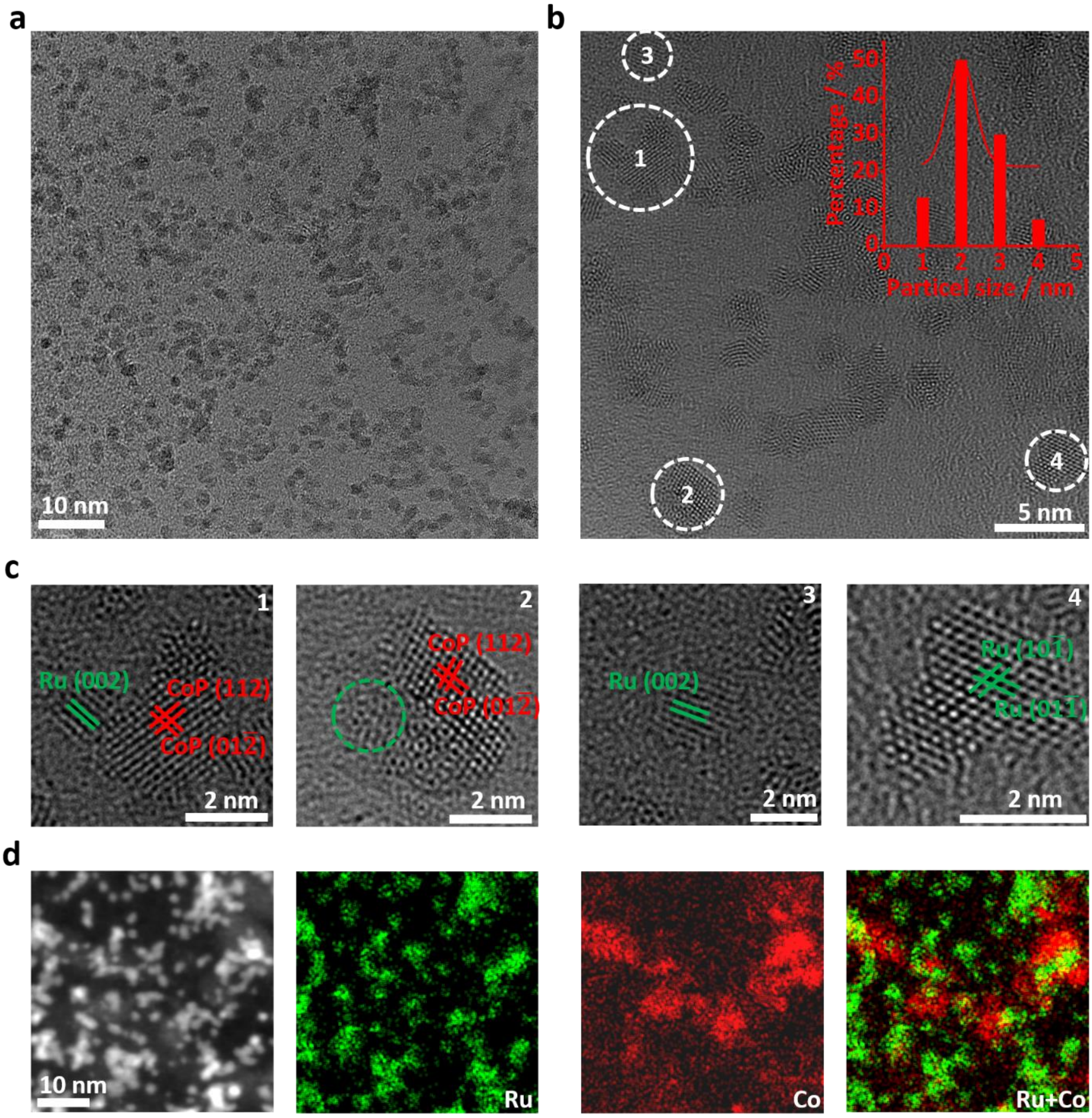

Fig. S7 Morphology and microstructure of Ru/CoP. (a) TEM image. (b) HRTEM image. Inset: particle size distribution of Ru. (c) Zoom viewed of some NPs. (d) STEM-HAADF image and elemental maps of Ru, Co and their overlay.

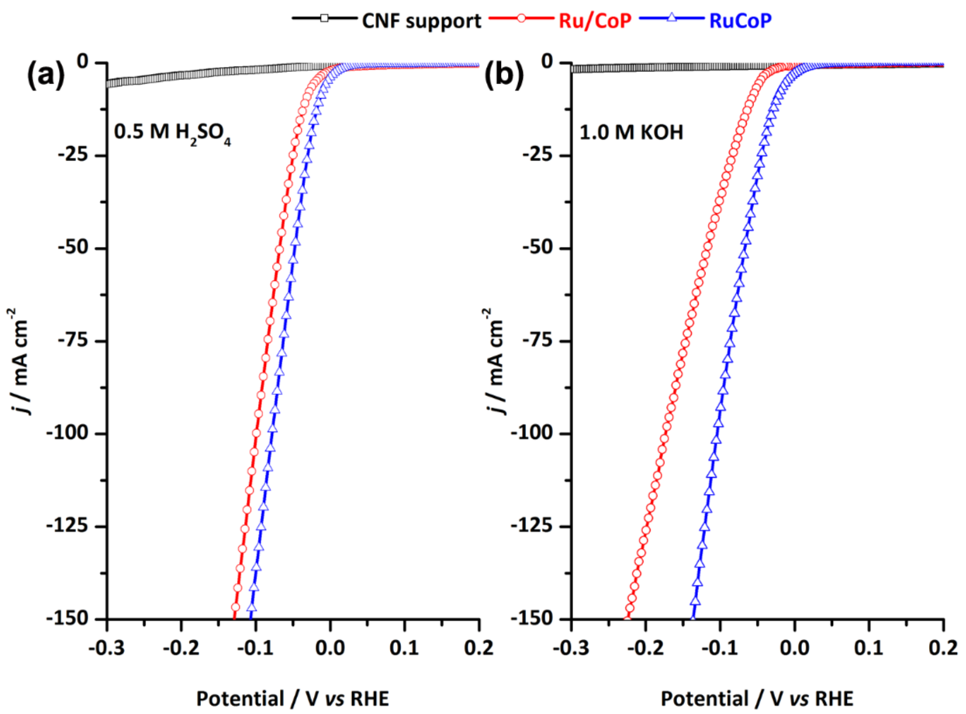

Fig. S8 *iR*-corrected linear scan voltammograms of the CNF supports measured in (a) 0.5 H_2SO_4 and (b) 1.0 M KOH. For comparison, the curves of the hybrid RuCoP and Ru/CoP catalysts are also presented.

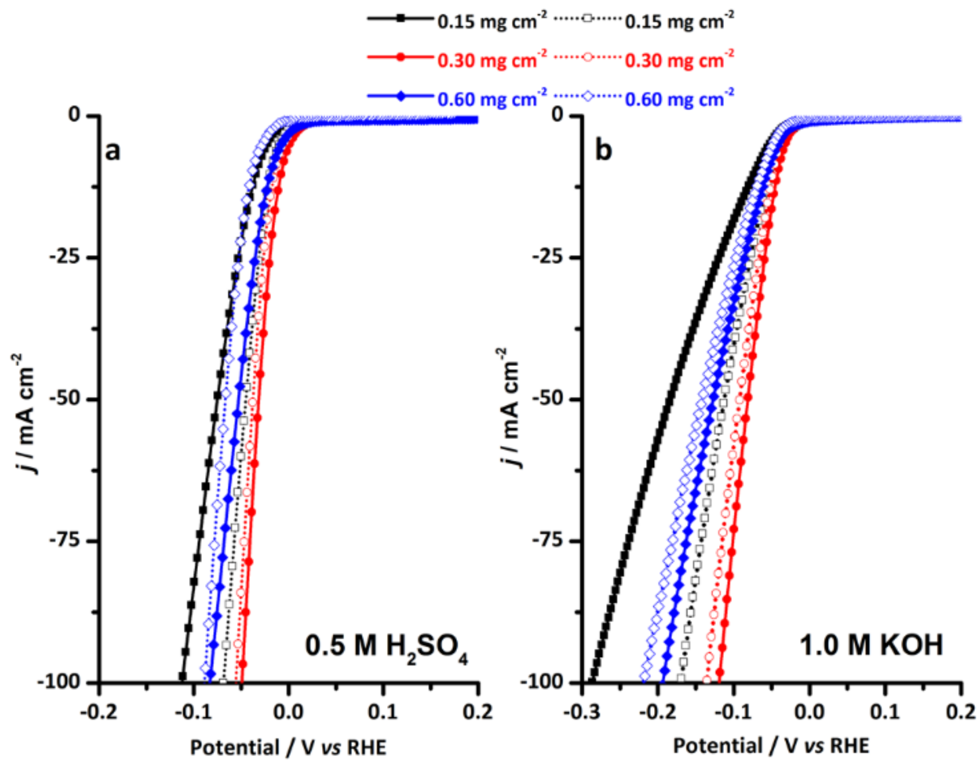

Fig. S9 *iR*-corrected polarization curves of commercial Pt/C catalysts (solid lines for 20 wt % Pt loading and short dotted lines for 40 wt % Pt loading) with different mass loadings of 0.15, 0.30 and 0.60 mg cm^{-2} on GC substrates. Scan rate: 5 mV s^{-1}. Pt/C catalysts (20 wt % Pt) with a loading of 0.3 mg cm^{-2} show best HER activities in both acidic and alkaline solutions.

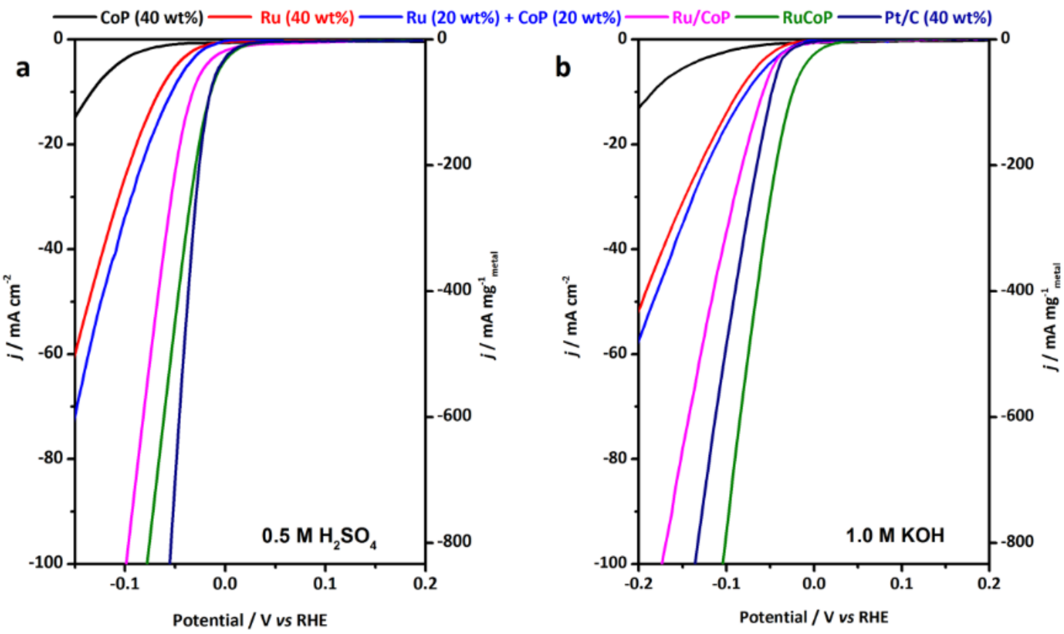

Fig. S10 Comparison of the apparent and mass activities of RuCoP, Ru/CoP and other control catalysts measured in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH. To make the comparison fair, all catalysts have a nominal metal loading of 40 wt % on the carbon supports.

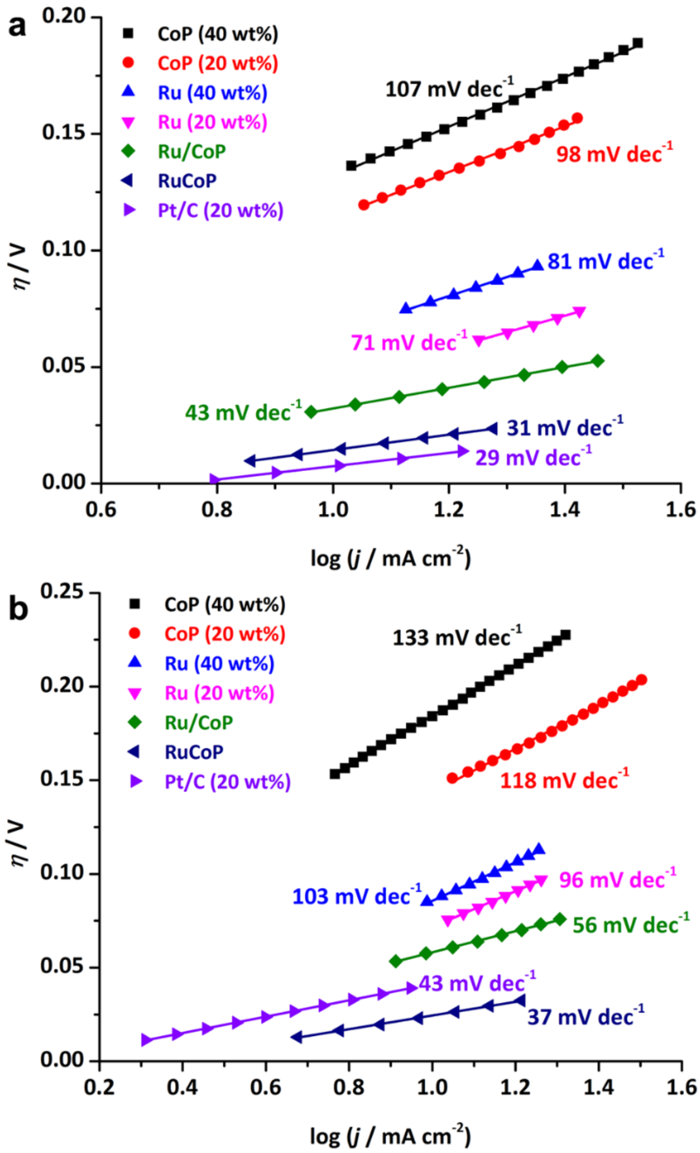

Fig. S11 Tafel plots of RuCoP, Ru/CoP and other control catalysts obtained in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH.

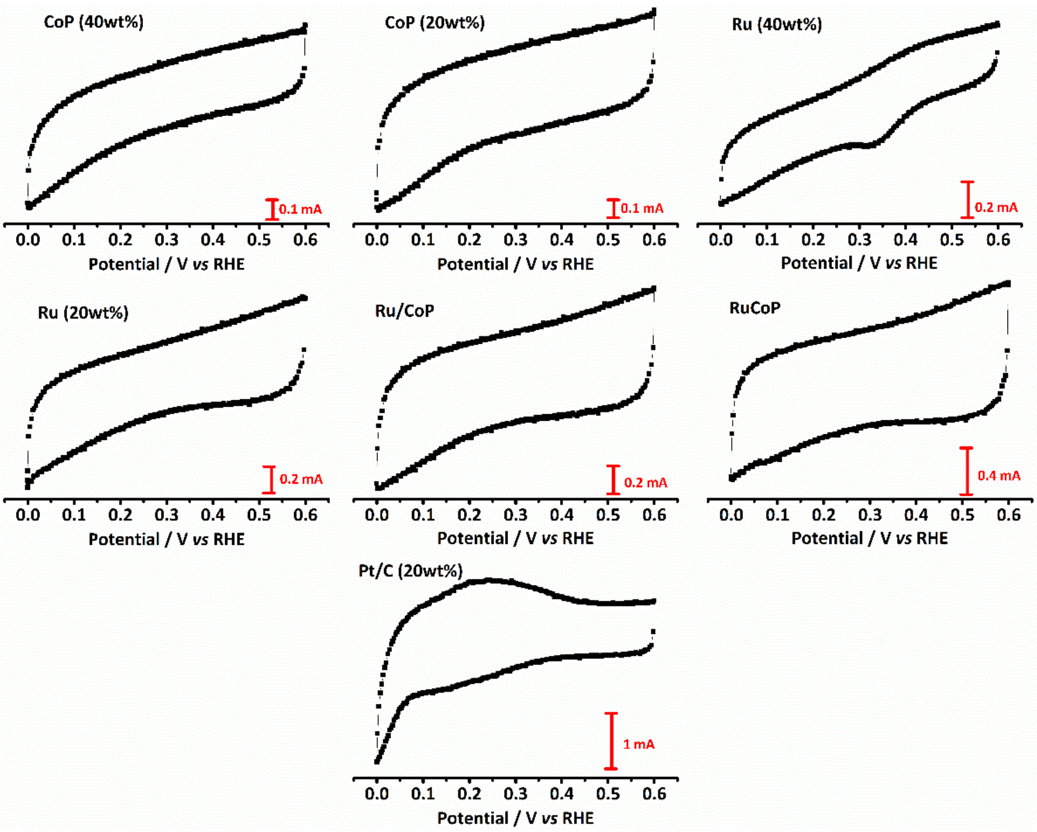

Fig. S12. Cyclic Voltammograms of CoP-40, CoP-20, Ru-40, Ru-20, Ru/CoP, RuCoP and Pt/C (20 wt % Pt) catalysts measured in PBS solution (pH = 7) at 50 mV s^{-1}.

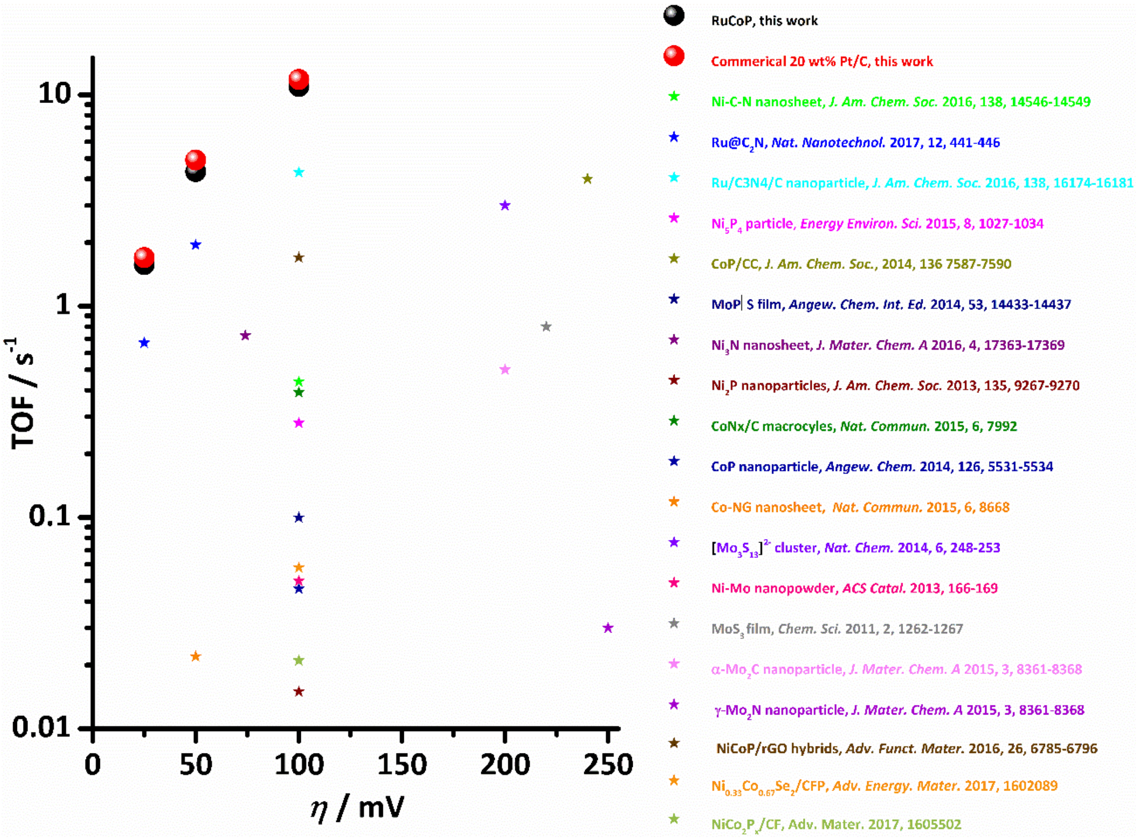

Fig. S13 Comparison of the TOF values of RuCoP catalysts with those of other state-of-the-art HER catalysts tested in 0.5 M H_2SO_4.

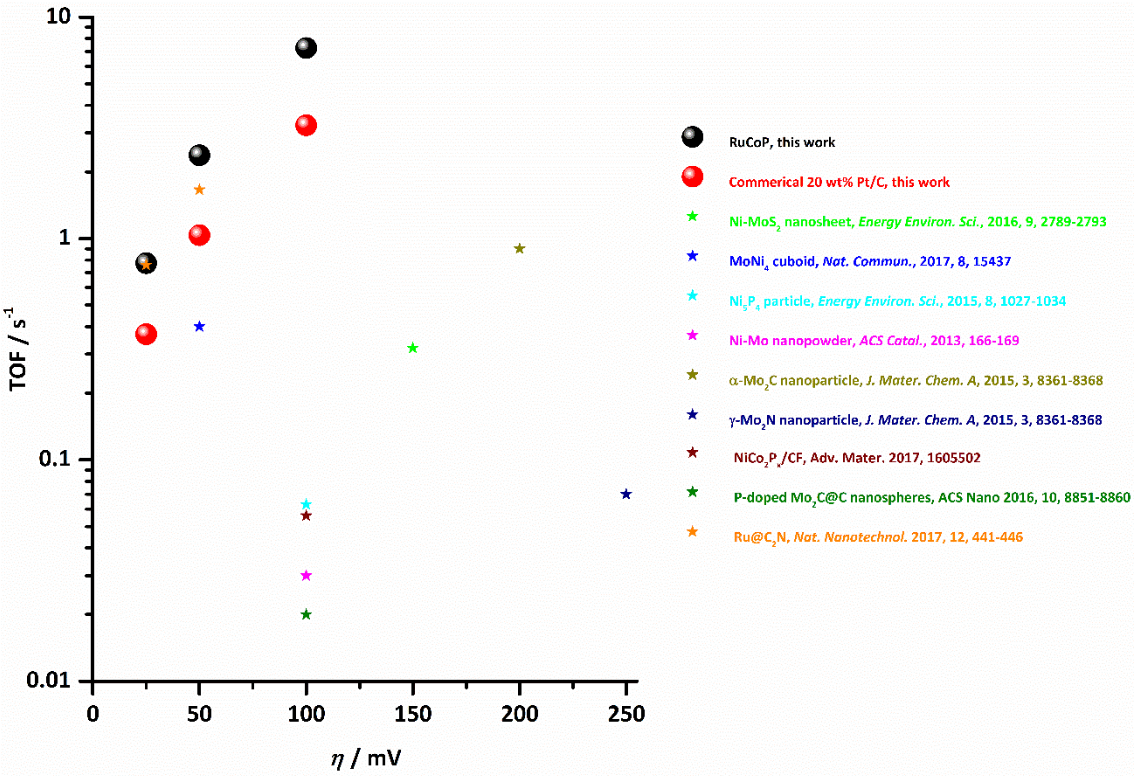

Fig. S14 Comparison of the TOF values of RuCoP catalysts with those of other state-of-the-art HER catalysts tested in 1.0 M KOH.

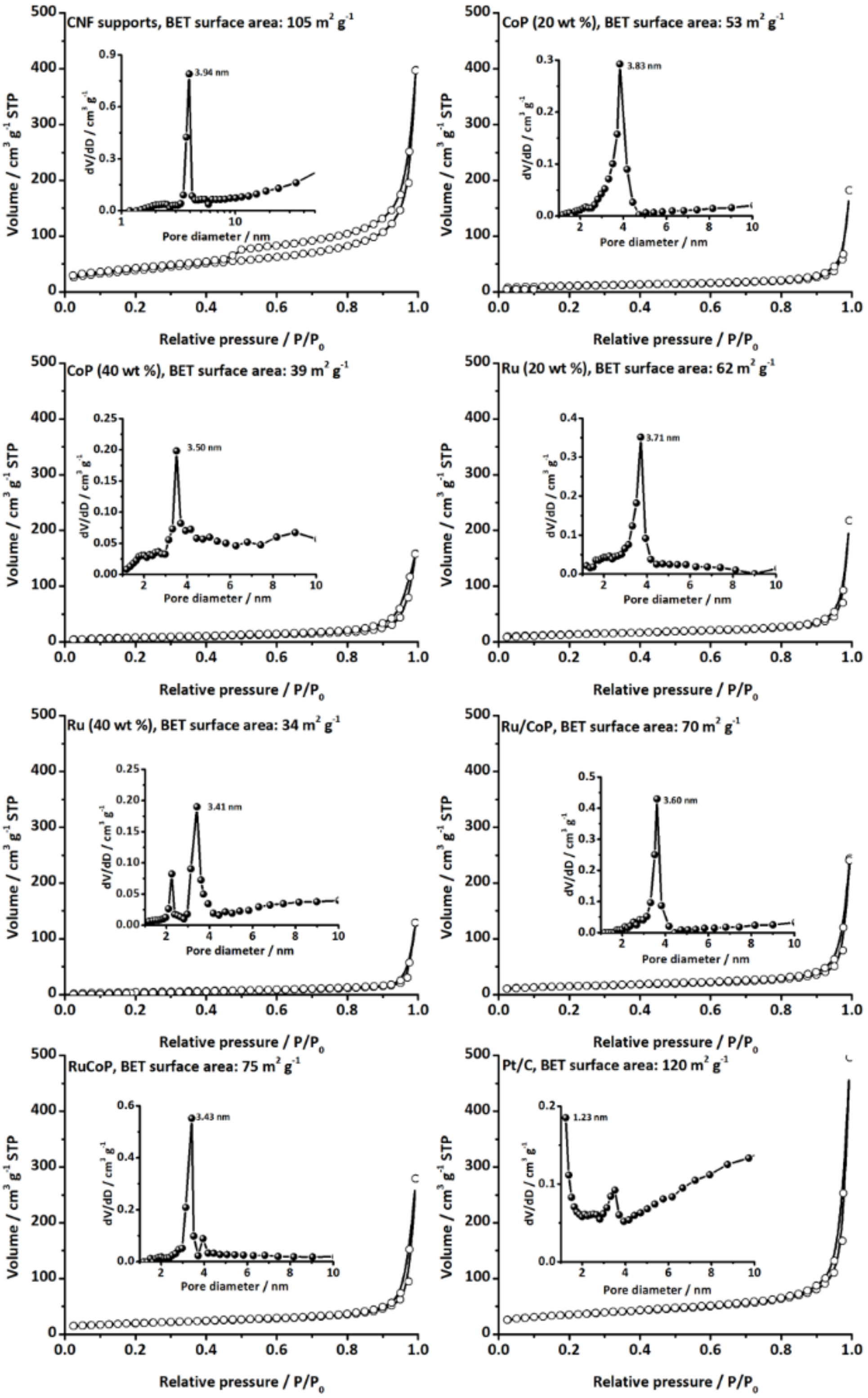

Fig. S15 N_2 adsorption/desorption isotherms of CNF supports, CoP-20, CoP-40, Ru-20, Ru-40, Ru/CoP, RuCoP and Pt/C (20 wt %) catalysts. The insets are corresponding pore size distribution plots.

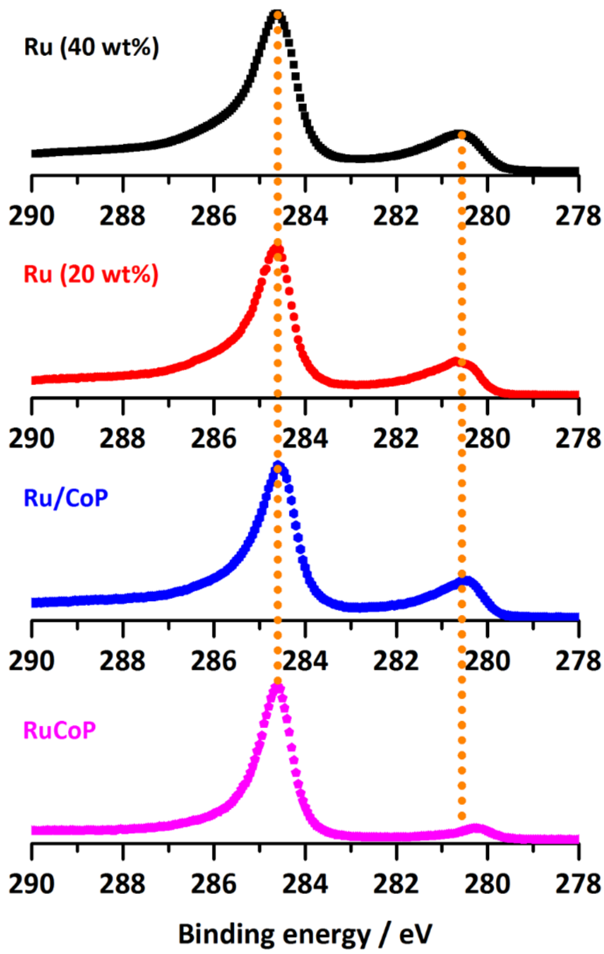

Fig. S16 Ru 3d-C1s XPS spectra of Ru-40, Ru-20, Ru/CoP, and RuCoP catalysts.

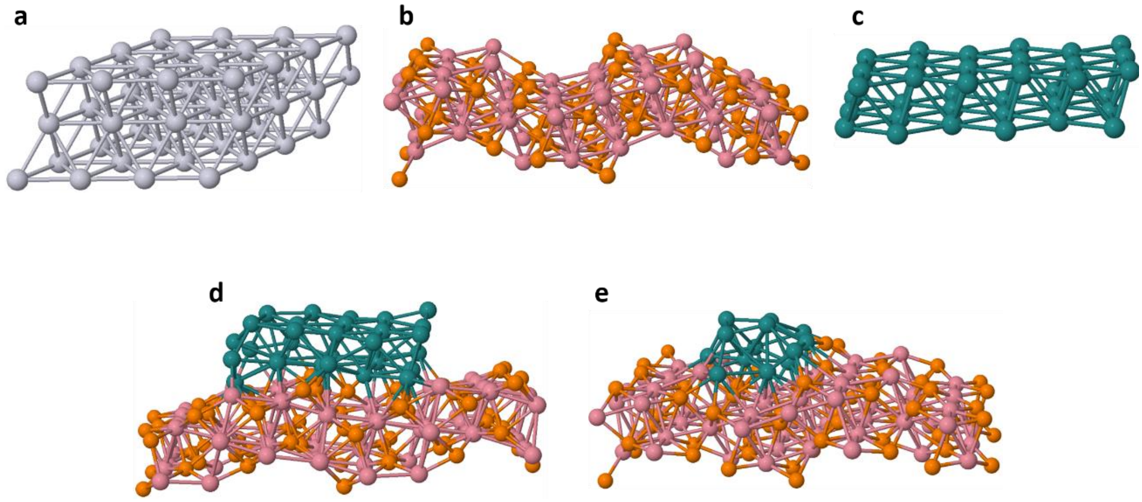

Fig. S17 The model catalysts optimized for DFT calculations. (a) Pt (111) – most active crystalline planes of Pt for HER, (b) a slab of CoP (111) mimicking the pristine CoP, (c) a slab of Ru (001) mimicking the pristine Ru, (d) a slab of Ru (001) on a slab of CoP (111) mimicking the Ru/CoP catalyst, and (e) an ultrafine Ru cluster (13 atoms) on a slab of Co (111) mimicking the RuCoP hybrid catalyst. The grey, dark pink, orange, dark green spheres represent platinum, cobalt, phosphorus and Ru atoms, respectively.

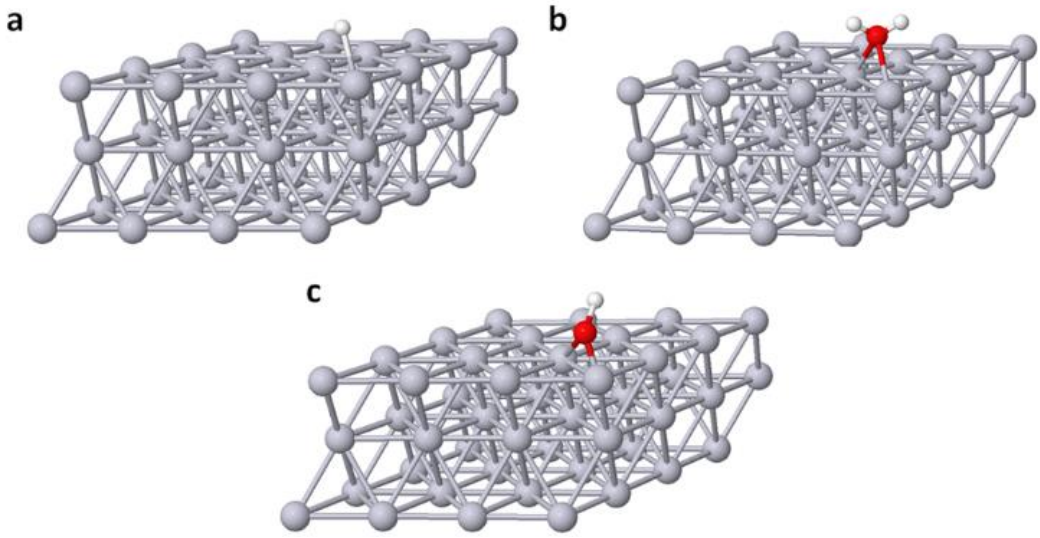

Fig. S18 (a) The hydrogen ($E_{ads,H}$ = -0.50 eV), (b) H_2O ($E_{ads,H2O}$ = -0.34 eV), and (c) OH ($E_{ads,OH}$ = -2.43 eV) adsorption energies on the Pt (111) surface. The white and red spheres represent hydrogen and oxygen atoms, respectively.

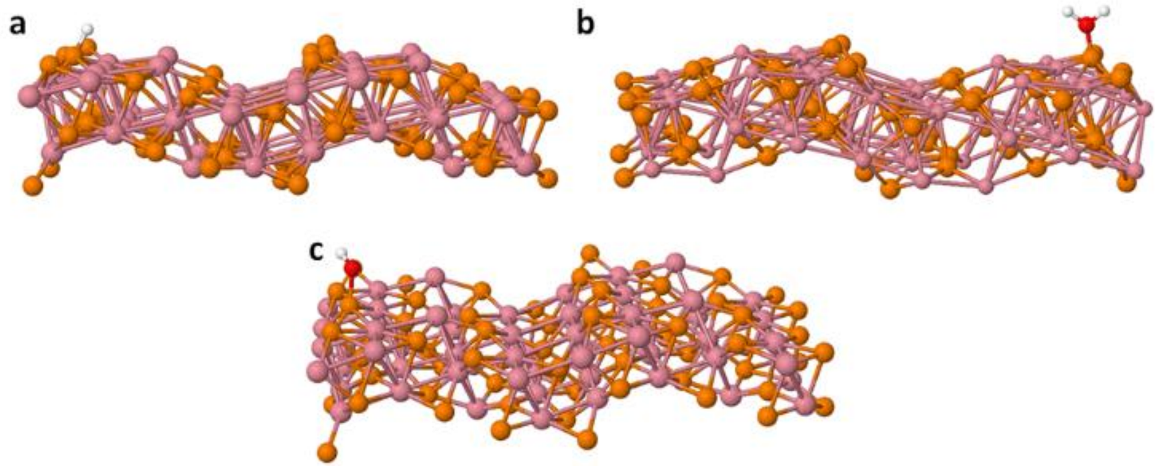

Fig. S19 (a) The hydrogen ($E_{ads,H}$ = -0.13 eV), (b) H_2O ($E_{ads,H2O}$ = -0.59 eV), and (c) OH ($E_{ads,OH}$ = -4.55 eV) adsorption energies on the CoP (111) surface. The white and red spheres represent hydrogen and oxygen atoms, respectively.

Supplementary tables

Table S1. Actual metal loading, surface charge and physical surface area of each catalyst.

Catalyst (nominal loading)	Co (actual loading, wt %)[a]	Ru (actual loading, wt %)[a]	Surface charge (μC)[b]	Physical surface area ($m^2\ g^{-1}$)[c]
CoP (40 wt %)	33.8	/	2735	39
CoP (20 wt %)	18.2	/	3095	53
Ru (40 wt %)	/	34.5	3626	34
Ru (20 wt %)	/	19.0	3791	62
Ru/CoP	17.6	18.4	4937	70
RuCoP	18.8	17.7	5478	75
Pt/C (20 wt %)	/	/	8378[d]	120[d]

[a] The values were determined from the ICP-MS analyses.
[b] The values were estimated in accordance with **Fig. S12**.
[c] The values were obtained by N_2 absorption/desorption isotherms (**Fig. S15**).
[d] The large surface area of Pt/C (20 wt%) can be partly attributed to the larger surface area of the C supports (230 – 240 $m^2\ g^{-1}$, *J. Phys. Chem. B* **2003**, 107, 6292), compared to the CNF supports (105 $m^2\ g^{-1}$, **Fig. S15a**).

Table S2. Comparison of the η_j and Tafel slope of RuCoP with other state-of-the-art catalysts in 0.5 M H_2SO_4 and 1.0 M KOH.

Electrolyte	Catalyst	Substrate	Loading (mg cm^{-2})	j (mA cm^{-2})	η_j (mV)	Tafel slope (mV dec^{-1})	Reference
0.5 M H_2SO_4	**RuCoP**	**Glassy carbon electrode**	**Ru ca. 0.06**	**10 20 50 100**	**11 25 47 77**	**31**	**This work**
	Pt-MoS_2 nanosheet	Glassy carbon electrode	Pt, ca. 0.075	10	ca. 53	40	*Nat. Commun.*, 2013, **4**, 1444
	MoP|S film	Ti foil	3	10	64	50	*Angew. Chem. Int. Ed.*, 2014, **53**, 14433-14437
	Pt MLAg NF/Ni foam	Ni foam	⁄	10	ca. 70	53	*Sci. Adv.*, 2015, **1**, e1400268
	NiAu/Au nanaoparticle	Glassy carbon electrode	ca. 0.20	10	50	36	*J. Am. Chem. Soc.*, 2015, **137**, 5859-5862
	Ni_5P_4 pellet	Ti foil	177	10	23	33	Energy Environ. Sci., 2015, **8**, 1027-1037
	WO_2-Carbon mesoporous nanowires	Glassy carbon electrode	0.35	10 20	58 78	46	*J. Am. Chem. Soc.*, 2015, **137**, 6983-6986
	Mo_2C@NPC/NPRGO nanocomposite	Glassy carbon electrode	0.14	10	34	33.6	*Nat. Commun.*, 2016, **7**, 11204
	$NiMo_4N_5$ nanocrystals	Glassy carbon electrode	1.0	20	43	39	*Nano Energy*, 2016, **22**, 111-119
	ALD50Pt/NGNS	Rotating disk electrode	ca. 0.15	10	38	29	*Nat. Commun.*, 2016, **7**, 13638
	Ru/C_3N_4/C nanoparticle	Rotating disk electrode	Ru, ca. 0.041	10	70	⁄	*J. Am. Chem. Soc.*, 2016, **138**, 16174-16181
	Pt_2Pd/NPG700 nanoparticle	Rotating disk electrode	ca. 0.16	10	58	31	*Carbon*, 2017, **114**, 740-748
	Ru@C_2N nanoparticle	Rotating disk electrode	Ru, ca. 0.082	10	13.5	30	*Nat. Nanotechnol.*, 2017, **12**, 441-446
	Ru-MO_2 nanoparticle	Glassy carbon electrode	0.285	10	55	44	*J. Mater. Chem. A*, 2017, **5**, 5475-5485
	$Ni_{43}Ru_{57}$ nanoalloy	Glassy carbon electrode	0.28	10	41	31	*ACS Appl. Mater. Interfaces*, 2017, **9**, 17326-17336
	RuP_2@NPC nanoparticle	Glassy carbon electrode	1.0	10	38	38	*Angew. Chem. Int. Ed.*, 2017, **56**, 11559-11564
	$Ni_{0.33}Co_{0.67}Se_2$/CFP	Carbon fiber paper	⁄	10	65	35	*Adv. Energy Mater.*, 2017, **7**, 1602089
	$Ni_{0.89}Co_{0.11}Se_2$ MNSN/NF	Ni foam	2.62	10	52	39	*Adv. Mater.*, 2017, **29**, 1606521
	N,S-Carbon nanosheets	Glassy carbon electrode	⁄	10	290	76.9	*ACS Nano*, 2017, **11**, 7293-7300
1.0 M KOH	**RuCoP**	**Glassy carbon electrode**	**Ru, ca. 0.06**	**10 20 50 100**	**23 38 66 102**	**37**	**This work**
	Pt nanowire/SL-$Ni(OH)_2$	Glassy carbon electrode	Pt, 0.016	10	70	⁄	*Nat. Commun.*, 2015, **6**, 6430
	NiSe/NF	Ni foam	2.8	10	96	120	*Angew.Chem., Int. Ed.*, 2015, **54**, 9351-9355
	Ni_5P_4 pellet	Ti foil	177	10	49	98	Energy Environ. Sci., 2015, **8**, 1027-1037
	P-doped Mo_2C@C nanospheres	Glassy carbon electrode	0.90	10	47	71	*ACS Nano*, 2016, **10**, 8851-8860

Pt_3Ni_3 nanowire	Rotating disk electrode	Pt, 0.015	10 ca. 40	40 70	⁄	*Angew. Chem. Int. Ed.*, 2016, **128**, 13051-13055
Ni-MoS_2 nanosheet	Carbon cloth	0.89	10	98	60	*Energy Environ. Sci.*, 2016, **9**, 2789-2793
Ni-C-N nanosheets	Glassy carbon electrode	0.2	10	30.8	40	*J. Am. Chem. Soc.*, 2016, **138**, 14546-14569
Ultrathin Ni nanosheets	Carbon cloth	0.53	10	80	70	*Chem*, 2017, **3**, 122-133
RuCo@NC nanoparticle	Glassy carbon electrode	0.275	10	28	31	*Nat. Commun.*, 2017, **8**, 14969
$Ni_{0.33}Co_{0.67}Se_2$/CFP	Carbon fiber paper	⁄	10	106	60	*Adv. Energy Mater.*, 2017, **7**, 1602089
$Ni(OH)_2/MoS_2$ heterostructure	Carbon cloth	4.8	10	80	60	*Nano Energy*, 2017, **37**, 74-80
3D core–shell Cu@NiFe LDH/CF	Copper foam	⁄	10 100	116 192	58.9	*Energy Environ. Sci.*, 2017, **10**, 1820-1827
N,S-Carbon nanosheets	Glassy carbon electrode	⁄	10	380	103	*ACS Nano*, 2017, **11**, 7293-7300
$NiCo_2P_x$/CF	Carbon fiber paper	5.9	10	58	34.3	*Adv. Mater.*, 2017, **29**, 1605502
$Ni_{0.89}Co_{0.11}Se_2$ MNSN/NF	Ni foam	2.62	10	85	52	*Adv. Mater.*, 2017, **29**, 1606521
RuP_2@NPC nanoparticle	Glassy carbon electrode	1.0	10	52	69	*Angew. Chem. Int. Ed.*, 2017, **56**, 11559-11564