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Supporting Information (SI) for

Ru decorated with NiCoP: an efficient and durable hydrogen evolution reaction electrocatalyst in both acidic and alkaline conditions

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Experimental Section

Chemicals

Dodecylamine (DDA), Oleic acid (OA), 20% Pt/C and 5 wt% Nafion were purchased from Alfa Aesar. $Co(acac)_2$, $Ni(HCOO)_2$, $Fe(Ac)_2$ and $RuCl_3{\cdot}nH_2O$ were purchased from ShangHai Guoyao Chemical Industry Co. Ltd. Trioctyphosphine (TOP, 90%) was purchased from Aladdin Industrial Corporation. Unless otherwise stated, all the above chemicals were used as received without further purification.

Synthesis of NiCoP@Ru. The NiCoP@Ru were prepared via a simple one-pot synthesis method. Firstly, $Ni(HCOO)_2$ (0.1116 g, 0.75 mmol), $Co(acac)_2$ (0.1782 g, 0.70 mmol), $RuCl_3{\cdot}nH_2O$ (0.1037 g, 0.5 mmol), TOP (5 mL), OA (1.5 mL) and DDA (3 mL) were mixed homogenously in a three-necked flask reactor. Then the reactor was heated to 320 ºC in sand bath and maintained at this temperature for 30 min. Then, the reactor was naturally cooled to 50 °C. The reactor was again heated to 320 ºC in sand bath and maintained at this temperature for 30 min. After the reaction, the generated black precipitate was centrifuged and separated with ethanol and heptane for several times. Finally, the as-obtained catalyst was dried in a vacuum oven overnight.

Synthesis of other $Ni_xCo_yP@Ru_z$. The synthesis of other $Ni_xCo_yP@Ru_z$ was similar to that of NiCoP@Ru with different molar ratio of the introduced metal solid precursors.

Synthesis of NiCoP. The synthesis of NiCoP was similar to that of NiCoP@Ru but the $RuCl_3{\cdot}nH_2O$ was not added.

Synthesis of Ru. The synthesis of Ru was similar to that of NiCoP@Ru but the $Ni(HCOO)_2$, $Co(acac)_2$ and TOP were not added.

Synthesis of FeCoP@Ru. The synthesis of FeCoP@Ru was similar to that of NiCoP@Ru, $Fe(Ac)_2$ instead of $Ni(HCOO)_2$.

Sample Characterizations

The transmission electron microscopy (TEM) image was performed using a JEM-200CX instrument (Japan), and the corresponding acceleration voltage was 200 kV. The high resolution transmission electron microscopy (HRTEM), together with X-ray energy-dispersive spectra (EDS), elemental mapping, scanning transmission electron microscopy (STEM) and EDS line-scan images was acquired using JEOL-2100F apparatus at an acceleration voltage of 200 kV. The powder X-ray diffraction (XRD) pattern was recorded using a D/max 2500VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation (λ = 0.154060 nm), and the corresponding scan range was 5o to 90o in 2θ value. The X-ray photoelectron spectra (XPS) were recorded on a scanning X-ray microprobe (PHI 5000 Versa, ULACPHI, Inc.) that uses Al Kα radiation. The binding energy of the C1s peak (284.6 eV) was employed as a standard to calibrate the binding energies of other elements. The electrochemical impedance spectra (EIS) test was carried out on an Autolab PGSTAT302N system in 0.5 M H_2SO_4.

Electrochemical HER measurements

The electrochemical HER experiment was carried out on a CHI 660E electrochemical workstation (Shanghai, Chenhua Co.) with a standard three electrode system. A graphite rod electrode served as the counter electrode, while Ag/AgCl (3 M KCl) acted as the reference electrode and a glassy carbon electrode (GCE) (3 mm in diameter) was used as the working electrode. The catalyst dispersions were prepared by mixing a certain amount of catalyst with the appropriate amount of water, ethanol, and Nafion (1.0 wt%) with a volume ratio of 3.8:1:0.2 under sonication for 40 min to form a homogeneous ink with a concentration of 5 mg mL^{-1}. The catalyst suspension (4 μL) was dropped onto the GCE surface and air dried. All of the modified electrodes were pretreated by cycling the potential between -0.80 and 0.10 V for 100 cycles to remove any surface contamination prior to the electrochemical test. Cyclic voltammetry (CV) measurements were conducted in N_2-saturated 0.5 M H_2SO_4 and 1.0 M KOH aqueous solutions. All the potentials were referenced to a reversible hydrogen electrode (RHE).

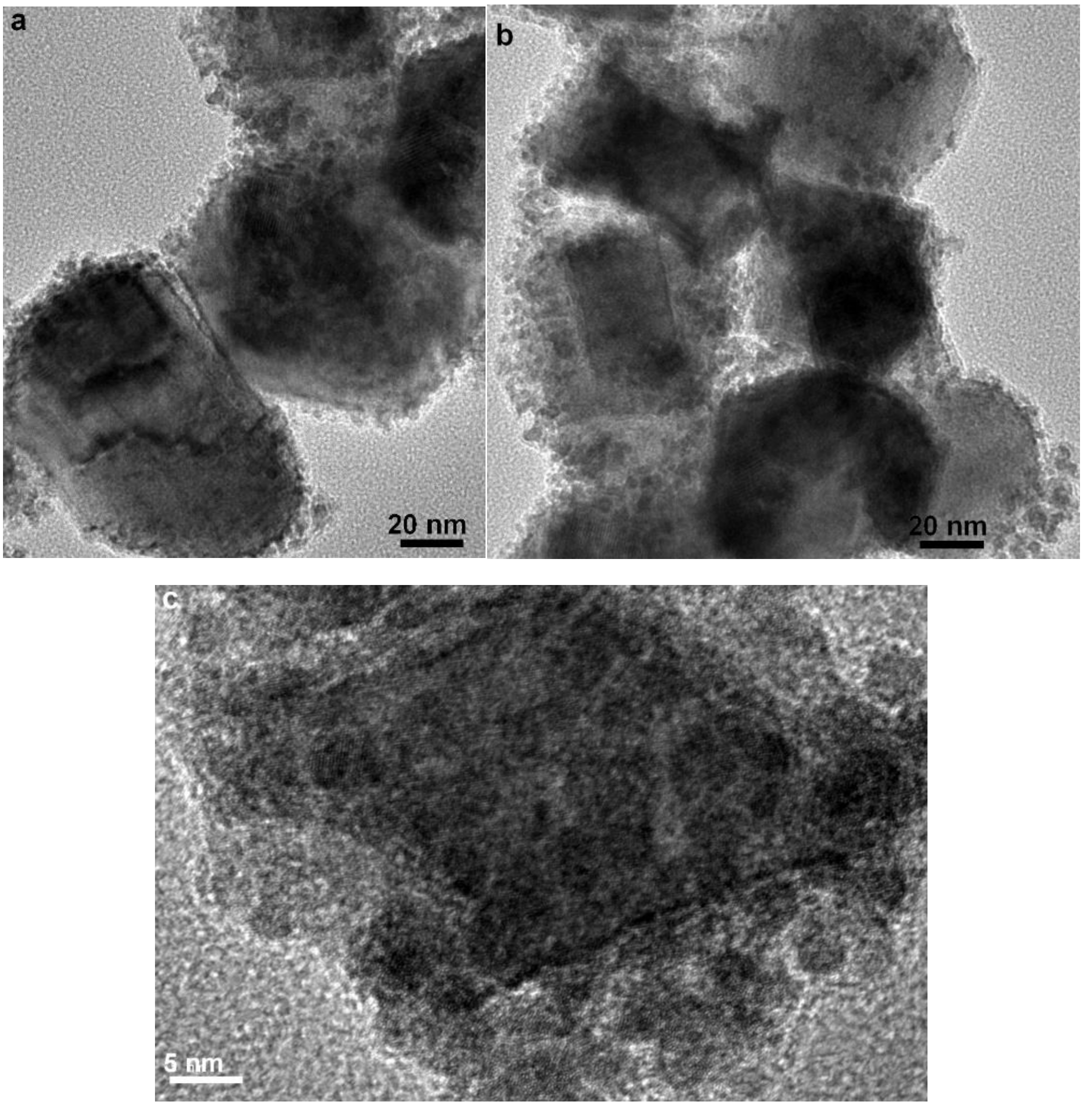

Fig. S1 (a) and (b) TEM and (c) HRTEM images of the NiCoP@Ru.

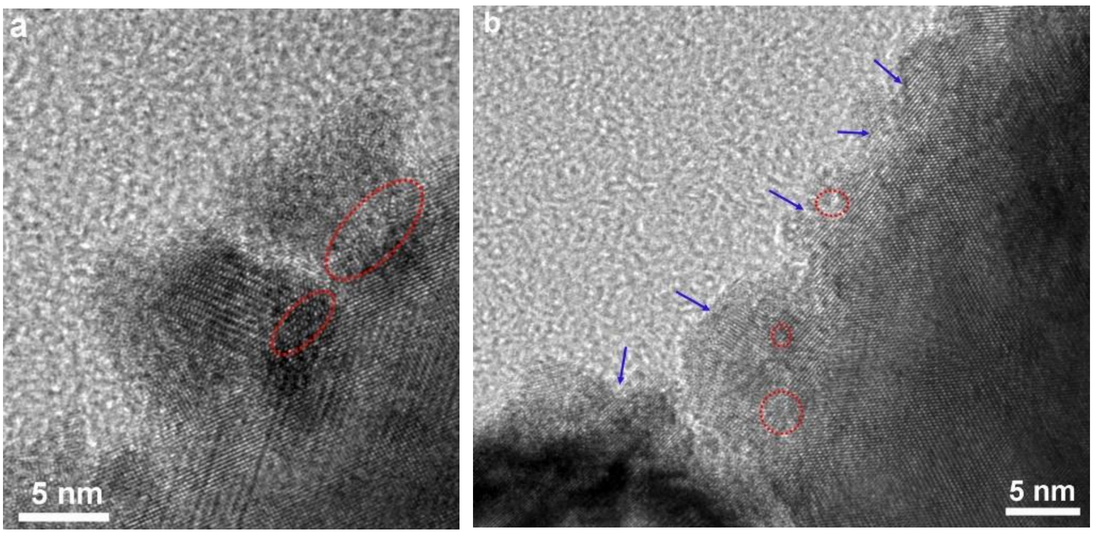

Fig. S2 (a) and (b) HRTEM images of the NiCoP@Ru.

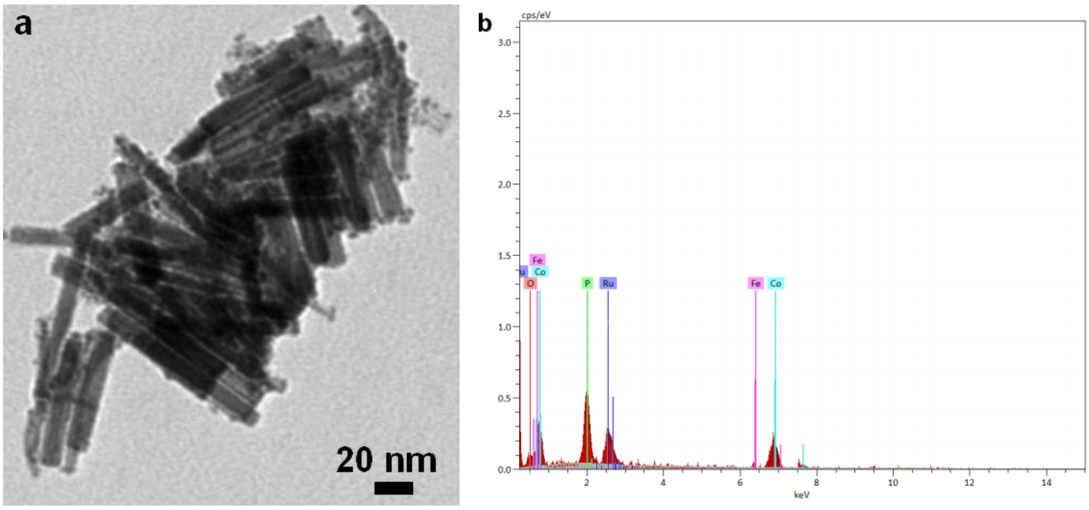

Fig. S3 (a) TEM image and (b) EDS of the FeCoP@Ru.

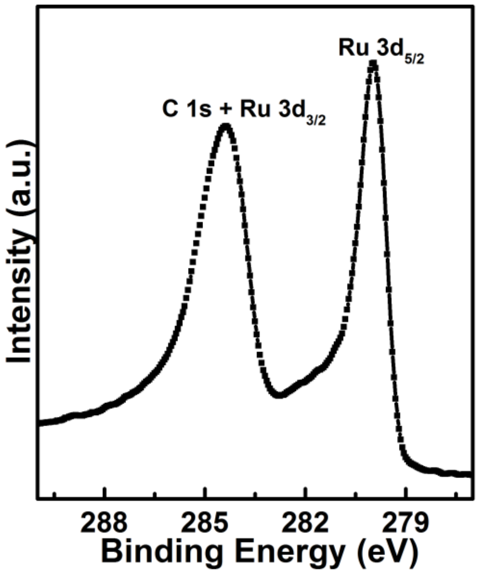

Fig.S4 high-resolution XPS spectra for Ru 3d of NiCoP@Ru.

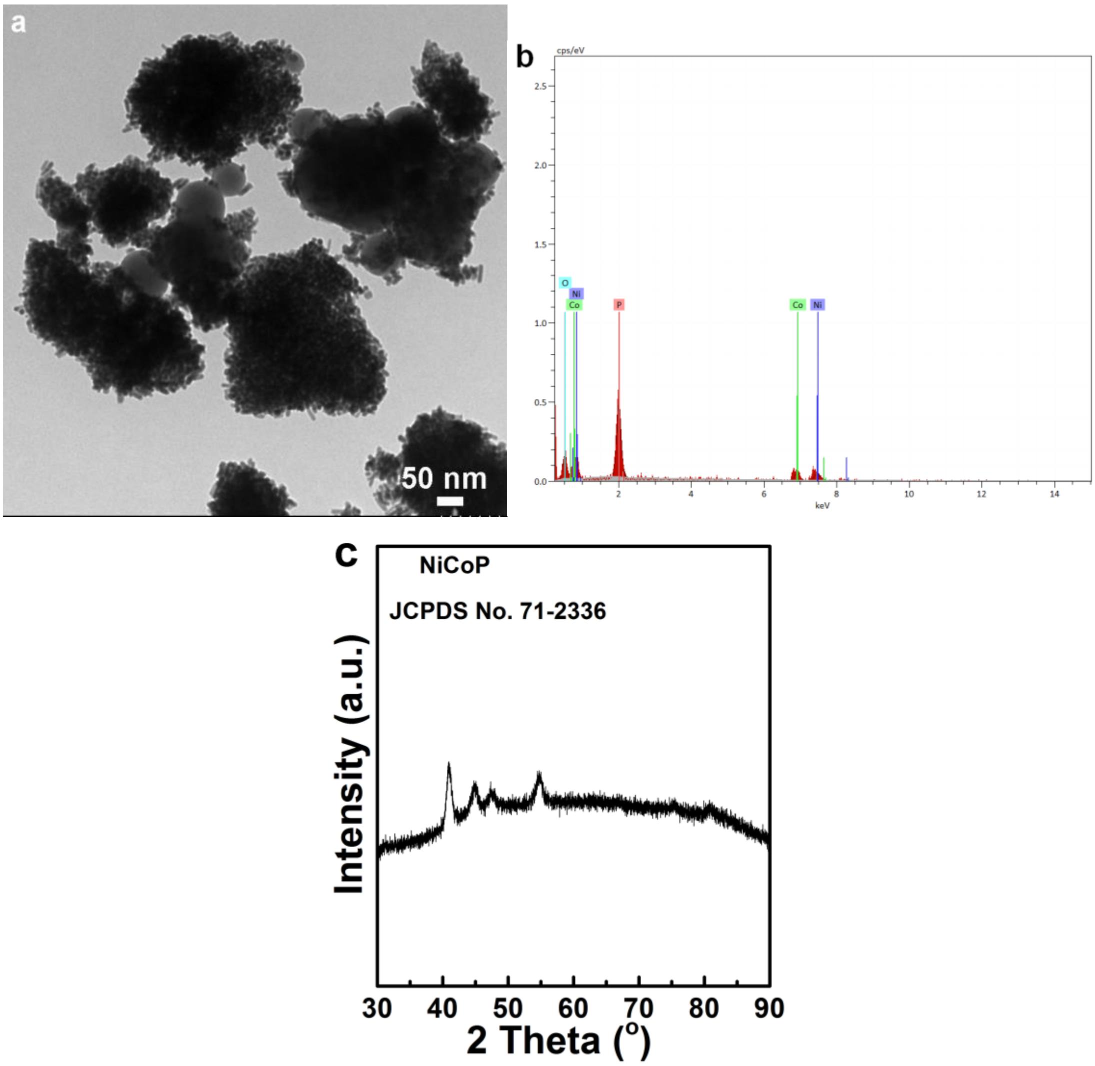

Fig. S5 (a) TEM image, (b) EDS and (c) XRD pattern of the NiCoP.

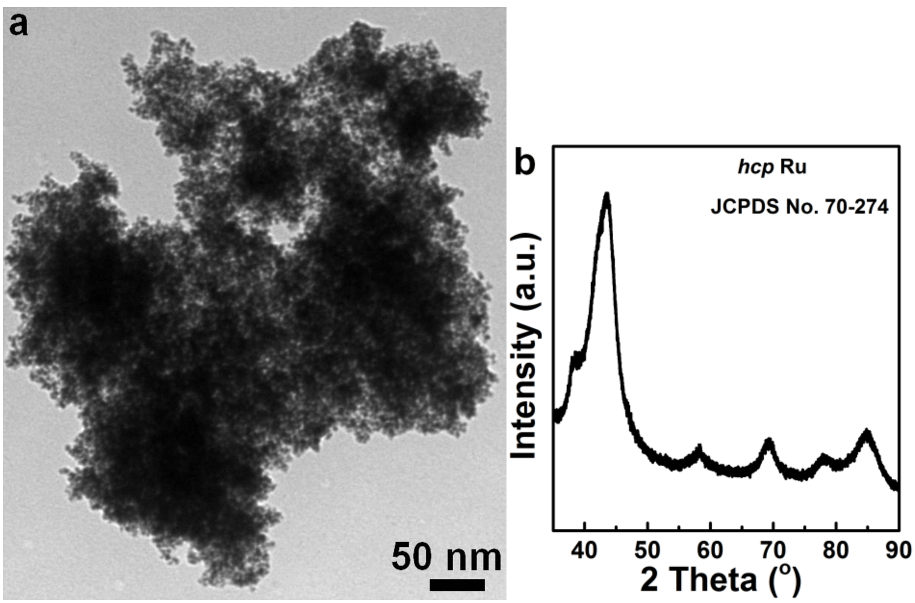

Fig. S6 (a) TEM image and (b) XRD pattern of the Ru.

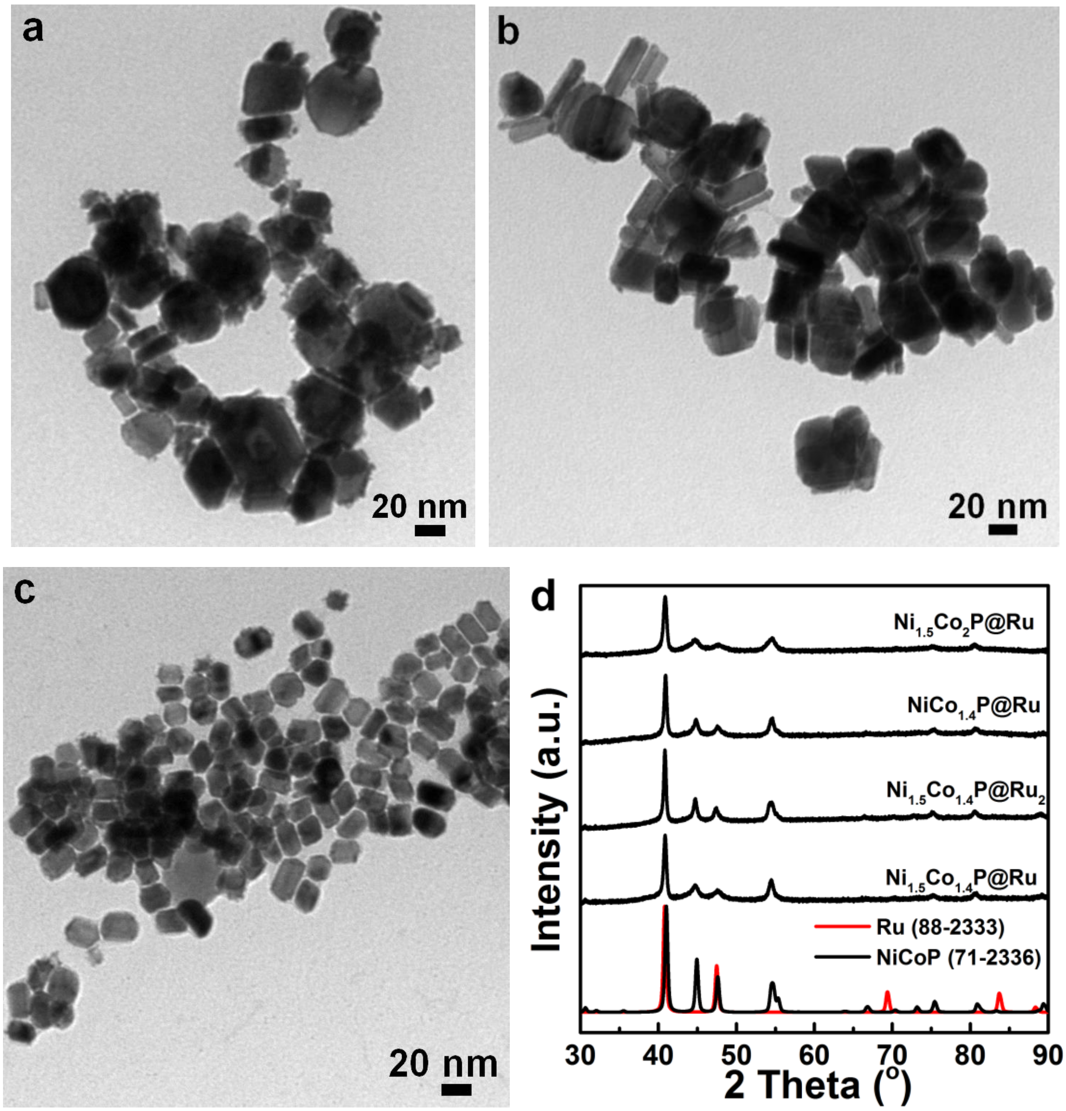

Fig. S7 TEM images of (a) $Ni_{1.5}Co_{1.4}P@Ru_2$, (b) $NiCo_{1.4}P@Ru$, and (c) $Ni_{1.5}Co_2P@Ru$ and (d) XRD patterns of the $Ni_xCo_yP@Ru_z$.

Table S1. Comparisons of electrocatalytic HER properties of some recently reported catalysts in 0.5 M H_2SO_4

Catalyst	Tafel slope [mV dec^{-1}]	η_{10} [mV][a]	j_0 [mA cm^{-2}][b]	Ref.
$Ni_{1.5}Co_{1.4}P@Ru$	49	48	1.26	This work
$Ni_{1.5}Co_{1.4}P$	39	99	2.5×10^{-4}	
Ru	134	243	0.15	
$NiCo_2P_x$	59.6	104	~	*Adv. Mater.*, 2017, **29**, 1605502.
ultrathin porous CoP nanosheets	44	56	0.61	*Chem. Sci.*, 2017, **8**, 2769-2775.
Mo-Ni_2P NWs/NF	109	67	~	*Nanoscale*, 2017, DOI: 10.1039/C7NR03515B.

$(CoP)_{0.54}$-$(FeP)_{0.46}$-NRs/G	52	57	0.489	*small 2017*, **13**, 1700092.
Ni_2P/NiCoP@NCCs	79	136	~	*J. Mater. Chem. A*, 2017, **5**, 16568-16572.
Ce-doped CoP	54	54	~	*Nano Energy*, 2017, **38**, 290-296.
CoP@NC	59	129	~	*ACS Catal. 2017*, **7**, 3824-3831.
NiCoP	50	59	~	*Adv. Funct. Mater.*, 2016, **26**, 6785-6796.
$Co_{1.6}Ni_{0.4}$P/CNT	46.7	91	0.0186	*J. Mater. Chem. A*, 2016, **4**, 14675-14686.
MoS_2@MoP	76	108	~	*Nanoscale*, 2016, **8**, 11052-11059.
CoP	50	75±2	~	*Chem. Mater.*, 2015, **27**, 3769.
CoPS film	57	128	0.056	*Nature Mater.*, 2015, **14**, 1245.
CoPS NPIs	56	48	0.984	
CoP-N-C	42	91	0.16	*ChemCatChem*, 2015, **7**, 1920-1925.
Cu_3P NW/CF	67	143	0.18	*Angew. Chem. Int. Ed.*, 2014, **126**, 9731.
CoP/CNT	54	122	0.13	*Angew. Chem. Int. Ed.*, 2014, **53**, 6710.

[a]The potential measured versus RHE.

[b]j_0 values were calculated from Tafel curves using an extrapolation method.

Table S2. Comparisons of electrocatalytic HER properties of some recently reported catalysts in alkaline electrolyte

Catalyst	Tafel slope [mV dec^{-1}]	η_{10} [mV]	Electrolyte	Ref.
$Ni_{1.5}Co_{1.4}$P@Ru	50	52 (η_{10})	1.0 M KOH	This work
		105 (η_{50})	1.0 M KOH	
$Ni_{0.89}Co_{0.11}Se_2$ MNSN/NF	52	85	1.0 M KOH	*Adv. Mater.*, 2017, **29**, 1606521.
CuCoP/N-C	122	220	1.0 M KOH	*Adv. Energy Mater.*, 2017, **7**, 1601555.
Hollow Cu_{2-x}S@Ru NPs	48	82	1.0 M KOH	*Small*, 2017, **13**, 1700052.
Mn-Co-P/Ti	52	76	1.0 M KOH	*ACS Catal.*, 2017, **7**, 98-102.
NiCoP/CC	66.5	62	1.0 M KOH	*ACS Catal.*, 2017, **7**,

				4131-4137.
Mn-Ni$_2$P/NF	135	103 (η_{20})	1.0 M KOH	*Chem. Commun.*, 2017, **53**, 11048-11051.
NiCoP-2.5-300 hollow quasi-polyhedra	42	124	1.0 M KOH	*ACS Appl. Mater. Interfaces* 2017, **9**, 5982-5991.
NiCoP quasi-hollow nanocubes	60.6	150	1.0 M KOH	*Chem. Commun.*, 2016, **52**, 1633.
Ni-P/carbon paper	85.4	100	1.0 M KOH	*Adv. Funct. Mater.*, 2016, **26**, 4067.
Ni$_2$P/Ni/NF	72	98	1.0 M KOH	*ACS Catal.*, 2016, **6**, 714-721.
NiCoP/rGO	124.1	209	1.0 M KOH	*Adv. Funct. Mater.*, 2016, **26**, 6785-6796.
Ni$_2$P/NF	~	220	1.0 M KOH	*Energy Environ. Sci.*, 2015, **8**, 2347-2351.
Ni$_5$P$_4$/Ni foil	53	150	1.0 M KOH	*Angew. Chem. Int. Ed.*, 2015, **127**, 12538.
Co$_{0.59}$Fe$_{0.41}$P nanocubes	72	99	1.0 M KOH	*Nanoscale*, 2015, **7**, 11055-11062.

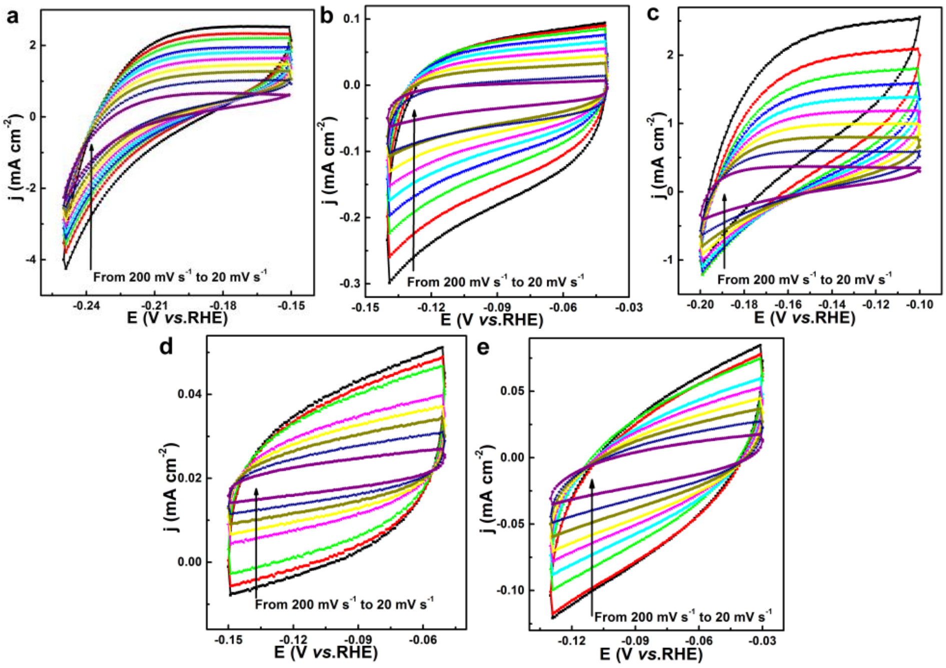

Fig. S8 CVs of (a) Co$_{1.4}$Ni$_{1.5}$P@Ru$_2$, (b) Co$_{1.4}$NiP@Ru, (c) Co$_2$Ni$_{1.5}$P@Ru, (a) Co$_{1.4}$Ni$_{1.5}$P, and (e) Ru with various scan rates (20-200 mV s^{-1}).

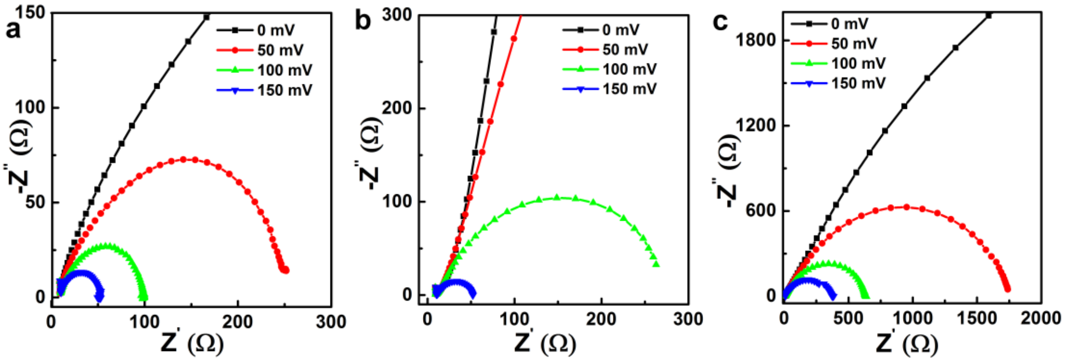

Fig. S9 Nyquist plots of (a) $Ni_{1.5}Co_{1.4}P$@Ru, (b) $Ni_{1.5}Co_{1.4}P$, and (c) Ru.