Supporting Information for

Cobalt phosphide-based electrocatalysts: Synthesis and phase catalytic activity comparison for hydrogen evolution

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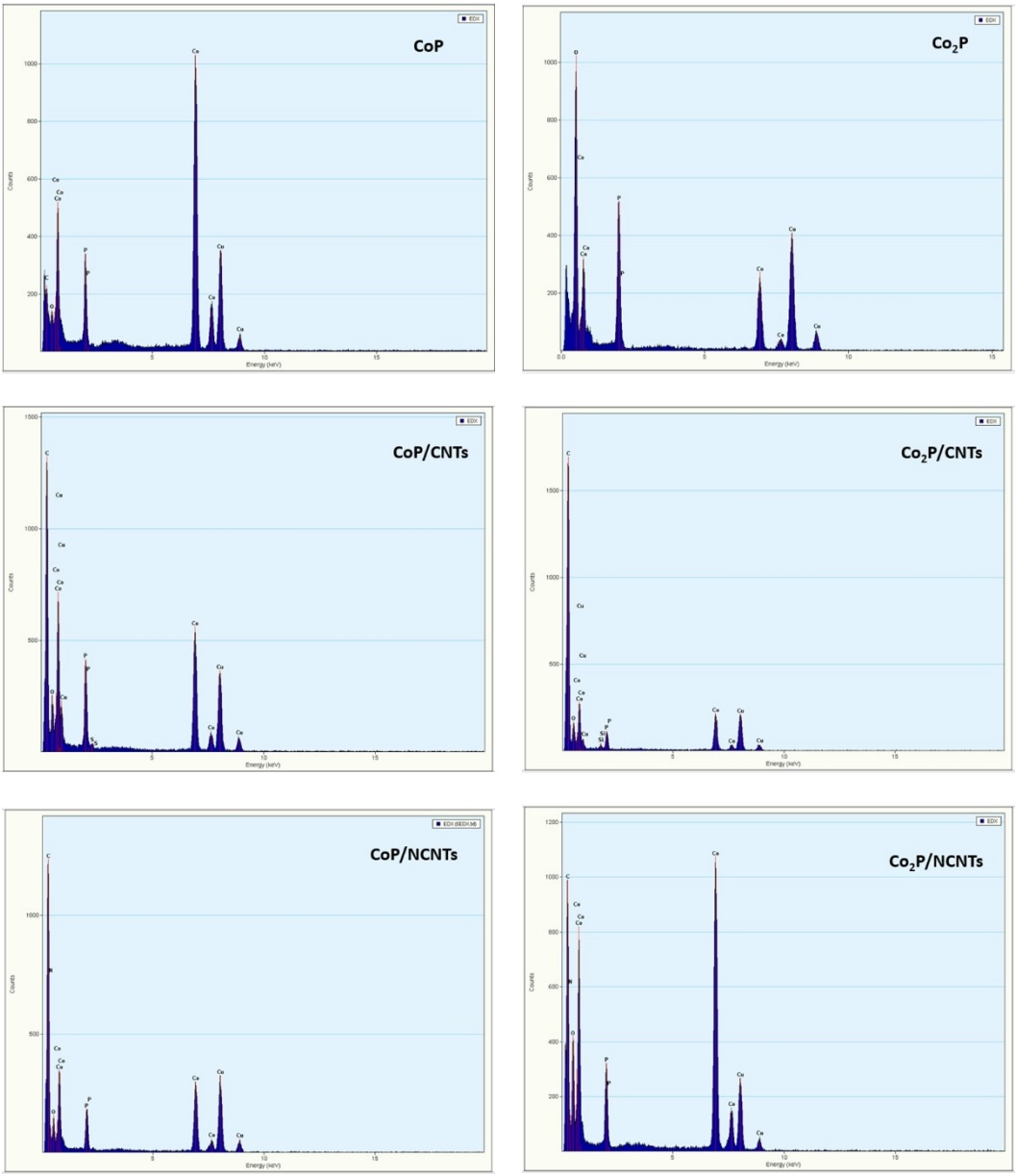

Fig. S1 EDX spectra of the as-synthesized cobalt phosphide-based catalysts.

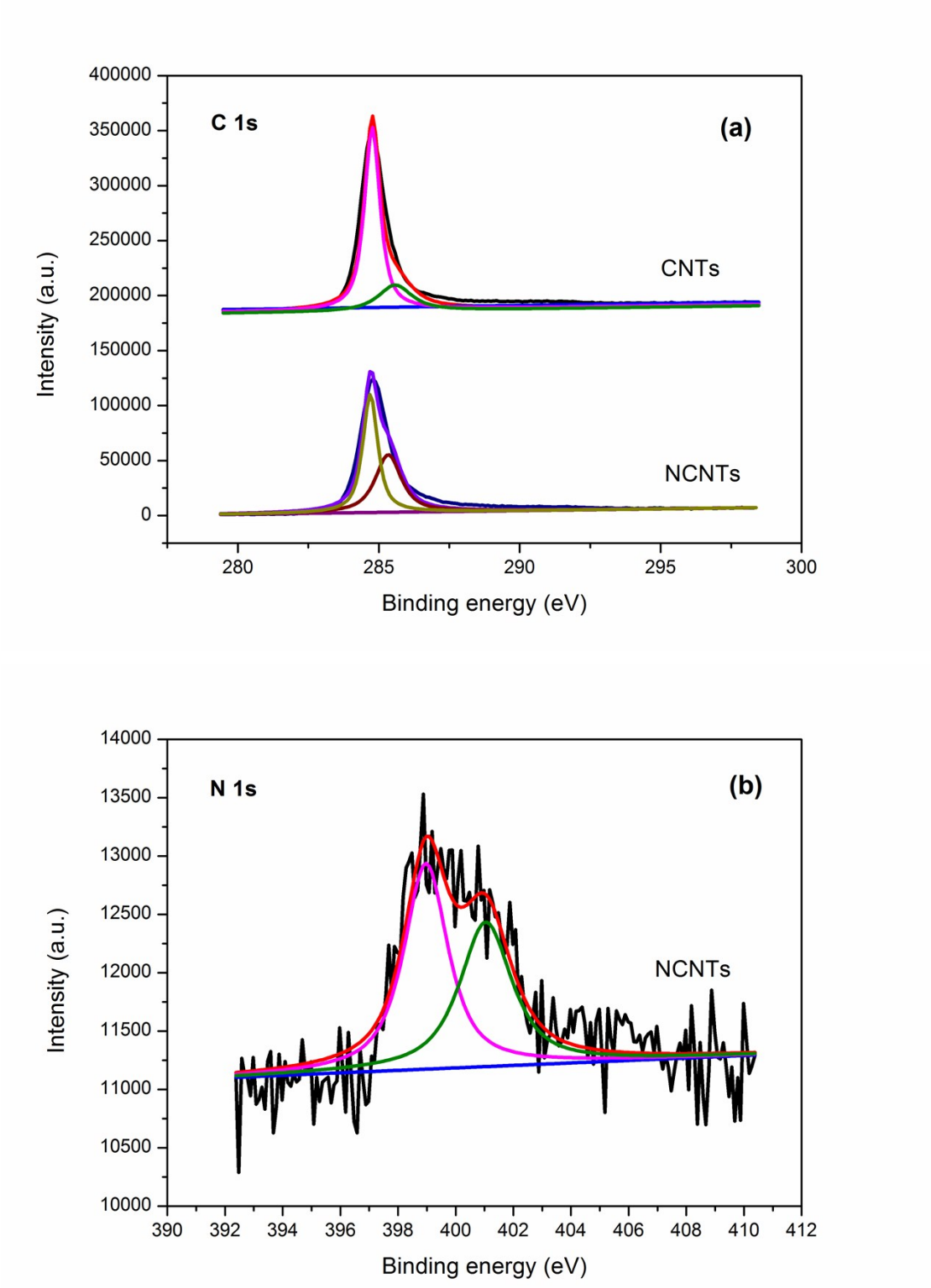

Fig. S2 XPS spectra in the C (1s) and N (1s) regions for the CNTs and NCNTs.

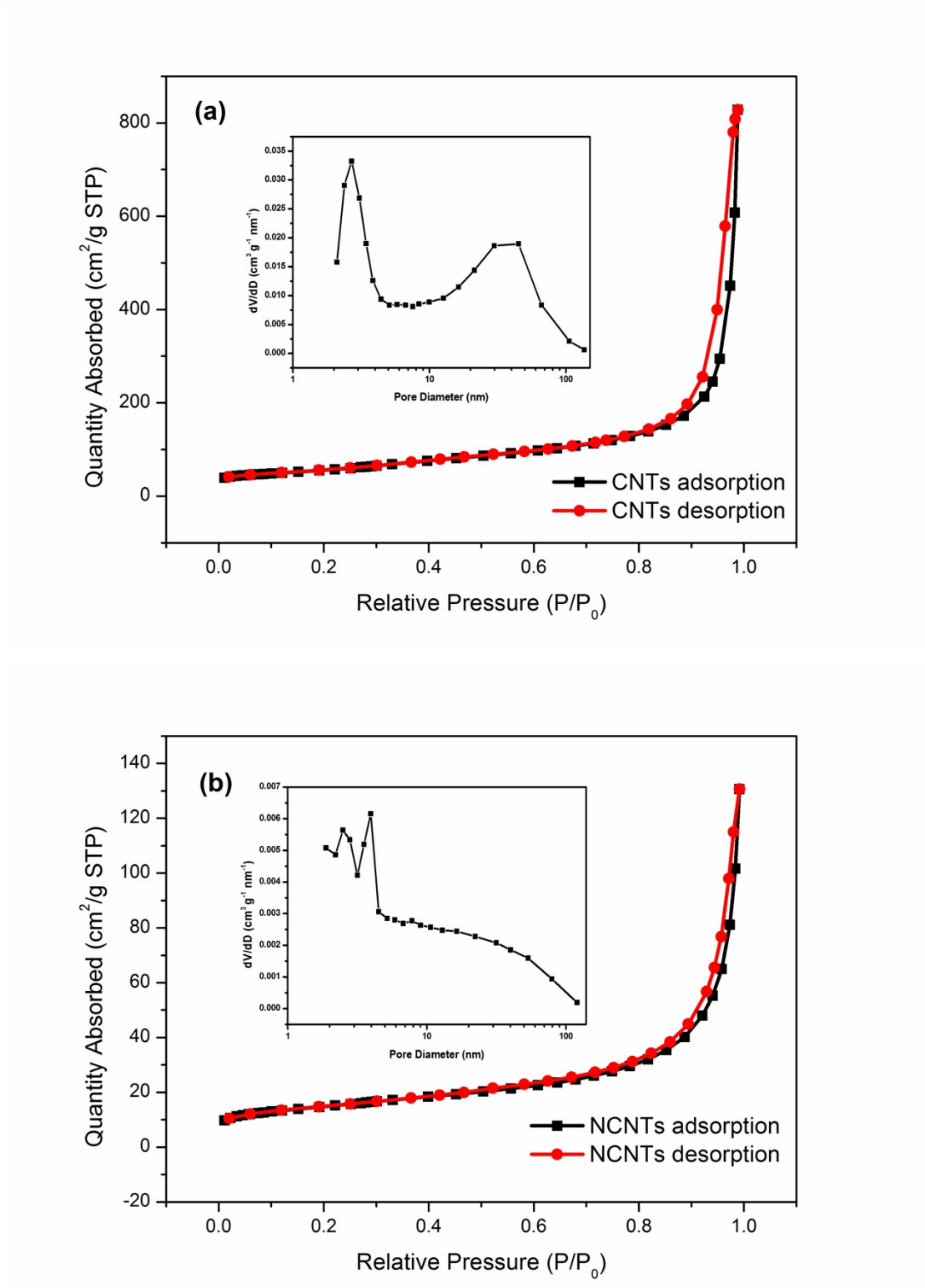

Fig. S3 N_2 adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore-size distribution (inset in Fig. S3) of (a) CNTs and (b) NCNTs

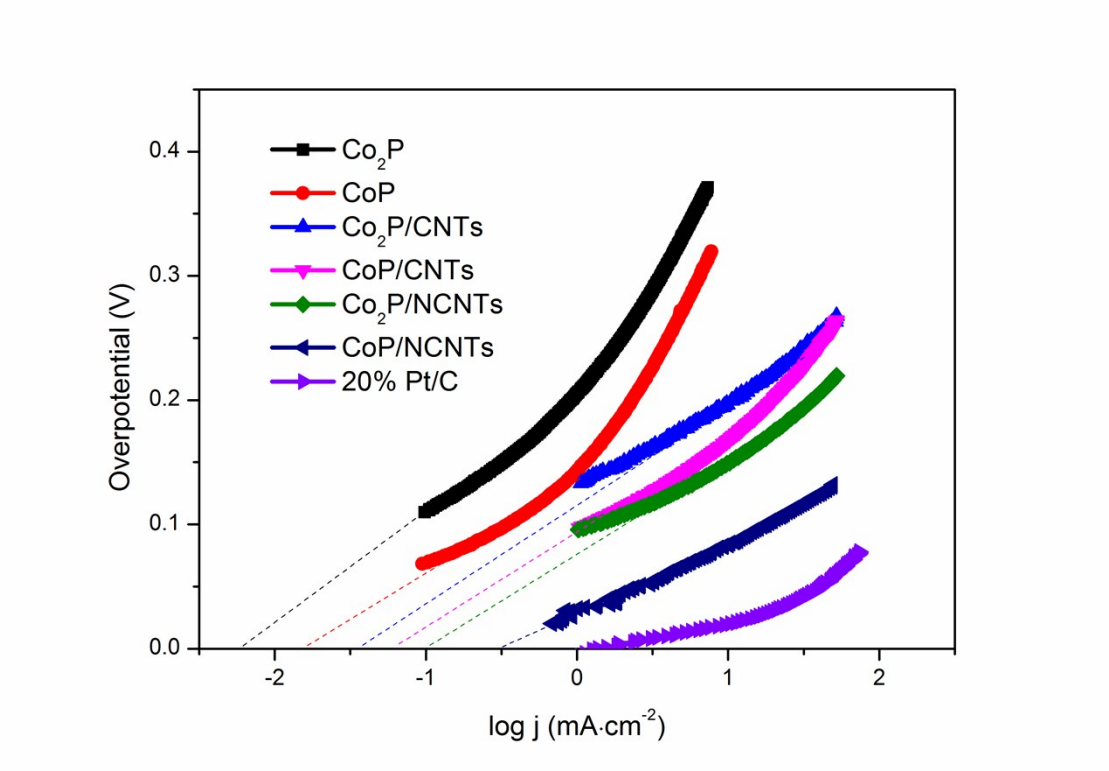

Fig. S4 Calculated exchange current density of the as-synthesized cobalt phosphide-based catalysts by using extrapolation methods.

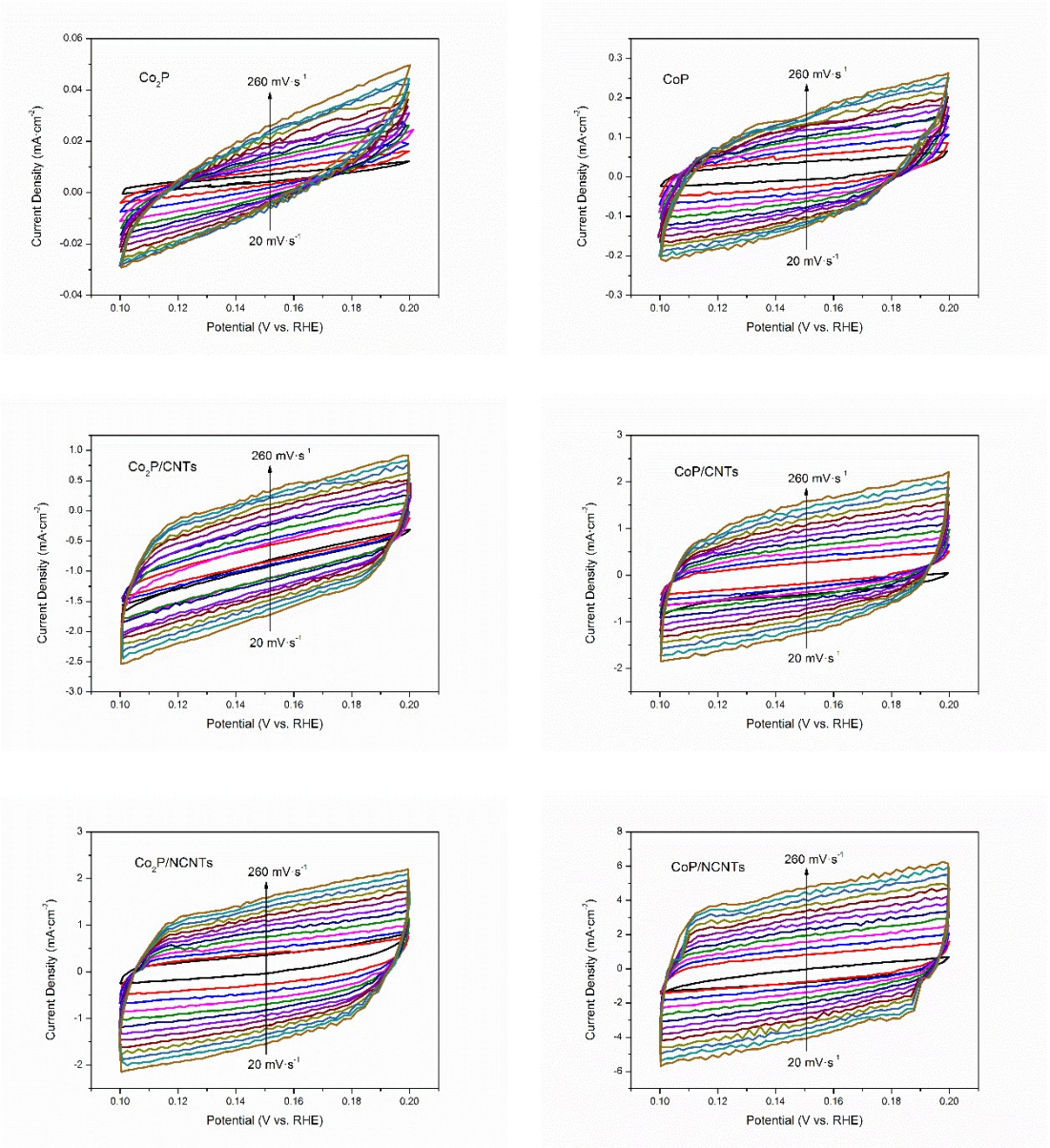

Fig. S5 Cyclic voltammetry curves of the as-synthesized cobalt phosphide-based catalysts in 0.5 M H_2SO_4 solution in the region of 0.1-0.2 V vs. RHE with different scan rates from 20 $mV \cdot s^{-1}$ to 260 $mV \cdot s^{-1}$.

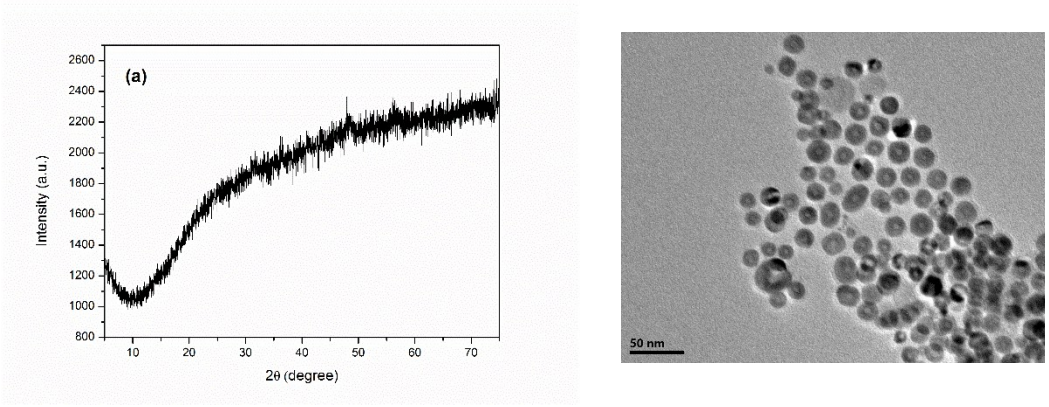

Fig. S6 XRD and TEM results of the as-synthesized CoP nanoparticles.

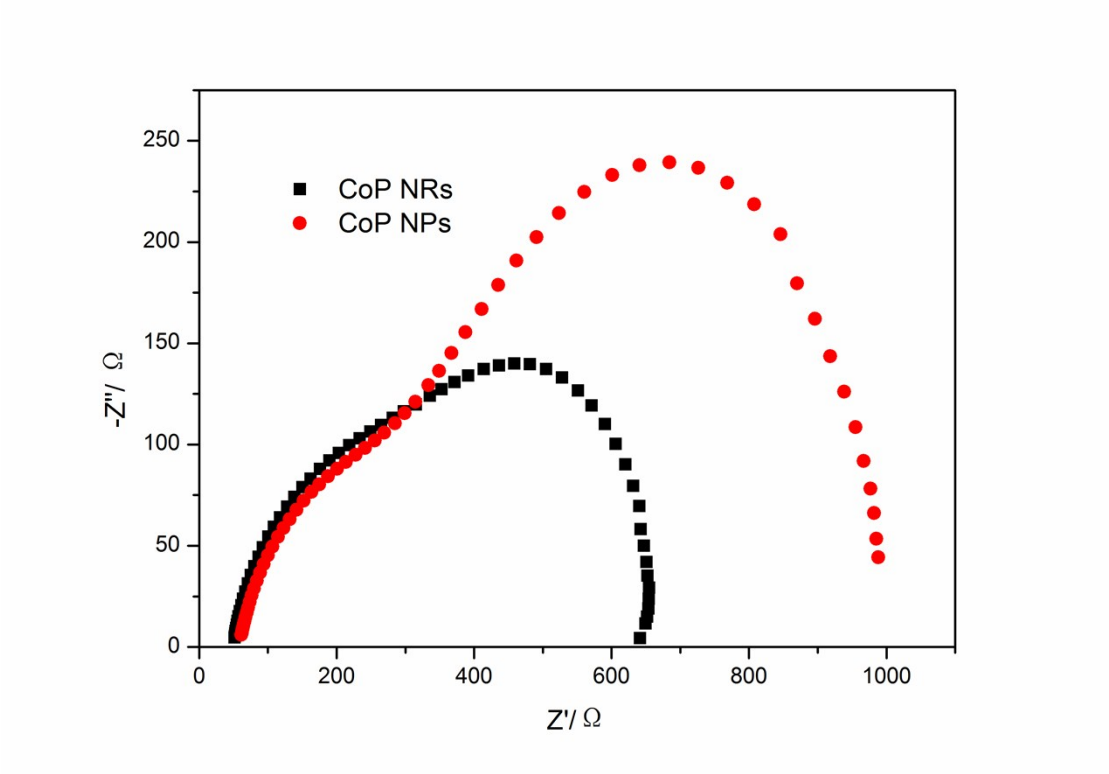

Fig. S7 Nyquist plots of the as-synthesized CoP NRs and CoP NPs in 0.5 M H_2SO_4 with an overpotential of 200 mV.

Table S1 Comparison of HER performance of some transition metal phosphide catalysts in 0.5 M H_2SO_4 solution.

Catalyst	Current density ($mA \cdot cm^{-2}$)	Overpotential (mV)	Tafel slope ($mV \cdot dec^{-1}$)	Reference
CoP/NCNTs	10	79	49	This work
CoP/CC	20	100	51	24
CoP Hollow Polyhedrons	10	159	59	25
urchin-like CoP	100	180	46	26
$Co_{0.59}Fe_{0.41}P$	10	72	52	27
CoP/RGO	10	156.89	70.2	28
CoP/MPC	10	141.73	69.8	28
CoP/MCV	10	134.34	63.1	28
CoP/OMC	10	112.18	56.7	28
CoP CPHs	10	133	51	29
CoP microspheres	10	226	76	30
Porous FeP	10	240	67	31
IPNTs	10	88	35.5	32
FeP NWs/rGO	10	107	58.5	33
Cu_3P nanowire/CF	10	143	67	34
MoP-CA2	10	125	54	35
Ni_2P/CNT	10	124	53	36
WP NAs/CC	10	130	69	37

Table S2 Calculations of the exchange current density of the as-synthesized cobalt phosphide-based catalysts and 20 % Pt/C catalyst by using extrapolation methods.

Catalyst	log(|j ($mA \cdot cm^{-2}$)|) at η=0 V	Exchange current density j_0 [$mA \cdot cm^{-2}$]
Co_2P	-2.2	0.0032
CoP	-1.77	0.017
Co_2P/CNTs	-1.41	0.039
CoP/CNTs	-1.17	0.068
Co_2P/NCNTs	-0.99	0.102
CoP/NCNTs	-0.5	0.32
20 % Pt/C	0.17	1.48

Table S3 ICP element composition and content analysis of the electrolyte after reaction.

	Co (mg/L)	P (mg/L)	S (mg/L)
Electrolyte after reaction	36.84	12.67	5103.68

Table S4 Values of elements in equivalent circuit resulted from fitting the EIS data of the as-synthesized CoP/NCNTs catalyst.

Potential (mV) vs. RHE	R_s (Ω)	Q ($F \cdot cm^{-2} \cdot S^{n-1}$)	n	R (Ω)
-60	9.85	3.9E-3	0.8	268.3
-80	9.95	4.5E-3	0.8	109.3
-100	9.87	4.9E-3	0.8	50.95
-120	10.16	5.4E-3	0.8	28.22
-140	10.37	5.7E-3	0.8	10.56