Electronic Supplementary Information

Sub-1 nm Pt nanoclusters on N and P co-doped carbon nanotubes for electrocatalytic hydrogen evolution reaction

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Experimental Section

Chemicals and Materials: HNO_3, H_2SO_4, $NaH_2PO_2 \cdot H_2O$, melamine, H_2PtCl_6 and H_2IrCl_6 are purchased from local suppliers. Carbon nanotubes used in this study were supplied by Nanotech Port Co. Ltd. (Shenzhen, China) with a purity of 97%. All water used in this work was purified using a Milli-Q water purification system which provides a resistance of 18.2 MΩ at 25 ℃. All chemicals were used as received without any further treatment.

Synthesis of Pt/NP-CNTs: In a typical synthesis, 1.5 g of raw carbon nanotubes (CNTs) was treated with 40 mL mixed acid solution (HNO_3 : H_2SO_4 = 1:3) in an ultrasonic water bath for 2 h to remove most of impurities. After filtration, washing and drying at 60 ℃, the as-prepared O-CNTs was sufficiently mixed with melamine (2 g) by grinding for 30 min and thermally treated at 750 ℃ for 3 h in Ar with a heating rate of 5 ℃ min^{-1}. The as-prepared sample was denoted as N-CNTs. Then, the obtained N-CNTs (0.5 g) was ground with $NaH_2PO_2 \cdot H_2O$ (5 g) for 30 min and heated at 300 ℃ for 2 h in Ar with a heating rate of 5 ℃ min^{-1} and cooled down to room temperature. After washing with water, filtering and drying at 60 ℃， the obtained black powder was marked as NP-CNTs. To prepare Pt/NP-CNTs, 200 mg NP-CNTs was dispersed in 60 ml deionized water with sonication, transformed in an oil bath and heated to 70 ℃ under N_2 atmosphere. Then, 1 mL H_2PtCl_6 solution (0.01 g mL^{-1}) was injected into the aqueous solution and stirred at 70 ℃ for 5 h. After filtration and drying at 60

℃, the mixture was placed in a tube furnace and annealed at 300 °C for 2 h under Ar atmosphere. The synthesized sample was denoted as Pt/NP-CNTs.

Synthesis of Ir/NP-CNTs: The synthetic procedure of Ir/NP-CNTs is similar to that of Pt/NP-CNTs just by replacing H_2PtCl_6 solution (0.01 g mL^{-1}) to H_2IrCl_6 solution (0.01 g mL^{-1}).

Characterization: Scanning electron microscopy (SEM) was performed on a Nova-450 electron microscope. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100F field emission electron microscope at 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted on a ULVAC PHI Quantera spectrometer with the binding energy calibrated with C 1s at 284.6 eV. X-ray diffraction (XRD) patterns were collected on a X'Pert 3 X-ray powder diffractometer operating at 40 kV and 40 mA with monochromatized Cu Kα radiation (λ=0.15418 nm). Raman spectra were recorded on a LabRam HR800 instrument with an excitation wavelength of 514.5 nm. The compositions of the catalysts were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher, USA).

Electrochemical measurements: HER performance tests were conducted on an Autolab electrochemical workstation (PGSTAT302N) with a 0.5 M H_2SO_4 solution as the electrolyte. A conventional three-electrode system was used with the Pt/NP-CNTs on Ni foam (0.5 cm×0. 5 cm) as the working electrode, a glassy-carbon (GC) as the counter electrode and an Ag/AgCl (1 M KCl) electrode as the reference electrode. All potentials reported were calculated versus the reversible hydrogen electrode (RHE). Linear sweep voltammograms (LSV) and cyclic voltammetry (CV) tests were recorded at a scan rate of 5 mV s^{-1} at room temperature. Electrochemical impedance spectroscopy (EIS) was measured in a frequency range from 100 kHz to 0.1 Hz with an amplitude of 10 mV on an Autolab electrochemical workstation.

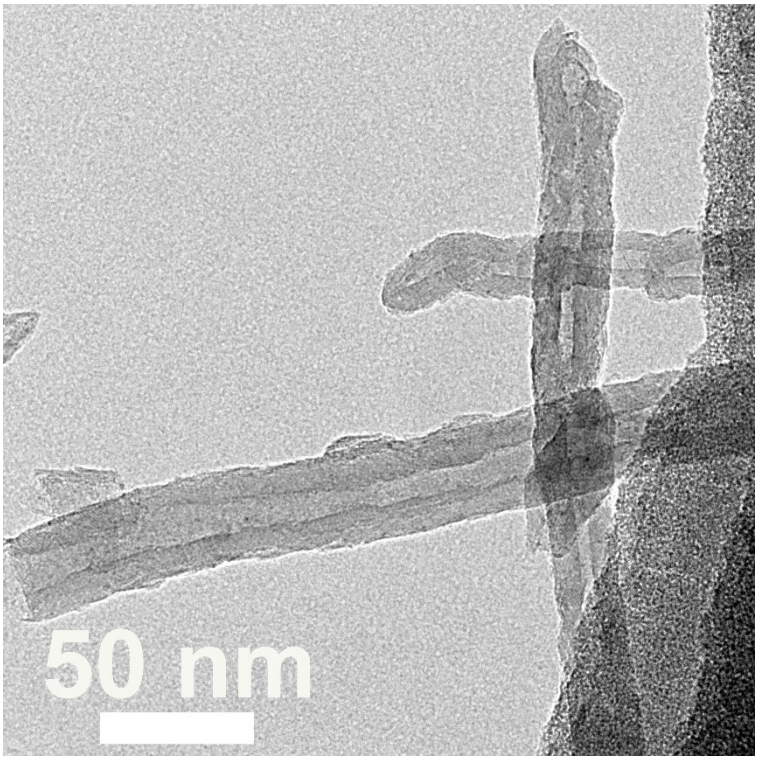

Figure S1. TEM image of O-CNTs.

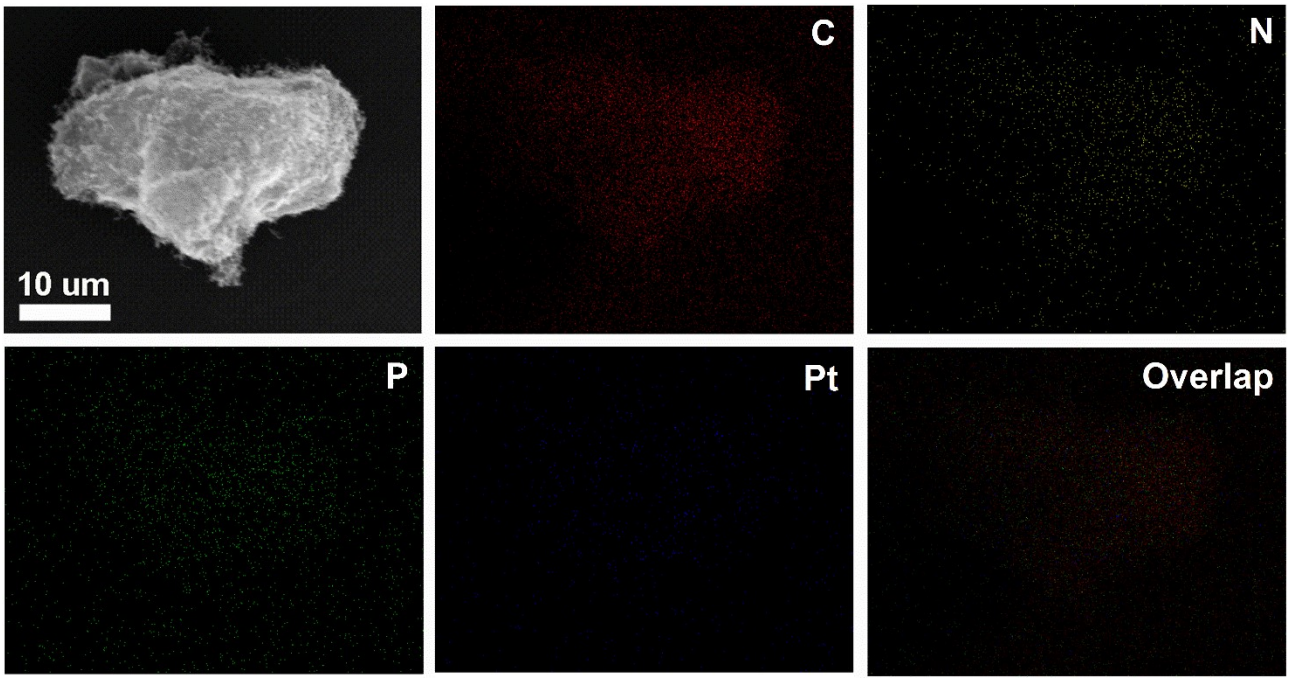

Figure S2. EDS mapping of Pt/NP-CNTs

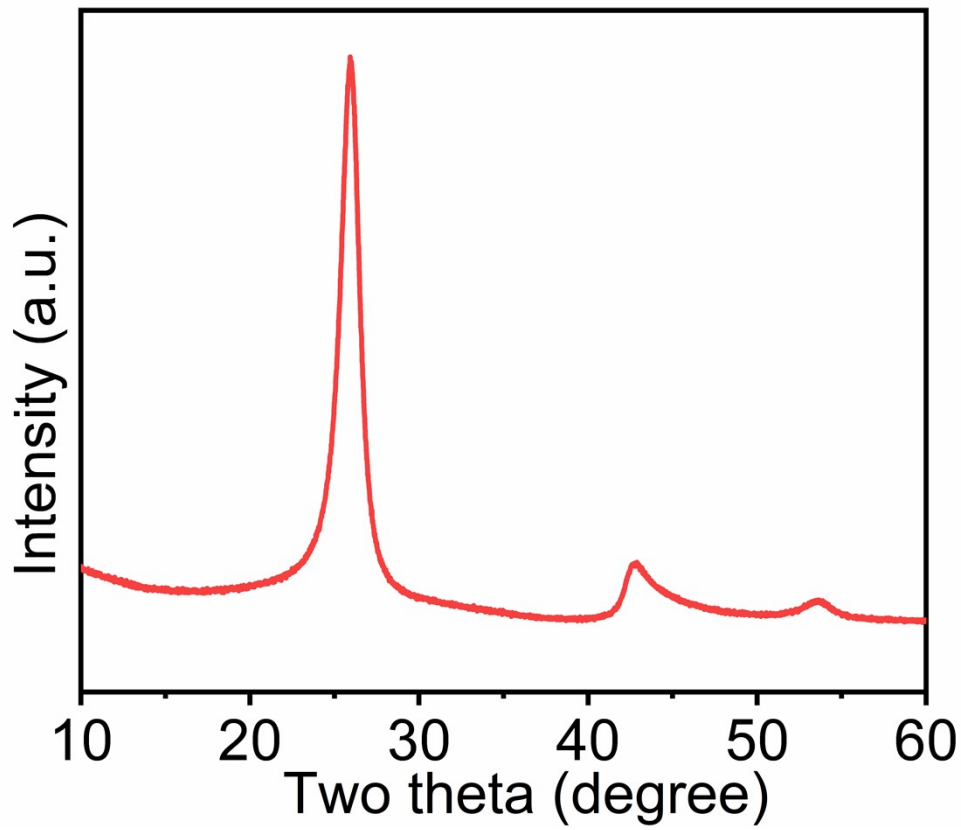

Figure S3. XRD pattern of Ir/NP-CNTs.

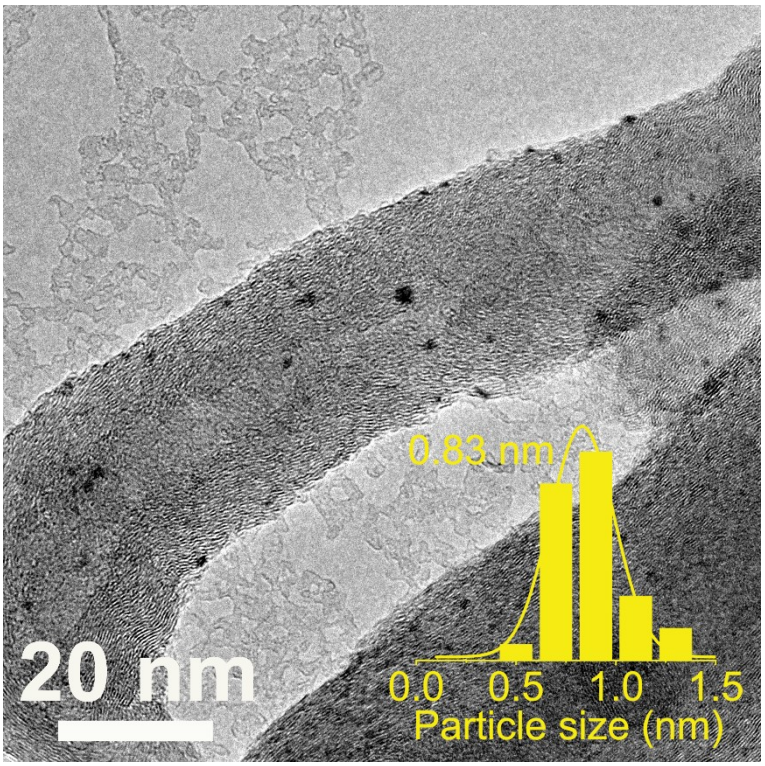

Figure S4. TEM image of Ir/NP-CNTs and corresponding Ir nanocluster size distribution (inset).

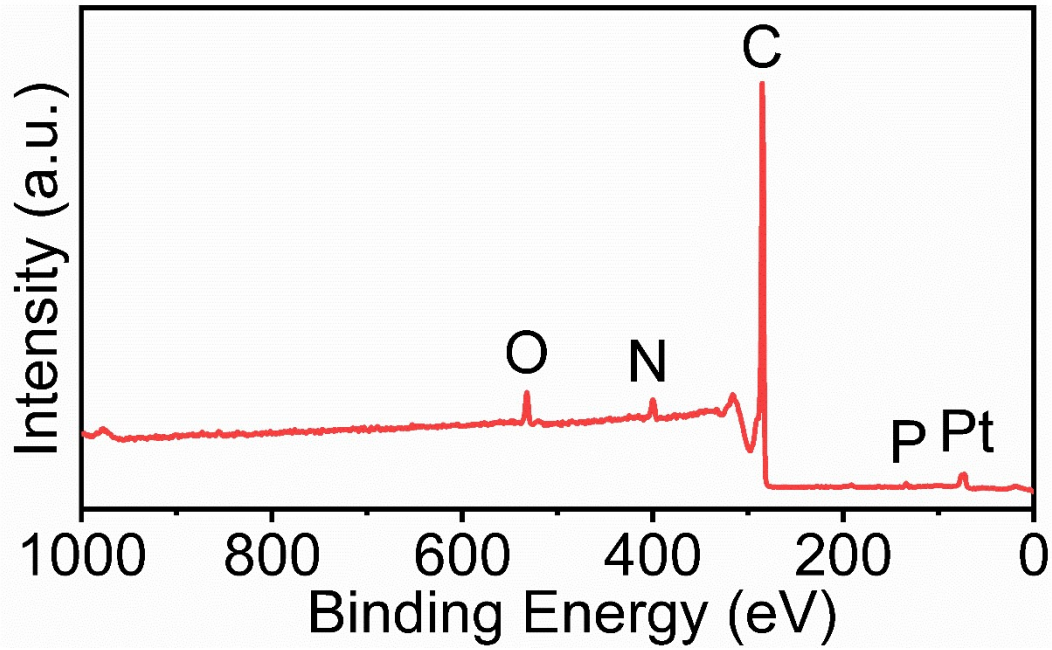

Figure S5. XPS survey spectrum of Pt/NP-CNTs.

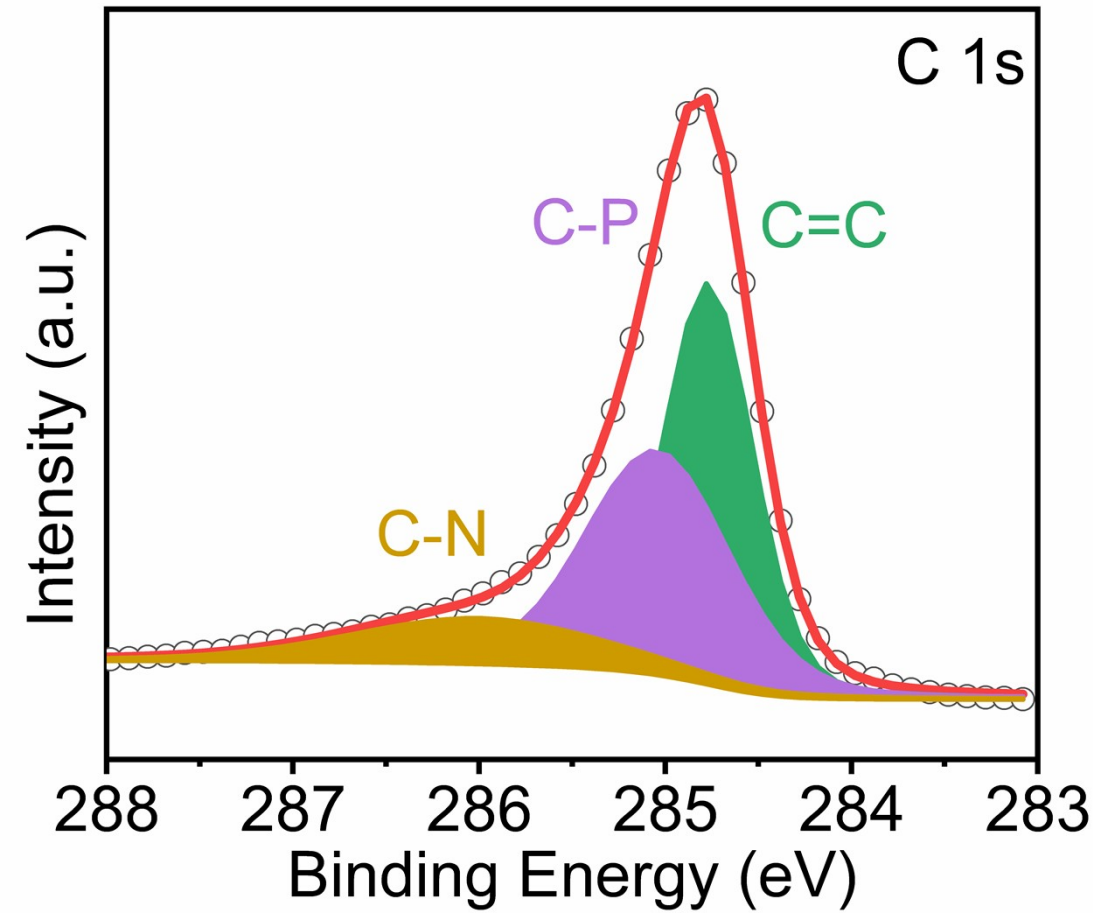

Figure S6. C 1s XPS spectrum of Pt/NP-CNTs.

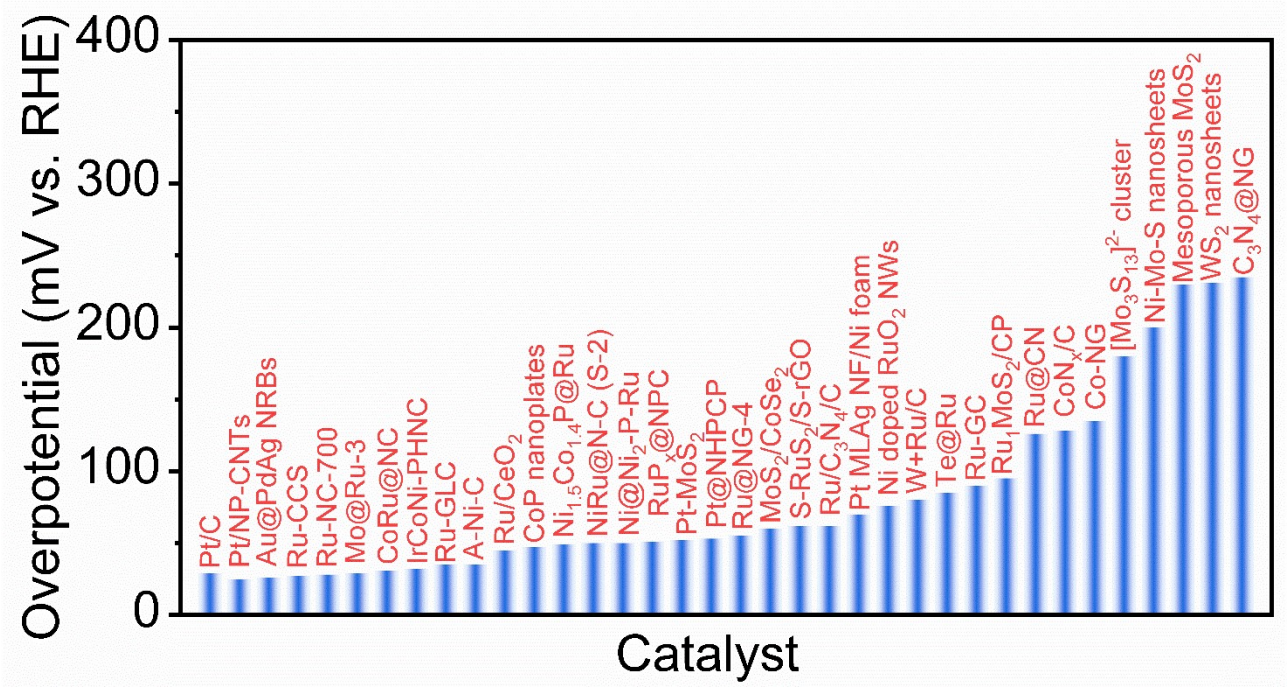

Figure S7. Overpotential comparison of recently reported representative HER electrocatalysts in acidic electrolytes.

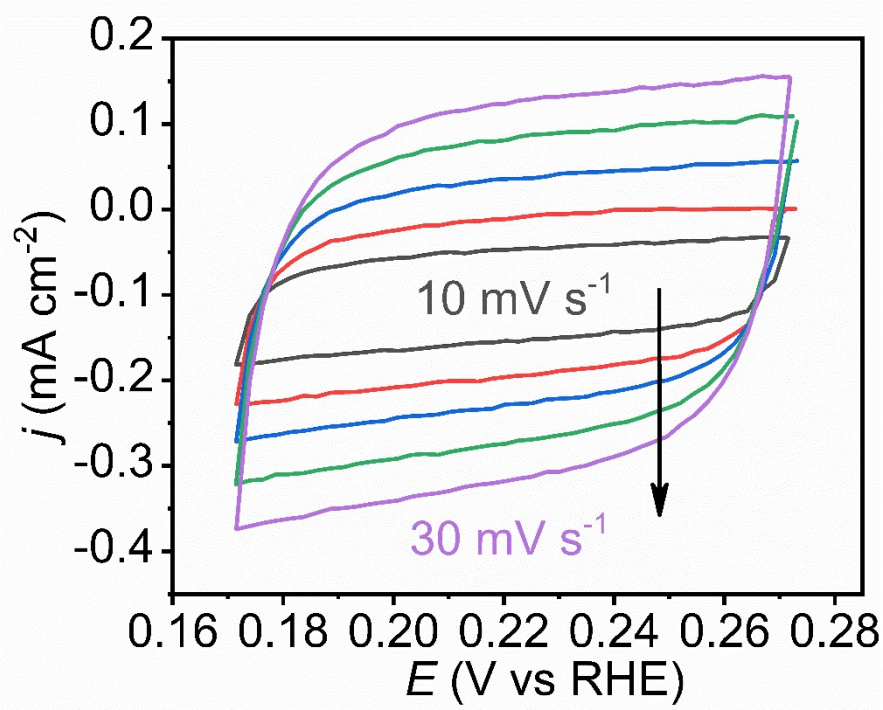

Figure S8. CV curves of Pt/NP-CNTs at different scan rates from 10 mV s^{-1} to 30 mV s^{-1} in the potential range of 0.17 to 0.27 (vs. RHE).

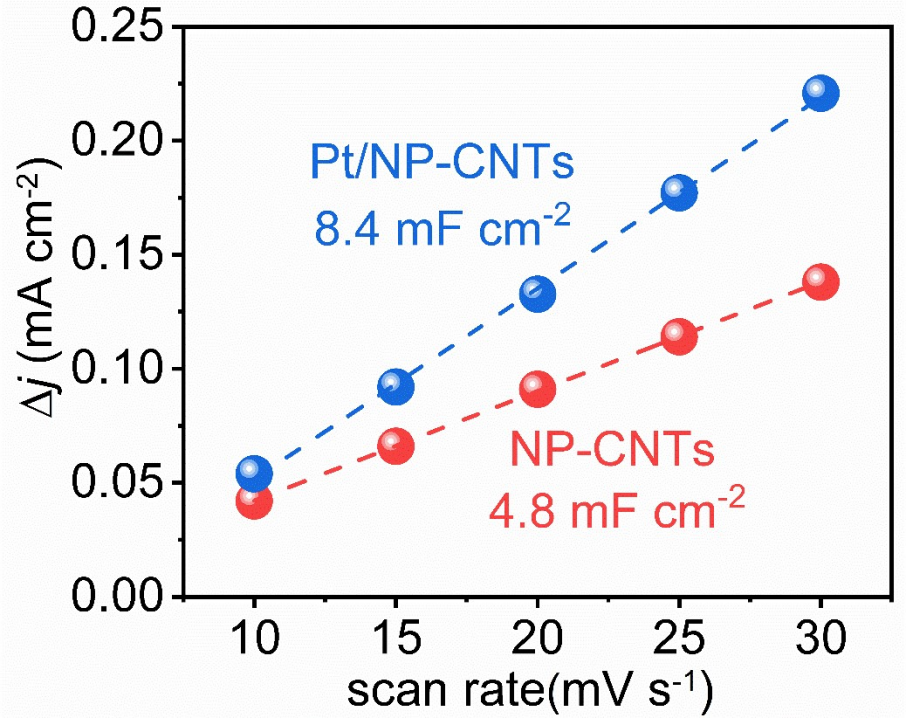

Figure S9. The extraction of the C_{dl} for NP-CNTs and Pt/NP-CNTs.

Table S1. The Ni contents in raw CNTs, O-CNTs, N-CNTs, NP-CNTs and Pt/NP-CNTs measured by ICP-AES.

Sample	Ni contents (wt%)
Raw CNTs	2.93
O-CNTs	0.92
N-CNTs	0.09
NP-CNTs	0.08
Pt/NP-CNTs	0.08

Table S2. Summary of recently reported representative HER electrocatalysts in acidic electrolytes.

No.	Catalysts	Overpotential at η_{10} (mV)	Tafel slope (mV dec^{-1})	References
1	Pt/C	29	29	This work
2	Pt/NP-CNTs	25	28	This work
3	Au@PdAg NRBs	26	30	J. Am. Chem. Soc., 2016, 138, 1414.

4	Ru-CCS	27	33	J. Mater. Chem. A, 2018, 6, 2311.
5	Ru-NC-700	29	28	Nat. Commun., 2019, 10, 631.
6	Mo@Ru-3	31	36	J. Mater. Chem. A, 2019, 7, 2780.
7	CoRu@NC	32	47	Nanotechnology, 2018, 29, 225403.
8	IrCoNi-PHNC	33	32	Adv. Mater., 2017, 29, 1703798.
9	Ru-GLC	35	46	ACS Appl. Mater. Interfaces, 2016, 8, 35132.
10	A-Ni-C	34	41	Nature Comm., 2016, 7, 10667.
11	Ru/CeO_2	47	41	ACS Appl. Mater. Interfaces, 2018, 10, 6299.
12	CoP nanoplates	48	57	Nat. Mater., 2015, 14, 1245-1251.
13	$Ni_{1.5}Co_{1.4}P$@Ru	49	49	Chem. Commun., 2017, 53, 13153.
14	NiRu@N-C (S-2)	50	36	J. 15Mater. Chem. A, 2018, 6, 1376.
15	$Ni@Ni_2$-P-Ru	51	35	J. Am. Chem. Soc., 2018, 140, 2731.
16	RuP_x@NPC	51	46	ChemSusChem, 2018, 11, 743-752.
17	Pt-MoS_2	53	40	Nat. Commun., 2013, 4, 1444.
18	Pt@NHPCP	57	27	Nano Energy, 2017, 40, 88-94.
19	Ru@NG-4	60	41	Sustain. Energy Fuels, 2017, 1, 1028.
20	$MoS_2/CoSe_2$	68	36	Nat. Commun., 2015, 6, 5982.
21	S-RuS_2/S-rGO	69	64	ACS Appl. Mater. Interfaces, 2018, 10, 34098.
22	$Ru/C_3N_4/C$	70	--	J. Am. Chem. Soc., 2016, 138, 16174.
23	Pt MLAg NF/Ni foam	70	53	Sci. Adv., 2015, 1, e1400268.
24	Ni doped RuO_2 NWs	78	--	J. Mater. Chem. A, 2019, 7, 6411.
25	W+Ru/C	85	46	ACS Appl. Mater. Interfaces, 2018, 10, 6354.
26	Te@Ru	86	36	Chem. Commun., 2019, 55, 1490.
27	Ru-GC	90	33	Electrochim. Acta, 2015, 167, 455.
28	Ru_1MoS_2/CP	96	--	Nanoscale, 2017, 9, 16616.

29	Ru@CN	126	--	Energy Environ. Sci., 2018, 11, 800.
30	CoN_x/C	133	57	Nat. Commun., 2015, 6, 7992.
31	Co-NG	147	82	Nat. Commun., 2015, 6, 8668.
32	$[Mo_3S_{13}]^{2-}$ cluster	180	40	Nature Chem., 2014, 6, 248.
33	Ni-Mo-S nanosheets	200	85.3	Sci. Adv., 2015, 1, e1500259.
34	Mesoporous MoS_2	233	50	Nat. Mater., 2012, 11, 963.
35	WS_2 nanosheets	234	55	Nat. Mater., 2013, 12, 850.
36	C_3N_4@NG	240	52	Nat. Commun., 2014, 5, 3783.