Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

In Situ Nitridated Porous Nanosheet Networked Co_3O_4-Co_4N Heteronanostructure Supported on Hydrophilic Carbon Cloth for Highly Efficient Electrochemical Hydrogen Evolution

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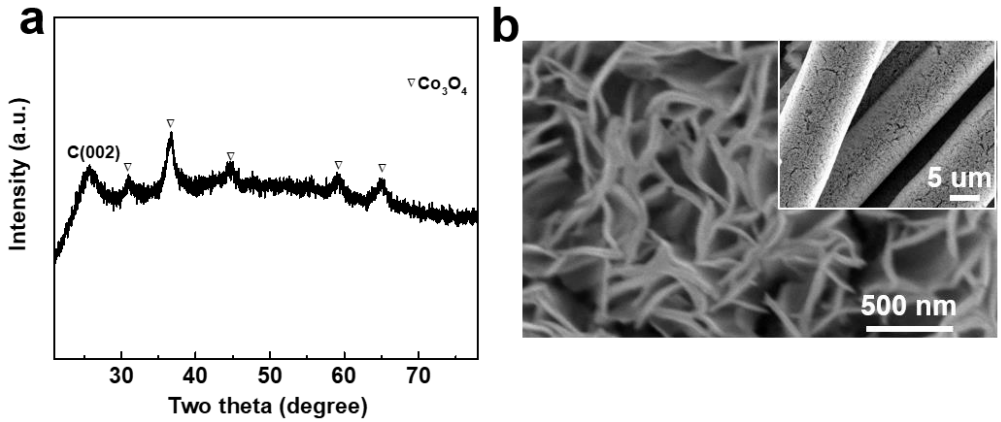

Fig. S1. (a) XRD pattern and (b) SEM images of Co_3O_4/HCC obtained by heat treatment of as-prepared α-$Co(OH)_2$/HCC at 300 °C for 1 h under air atmosphere. The Co_3O_4 nanosheets formed apparently an interconnected network structure.

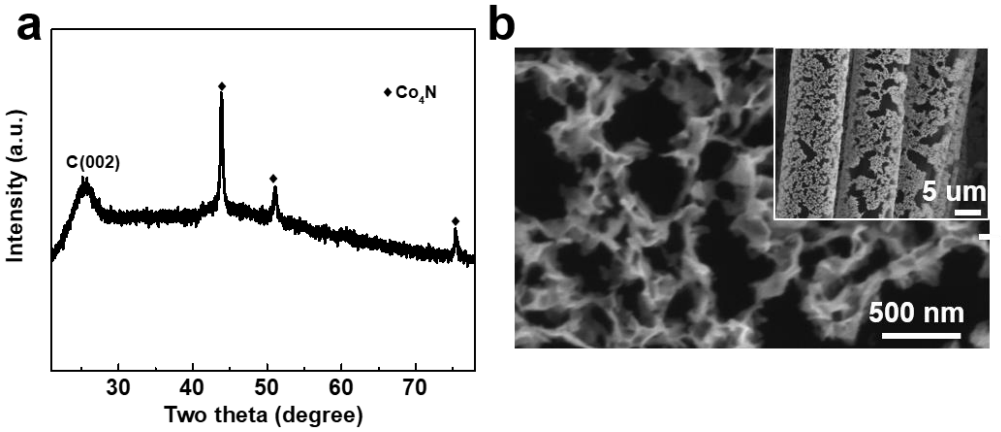

Fig. S2. (a) XRD pattern and (b) SEM images of Co_4N/HCC obtained by heat treatment of as-prepared α-$Co(OH)_2$/HCC at 400 °C for 1 h under NH_3 atmosphere. The Co_4N nanosheets also formed a networked structure.

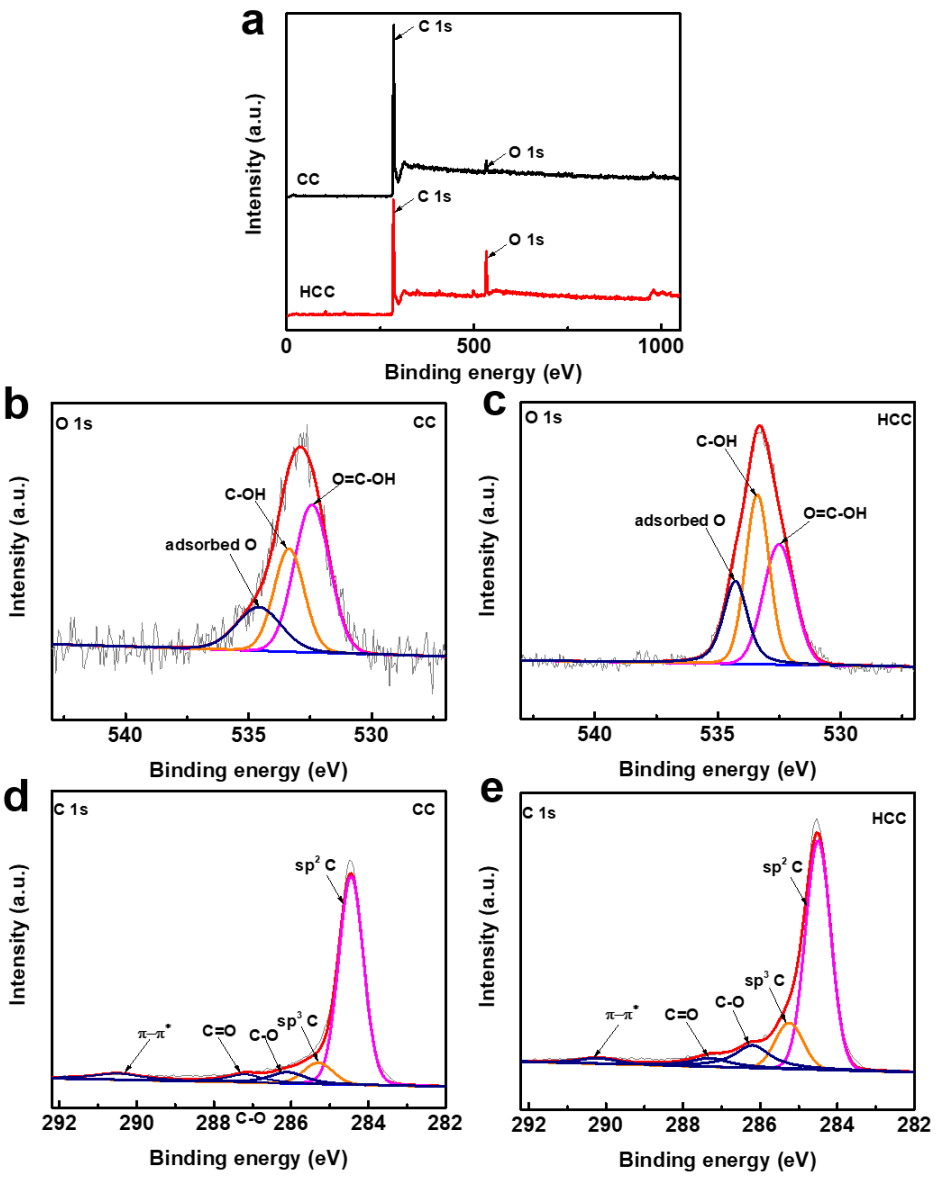

Fig. S3. (a) XPS survey spectra of CC and HCC. High-resolution spectra of O 1s (b) CC and (c) HCC, and high-resolution C 1s spectra of (d) CC and (e) HCC.

The C 1s peak in the XPS spectra can be split into five peaks at 284.5, 285.3, 286.1, 287.2, and 290.5 eV, which can be attributed to sp^2-bonded carbon, sp^3-bonded carbon, C-O groups, C=O groups, and π–π* shake-up satellites, respectively.[1] The O 1s peak can be deconvoluted into three components, i.e., the peak at 532.4 eV for the carboxyl group (COO^-), the peak at 533.3 eV for the hydroxyl (C-OH), and the peak at 534.6 eV for the chemisorbed oxygen.[2, 3] The content of C-OH and adsorbed oxygen increase after hydrogen plasma treatment. The increase in oxygen content can be attributed to edge-dangling bonds induced by the plasma treatment, which can either bind with oxygen to form oxygen-containing functional groups (e.g., C-OH) or adsorb water or oxygen when exposed to air.

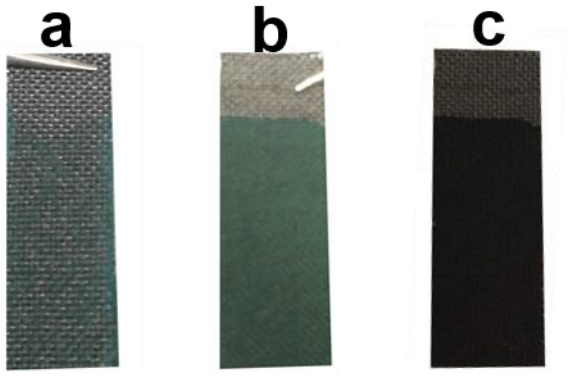

Fig. S4. Optical images of (a) α-$Co(OH)_2$ nanosheets grown on the untreated CC, (b) α-$Co(OH)_2$ nanosheets grown on HCC, and (c) Co_3O_4-Co_4N porous nanosheet networks grown on HCC.

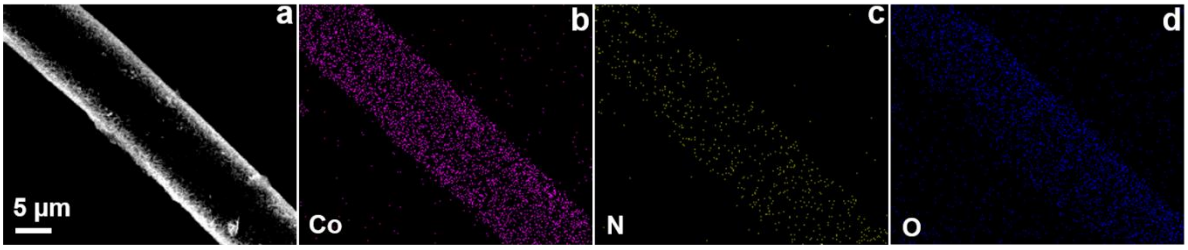

Fig. S5. SEM image and the corresponding elements mapping of Co_3O_4-Co_4N/HCC showing the distribution of (b) Co, (c) N, and (d) O over the surface of carbon fiber.

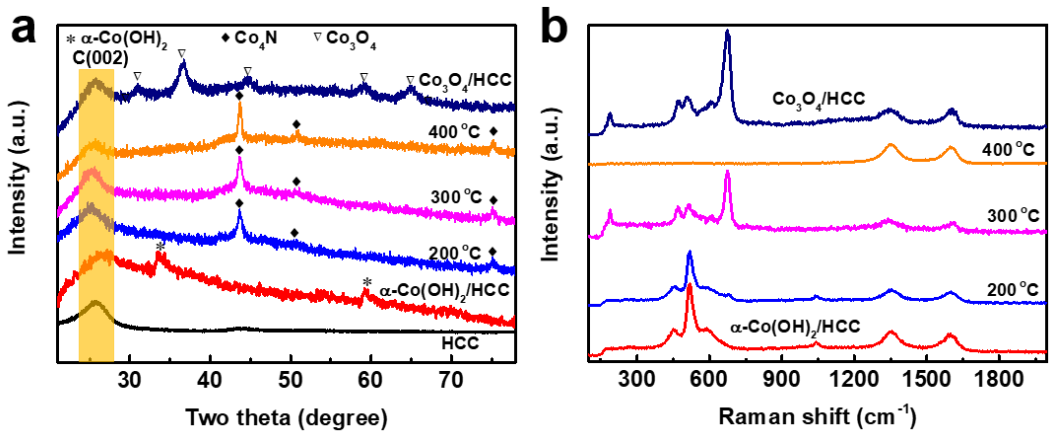

Fig. S6. (a) XRD patterns of HCC, α-$Co(OH)_2$/HCC, Co_3O_4/HCC, and the obtained products after nitrogen plasma treatment of α-$Co(OH)_2$/HCC at different temperatures. (b) The corresponding Raman spectra of the samples.

XRD patterns showed that all the products after nitrogen plasma treatment at 200 °C, 300 °C and 400 °C contained Co_4N phase. However, due to the poor sensitivity of Raman spectroscopy to Co_4N,[4] the Raman spectra of the corresponding samples only revealed α-$Co(OH)_2$ signal for the sample obtained at 200 °C, and Co_3O_4 signal for the sample obtained at 300 °C. For the sample obtained at 400 °C, no additional bands besides the characteristic D (~1350 cm^{-1}) and G (~1600 cm^{-1}) peaks of HCC substrate were observed. The combination of the XRD and Raman results suggested that the α-$Co(OH)_2$ was partially nitridated to Co_4N at 200 °C, and the decomposition and nitridation of α-$Co(OH)_2$ occurred simultaneously at an elevated temperature of 300 °C, leading to the formation of Co_4N-Co_3O_4 hybrid. When the temperature was increased to 400 °C, only Co_4N phase was obtained.

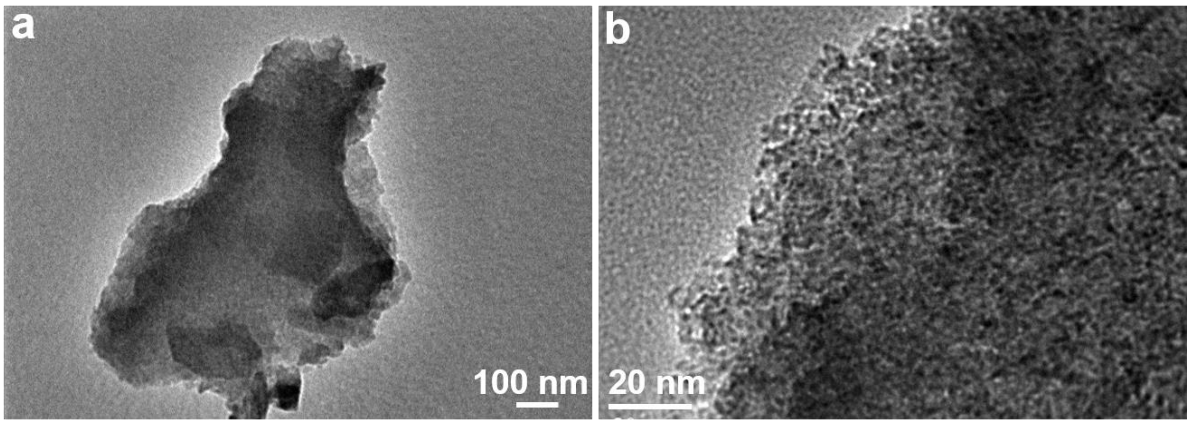

Fig. S7. TEM images of α-$Co(OH)_2$ nanosheets.

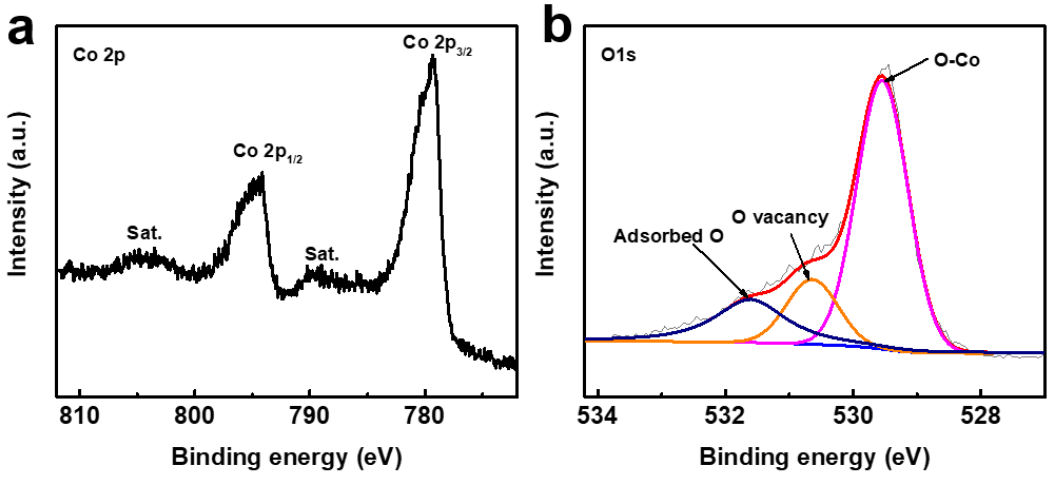

Fig. S8. High-resolution XPS spectra of (a) Co 2p and (b) O 1s of Co_3O_4.

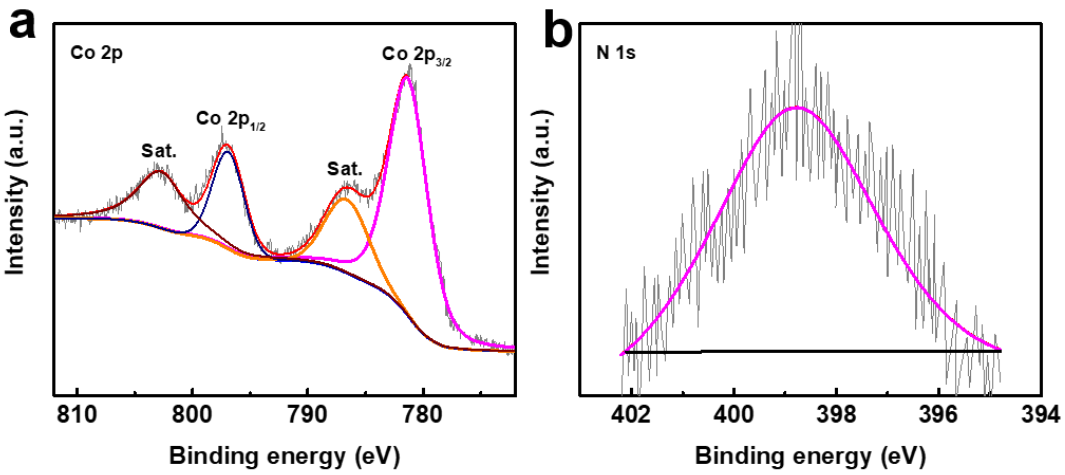

Fig. S9. High-resolution XPS spectra of (a) Co 2p and (b) N 1s of Co_4N.

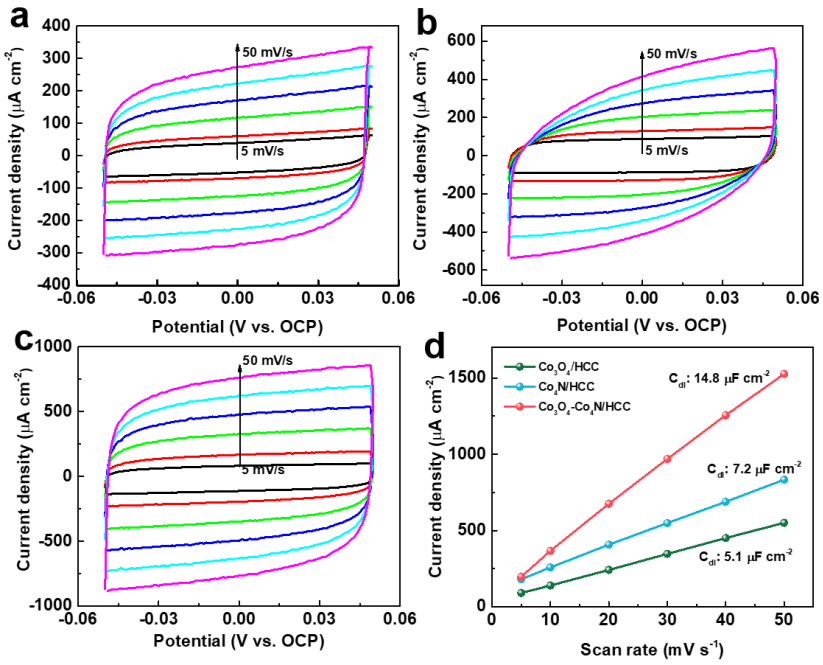

Fig. S10. (a) The CV curves of samples measured at different scan rates of 5, 10, 20, 30, 40, and 50 mV s^{-1} in CH_3CN with 0.15 M KPF_6. (a) Co_3O_4/HCC, (b) Co_4N/HCC, and (c) Co_4N-Co_3O_4/HCC. (d) The dependence of difference between the anodic and cathodic current densities at the open circuit potential (OCP) on the scan rate of potential obtained on Co_3O_4/HCC, Co_4N/HCC and Co_3O_4-Co_4N/HCC.

The double layer capacitance (C_{dl}) was calculated through the slope of linear dependences divided by 2,[5] which could be considered as an indication of the electrochemically active surface areas of the samples.

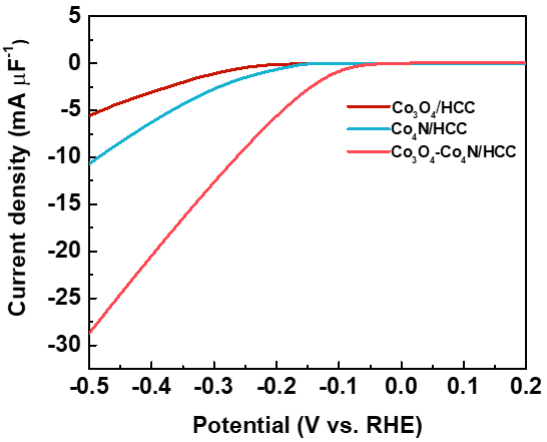

Fig. S11. Polarization curves normalized by the electrochemical double-layer capacitances of Co_3O_4/HCC, Co_4N/HCC, and Co_3O_4-Co_4N/HCC.

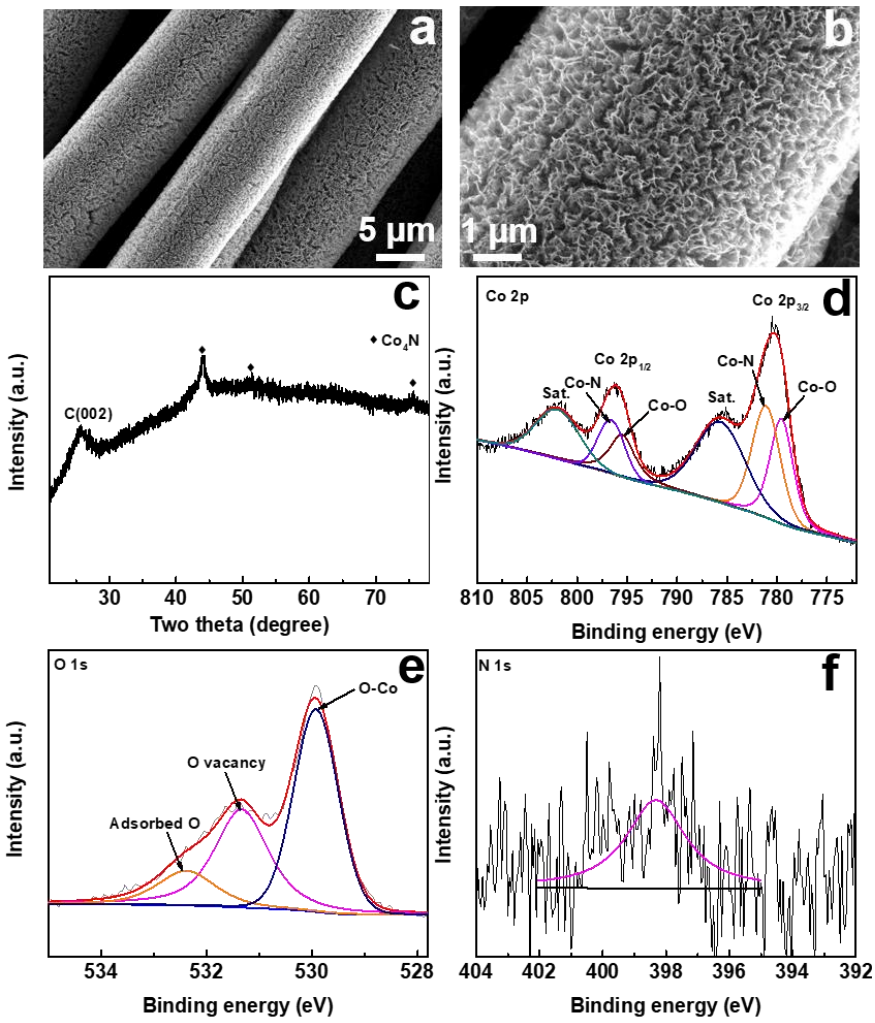

Fig. S12. (a, b) The SEM surface images and (c) XRD pattern of the Co_3O_4-Co_4N/HCC after HER stability measurement for 40 h in 1.0 M KOH solution. The corresponding high-resolution XPS spectra of (d) Co 2p, (e) O 1s and (f) N 1s of the sample.

Table S1. The C and O contents of CC and HCC from XPS measurement.

Sample	C percent(%)	O percent (%)	O/C ratio
CC	96.92	3.08	0.032
HCC	87.78	12.22	0.139

Table S2. EDX analysis on the elemental compositions of the samples prepared by nitrogen plasma treatment with different durations.

Samples	Atomic percentage (%)		
	Co	O	N
5 min	55.7	41.2	3.1
10 min	63.7	30.7	5.6
15min	70.2	21.3	8.5
20 min	74.0	15.4	10.6

Table S3. Comparison of the HER activity of the with other non-noble metal-based electrocatalysts with decent performance in basic condition.

Catalysts	Electrolyte	Current density (mA cm^{-2})	Overpotential (mV)	Tafel slope (mV dec^{-1})	Reference
Co_3O_4-Co_4N/HCC	1.0 M KOH	10	90	57.8	This work
Co-MoS_2/CC	1.0 M KOH	10	203	158	*Energy Environ. Sci.* **2016**, *9*, 2789.
Ni-P/carbon paper	1.0 M KOH	10	100	85.4	*Adv. Funct. Mater*. **2016**, *26*, 4067.
Fe-CoP/Ti	1.0 M KOH	10	78	75	*Adv. Mater.* **2017**, *29*, 1602441.
Ni-MoS_2/CC	1.0 M KOH	10	98	60	*Energy Environ. Sci.* **2016**, *9*, 2789.
MoC_x nano-octahedrons	1.0 M KOH	10	151	59	*Nat. Commum.* **2015,** *6*, 6512.
MoS_2/NiCo-LDH/CFP	1.0 M KOH	10	78	77	*Joule,* **2017**, *1,* 383.
Co-Ni_3N nanorods	1.0 M KOH	10	194	156	*Adv. Mater.* **2018**, *30,* 1705516.
CoP nanowires	1.0 M KOH	10	209	129	*J. Am. Chem. Soc.* **2014**, *136*, 7587.
$NiCo_2S_4$ nanowire/NF	1.0 M KOH	10	210	58.9	*Adv. Funct. Mater.* **2016**, *26*, 4661.
Ni-NiO/N-rGO	1.0 M KOH	10	135	46	*Adv. Funct. Mater*. **2015**, *25*, 5799.
Ni_2P/Fe_2P	1.0 M KOH	10	121	67	*Adv. Energy Mater.* **2018**, *8,*1800484.
Se-(NiCo)S_x/$(OH)_x$	1.0 M KOH	10	103	87.3	*Adv. Mater.* **2018**, *30,* 1705538.
Co/CoP	1.0 M KOH	10	253	73.8	*Adv. Energy Mater.* **2017**, *7,* 1602355.
Mn-Co-P	1.0 M KOH	10	76	52	*ACS Catal.* 2016, *7*, 98.
Ni_5P_4/Ni foil	1.0 M KOH	10	150	53	*Angew. Chem. Int. Ed.* **2015**, *127*, 12538.

$Ni_{0.89}Co_{0.11}Se_2$ MNSN/NF	1.0 M KOH	10	85	52	*Adv. Mater.* **2017,** *29,* 1606521.
NiMoN/CC	1.0 M KOH	10	109	95	*Adv. Energy Mater.* **2016**, *6*, 1600221.
N-Ni_3S_2/NF	1.0 M KOH	10	110	-	*Adv. Mater.* **2017**, *29,* 1701584.
V-Co_4N nanosheets	1.0 M KOH	10	37	44	*Angew. Chem. Int. Ed.* **2018**, *130,* 5170.
3D Ni–Mo alloy	1.0 M NaOH	20	34	-	*ChemElectroChem* **2014**, *1,* 1138.
Co–Mo–P	1.0 M KOH	10	30 ~ 35	63	*ChemCatChem* **2018**, *10,* 4832.
$MoNi_4/MoO_2$@Ni	1.0 M KOH	10	15	30	*Nat. Commun.* **2017**, *8,* 15437.

Table S4. The overpotential at the current density of 10 mA cm^{-2} (η_{10}), Tafel slope, MA, TOF, C_{dl}, and R_{ct} of the samples from electrocatalytic HER tests.

Catalysts	**η_{10} (mV)**	**Tafel slope (mV dec^{-1})**	**MA (A g^{-1})**	**TOF (s^{-1})**	**C_{dl} (μF cm^{-2})**	**R_{ct} (Ω)**
Co_3O_4-Co_4N/HCC	90	57.8	50.6	0.02	14.8	6
Co_4N/HCC	245	87.9	4.05	0.0016	7.2	16
Co_3O_4/HCC	348	136.7	0.95	0.00038	5.1	144

References

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