Electronic Supplementary Material (ESI) for ChemComm.

Ruthenium @ N-doped Graphite Carbon Derived from Carbon Foam for Efficient Hydrogen Evolution Reaction

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Table of the contents

1. Materials and methods

Materials

All chemicals were commercial and used without further purification: $RuCl_3 \cdot 5H_2O$, Co $(NO_3)_2 \cdot 6H_2O$, Ni $(NO_3)_2 \cdot 6H_2O$ and Pt/C (10 wt% Pt on Vulcan XC-72R) were purchased from Sigma-Aldrich.

Fabricating of M-NGC (Ru-NGC, Co-NGC, Ni-NGC)

Typically, the 100 mg carbon foam was impregnated in 5ml, 50mg/ml $RuCl_3.5H_2O$ or Co $(NO_3)_2.6H_2O$, Ni $(NO_3)_2.6H_2O$ after ultrasound for 30 min, the mix was freeze dried overnight. The M-NGC was subsequently fabricated by temperature programming to 800 °C for 2 h with a heating rate1 °C/min under the protection of an argon atmosphere.

Synthesis of Ru-NMC

The Ru-NMC sample was prepared in a similar way except that a heating rate (10 °C /min) was used.

Material characterization

The morphologies of the as-prepared products were characterized using high-resolution imaging performed on a JEOL 2100F and field-emission scanning electron microscopy S-4800, the energy dispersive x-ray spectroscopy (EDX) detector used for elemental mapping was X-Max 100 from Oxford. X-Ray powder diffraction was carried out using a Rigaku Dmax-2500X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) set-up equipped with a monochromatic Al Kα X-ray source (1486.6 eV; anode operating at 14.5 kV and 30.5 mA) and a high resolution Gammadata-Scienta SES 2002 analyzer.

Electrochemical measurements

A three-electrode system with a CHI 660 work station (Chenhua, Shanghai) was used to the electrochemical measurements. The catalysts (5 mg) were dispersed in 980 µL ethanol solution and 20 µl 5% Nafion, and untrasonic for half a hour to form a homogeneous suspension. The suspension (5 µL) were loaded onto a 3-mm-diameter glassy carbon electrode (mass loading: 0.36 mg/cm^2) . We used Ag/AgCl as a reference electrode and Pt wire as a counter electrode. All potentials in this article were calibrated by a reversible hydrogen electrode (RHE) under the same testing conditions immediately before the catalytic characterizations. The cyclic voltammograms of the HER activity were performed under a scan rate of 2 mV s^{-1} in 0.5 M H_2SO_4. The electrolyte solution was sparged with N_2 for 20 min before each test.

TOF calculate

The TOF (s^{-1}) can be calculated with the following equation[1]:

$$\mathrm{TOF} = \frac{(\#\ total\ hydrogen\ turnover * cm^{-2}\ geomrtric\ aera)}{(\#\ active\ site * cm^{-2}\ geomrtric\ aera)}$$

The Ru content of the Ru-NGC was calculated from the ICP-AES data:

$$\frac{2.0 \times 10^{-3} \times 6.55mg}{100} \times \frac{1\ \ mmol}{101.1\ \ mg} \times 6.02 \times 10^{23} \frac{sites}{mmol} = 7.8 \times 10^{16} site\ cm^{-2}$$

The number of total hydrogen turnovers (#H_2) was calculated from the current density according to the formula:

$$\#H_2 = (\mathrm{j}\frac{mA}{cm^2})(\frac{1Cs^{-1}}{1000mA})(\frac{1molH_2}{96500C})(\frac{1molH_2}{2mol * e^{-1}})(\frac{6.02 * 10^{23} H_2\ moleculars}{1mol\ H_2}$$

$$=3.12 \times 10^{15} (\frac{H_2 s^{-1}}{cm^2})\ \mathrm{per} \frac{mA}{cm^2}$$

For example, at an overpotential of 30 mV, the HER current density is 17 mA cm^{-2}, and the TOF of the Ru-NGC was calculated to be

$$TOF = \frac{3.12 \times 10^{15} \frac{H_2/s}{cm^2} per \times 17 \frac{mA}{cm^2}}{7.8 \times 10^{16} sites\ per\ cm^2} = 0.68 s^{-1}$$

DFT calculate

The simplified molecular model of the Ru-NGC was established based on STEM (Fig. 1) and XPS results (Fig. 2), in which the substrate of the NGC was perpendicular to the (001) facet of Ru, and the composite was formed mainly through the combination of nitrogen on the surface of Ru atoms. The dimension of a unit cell was 2.71 °A×2.71 °A × 4.28 °A. We used 4 layers of 8 atomic planes to simulate the (001) oriented Ru surface and 30 °A of sufficient vacuum space in the Z direction was applied to block the interaction between periodic structures.

2. Supporting figures

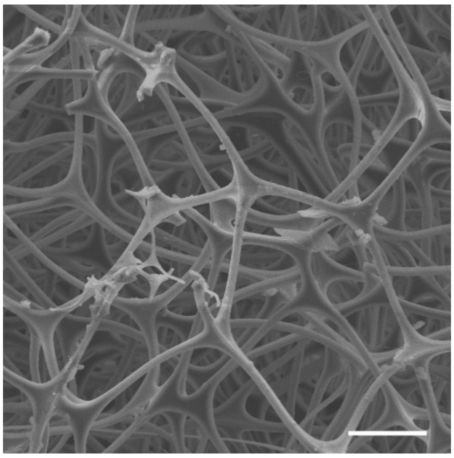

Fig. S1 Scanning electron microscopy (SEM) images of the original carbon foam (CF). Scale bar: 20 μm

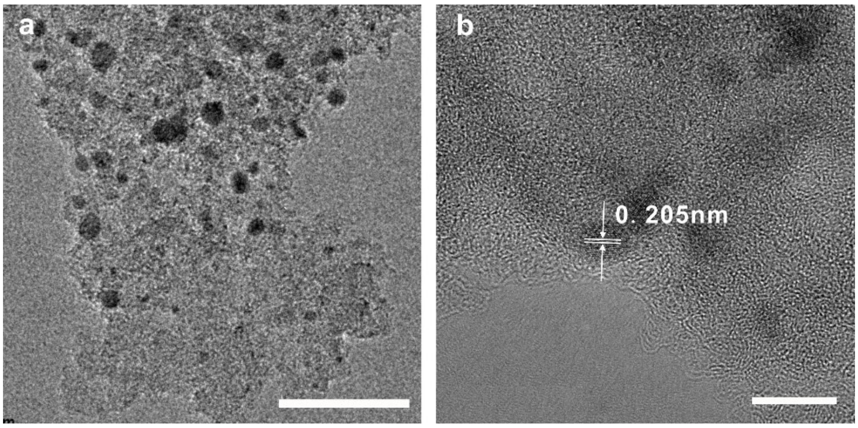

Fig. S2 TEM image (a) and HRTEM image (b) of Ru NPs encapsulated in nitrogen-doped amorphous carbon (Ru-NMC). Scale bar: (a), 50 nm (b), 10 nm.

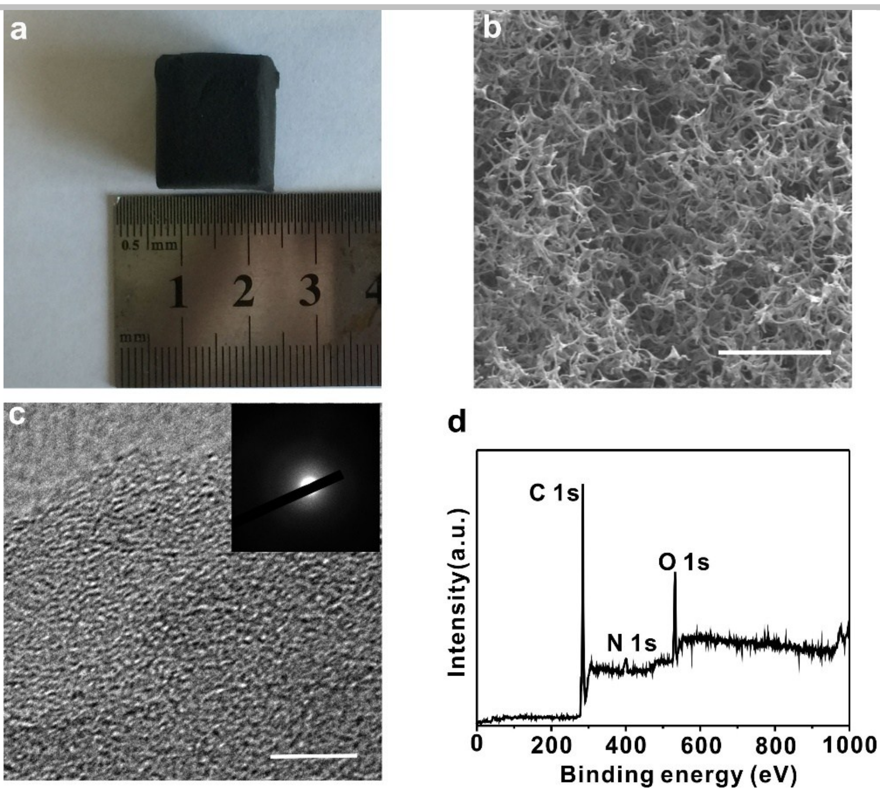

Fig. S3 (a) Digital image and (b) SEM image of blank sample nitrogen-doped carbon (NC) original from carbon foam (CF) after high temperature pyrolysis. (c) HR-TEM of NC and (d) X-ray photoelectron spectroscopy (XPS) measurements of NC. Scale bar: (b), 100 μm, (c) 5 nm.

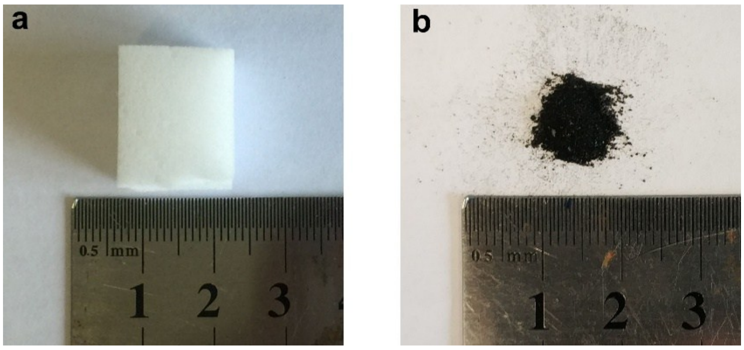

Fig. S4 Digital images of original CF (a) and Ru-NGC after high temperature annealing (b).

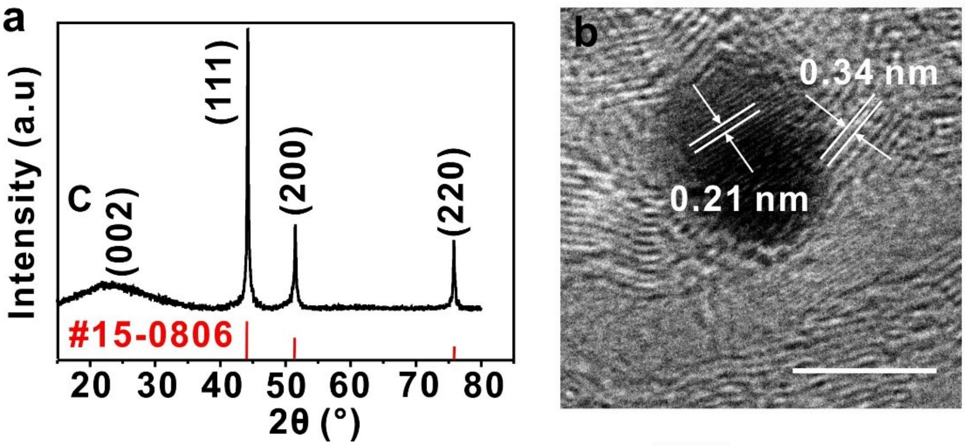

Fig. S5 The X-ray diffraction (XRD) pattern (a) and HRTEM of cobalt (Co) nanoparticles coated in nitrogen-doped graphite carbon (Co-NGC). Scale bar: (b), 2 nm.

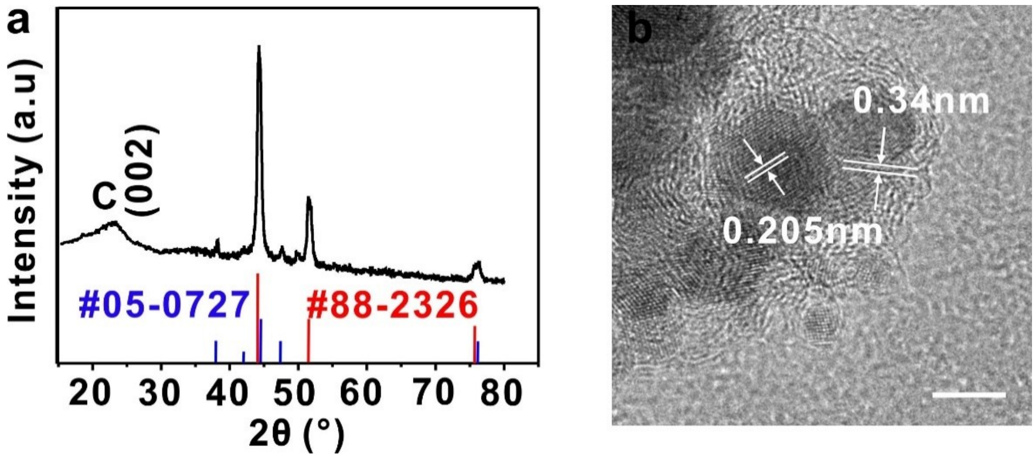

Fig. S6 The X-ray diffraction (XRD) pattern (a) and HRTEM of nickel (Ni) nanoparticles coated in nitrogen-doped graphite carbon (Ni-NGC). Scale bar: (b), 5 nm.

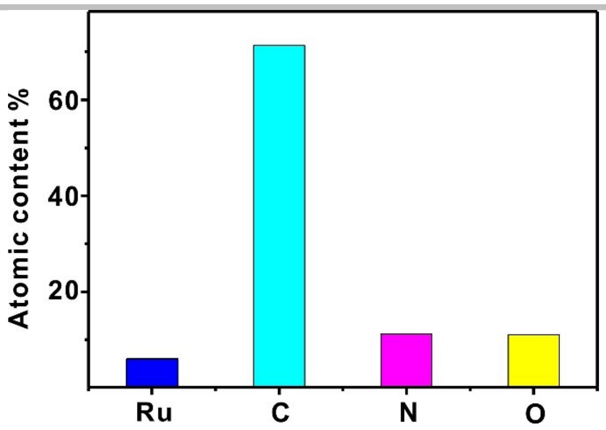

Fig. S7 Atomic content of Ru, C, N and O in the Ru-NGC measured by ICP-OES.

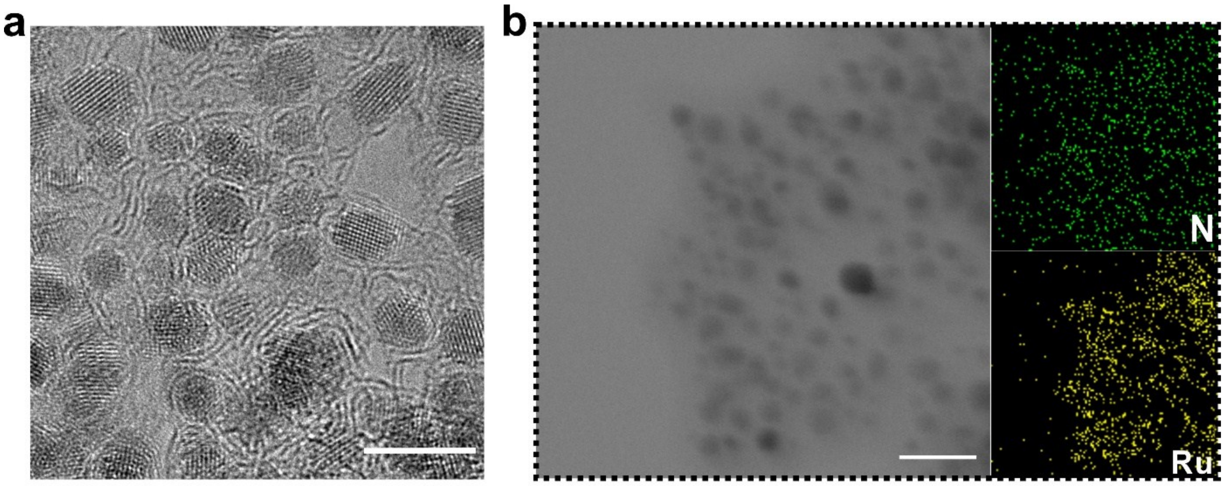

Fig. S8 (a) HR-TEM of Ru-NGC after electrolysis for 24 h in 0.5M H_2SO_4 and (b) EDS mapping of Ru-NGC after electrolysis for 24 h in 0.5M H_2SO_4. Scale bar: (a) and (b), 10 nm.

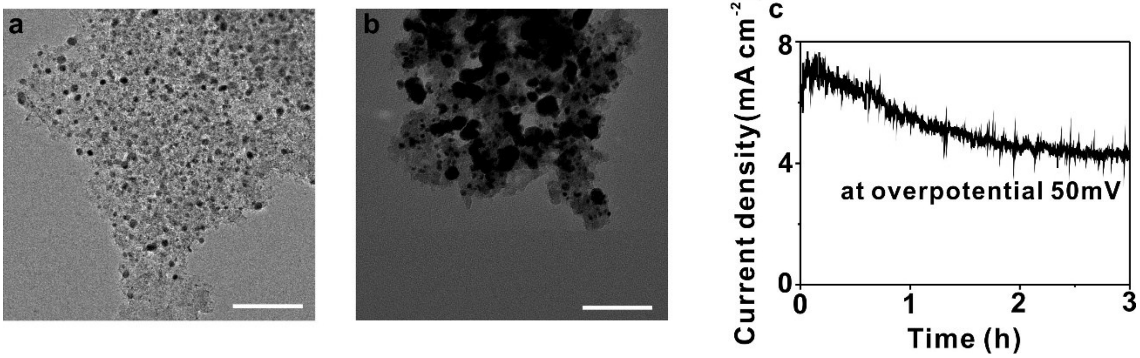

Fig. S9 TEM of Ru-NMC before (a) and after (b) electrolysis for 3 h and (c) i-t curve of Ru-NMC electrolysis for 3 h in 0.5M H_2SO_4. Scale bar: (a) and (b), 100 nm.

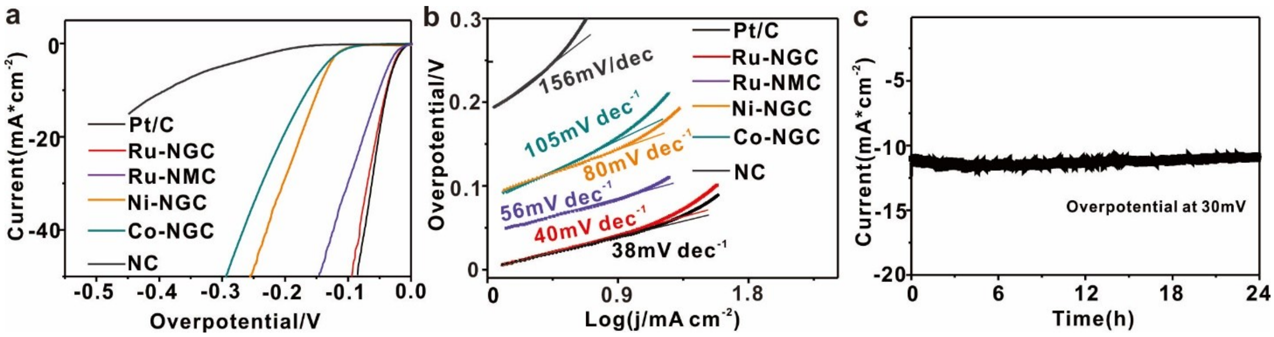

Fig. S10 (a) Tafel plots of Pt/C, Ru-NGC, Ru-NMC, Ni-NGC, Co-NGC and NC in 1.0 M KOH. (b) Ru-NGC electrocatalyst electrolysis in 1.0 M KOH at overpotential of 30 mV for 24 h.

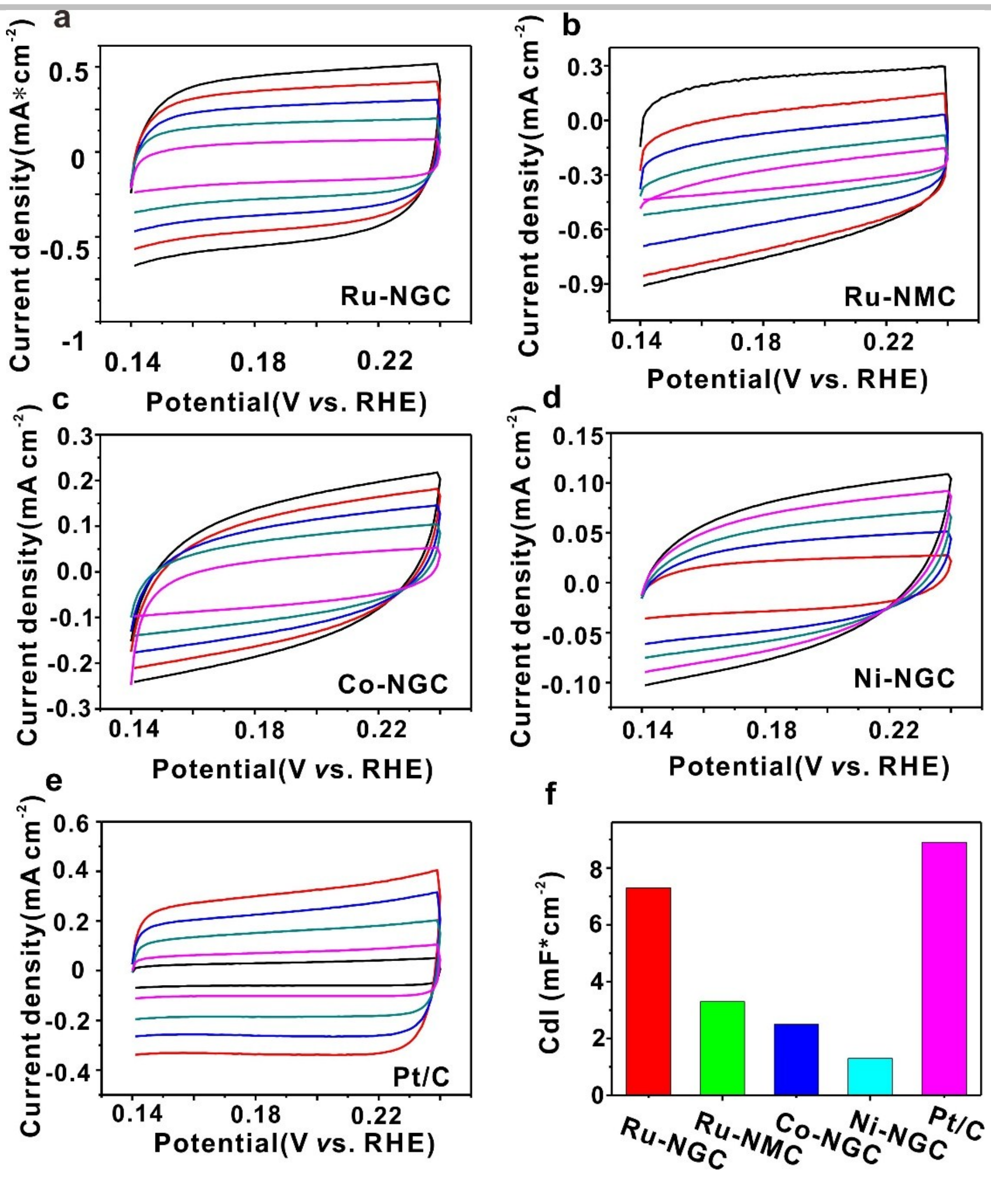

Fig. S11| Cyclic voltammetry curves of Ru-NGC (a), Ru-NMC (b), Co-NGC (c), Ni-NGC (d), Pt/C (e) at various scan rates from 20-100 mV s^{-1} in the region of 0.14−0.24 V versus RHE and (f), Cdl comparison of the five catalysts.

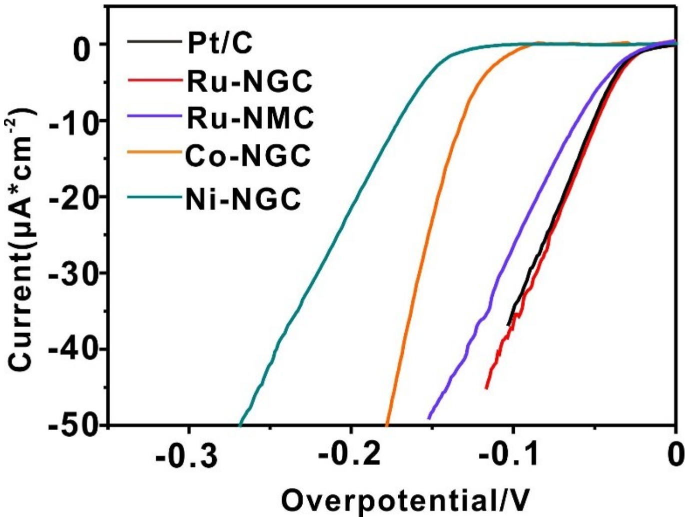

Fig. S12| ECSA-normalized HER polarization curves of the Pt/C, Ru-NGC, Ru-NMC, Co-NGC and Ni-NGC catalysts in 0.5M H_2SO_4.

3. Supporting tables

Table S1| HER catalytic data of Ru-NGC, Ru-NMC and Pt/C electrodes in 0.5M H_2SO_4.

Sample	$J_{\eta=30mV}$ (mA cm^{-2})	Double layer capacitance/Cdl	Active metal content (wt%)	TOF/s
Pt/C	21	8.9	10	1.04
Ru-NGC	17	7.3	6.55	0.68
Ru-NMC	3	3.3	6.23	0.13

Table S2 | Summary of some recently reported representative HER electrocatalysts in alkaline electrolytes

[a] The basic electrolyte is 1.0 M aq. KOH.
[b] The basic electrolyte is 0.1 M aq. KOH

Catalyst	Catalyst loading amount	Current density (mA	Overpotential at corresponding j	Tafel slope (mV dec^{-1})	References

		cm^{-2})	(mV)		
Ru-NGC	0.36 mg cm^{-2}	29	65	40	This work
Ru@C_2N	0.285 mg cm^{-2}	20	35.5	38	Nature Nanotech.12, 441-446 (2017)
CoMoSx[b]	50 µg cm^{-2}	5	~158	--	Nature Mater. 15, 197–203 (2016)
Co(OH)$_2$/Pt(111) [b]	--	10	248	--	Nature Mater. 11, 550–557 (2012)
NiRu@N–C	--	20	50	64	J. Mater. Chem. A 6, 1376 (2018)
RuP$_2$@NPC	1.0 mg cm^{-2}	10	52	69	Angew. Chem. Int. Ed. 56, 11559 (2017)
NiFeOx/CFP[a]	1.6 mg cm$^{−2}$	10	88	150	Nature Comm. 6, 7261 (2015)
np-CoP NWs-Ti	0.8 mg cm^{-2}	20	150	71	J. Am. Chem. Soc. 136, 7587 (2014)
CoP@BCN	0.4 mg cm^{-2}	10	215	52	Phys. Chem. Chem. Phys. 16, 16909 (2014)
CoNx/C	2 mg cm$^{−2}$	10	170	75	Nature Comm. 6, 7992 (2015)

4. Supporting refernces

1. Y. Liu, S. L. Liu, Y. Wang, Q. H. Zhang, L. Gu, S. C. Zhao, D. D. Xu, Y. F. Li, J. C. Bao, Z. H. Dai, *J. Am. Chem. Soc.* **2018**, *140*, 2731-2734.