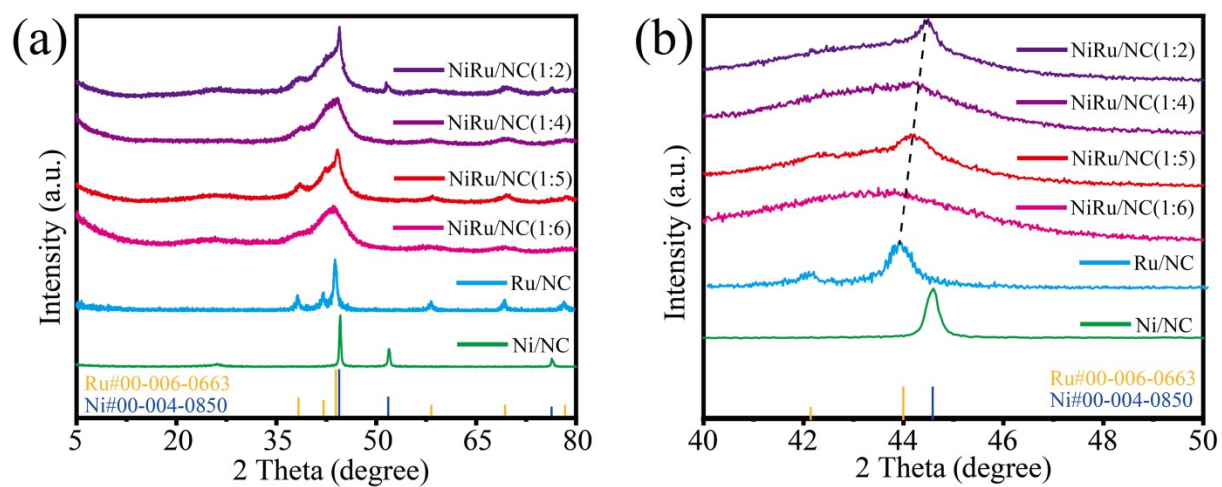
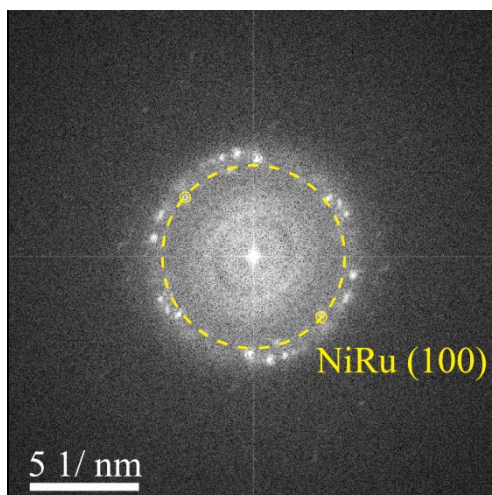


## Supplementary information

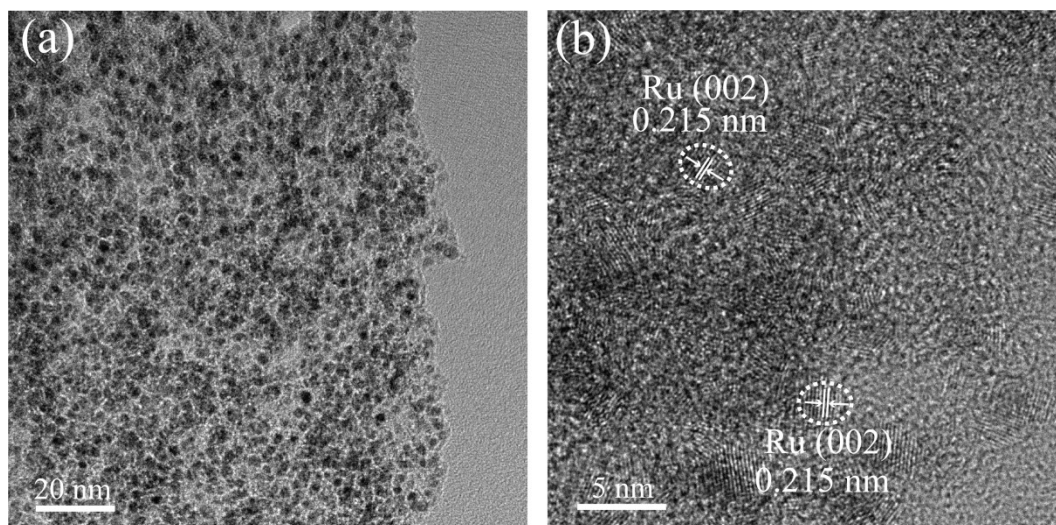


**Figure S1** NiRu alloy supported on nitrogen-doped carbon with different Ni/Ru ratio in synthesis

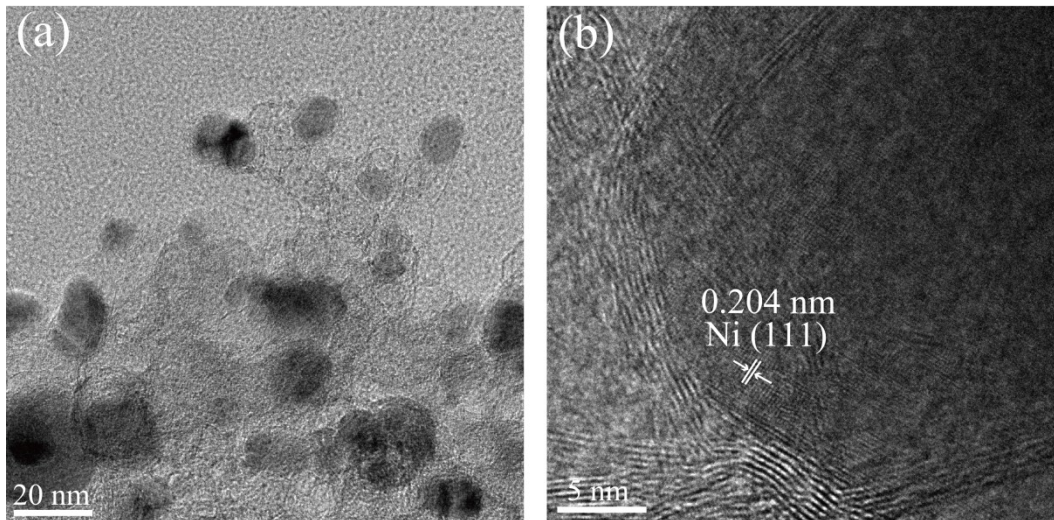
(a) XRD patterns, (b) local magnification



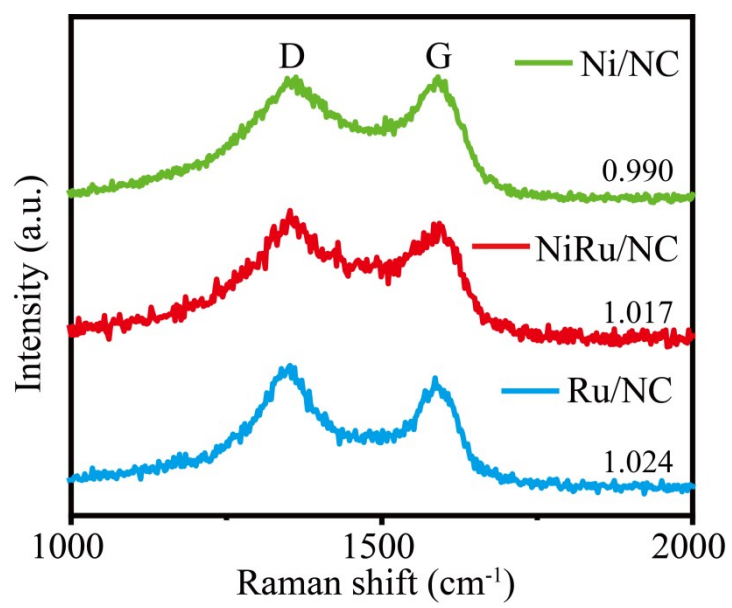
**Figure S2** Selected area electron diffraction (SAED) image of NiRu/NC from Figure 1d.



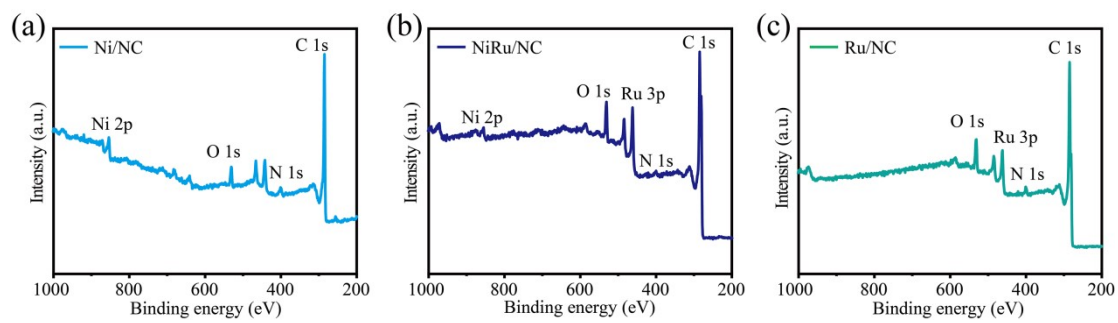
**Figure S3** a) and b) TEM and HRTEM image of Ru/NC.



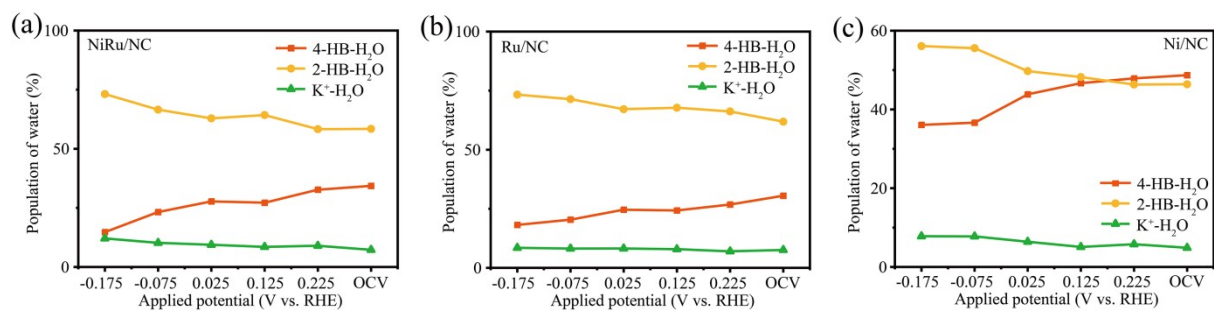
**Figure S4** a) and b) TEM and HRTEM image of Ni/NC.



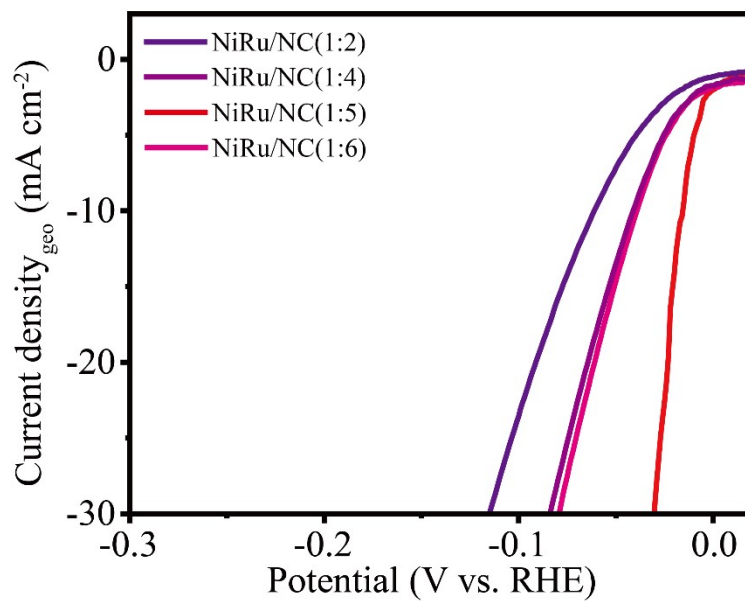
**Figure S5** Raman spectra of NiRu/NC, Ru/NC and Ni/NC.



**Figure S6** X-ray photoelectron spectroscopy studies. XPS full survey spectra of a) Ni/NC, b) NiRu/NC and c) Ru/NC

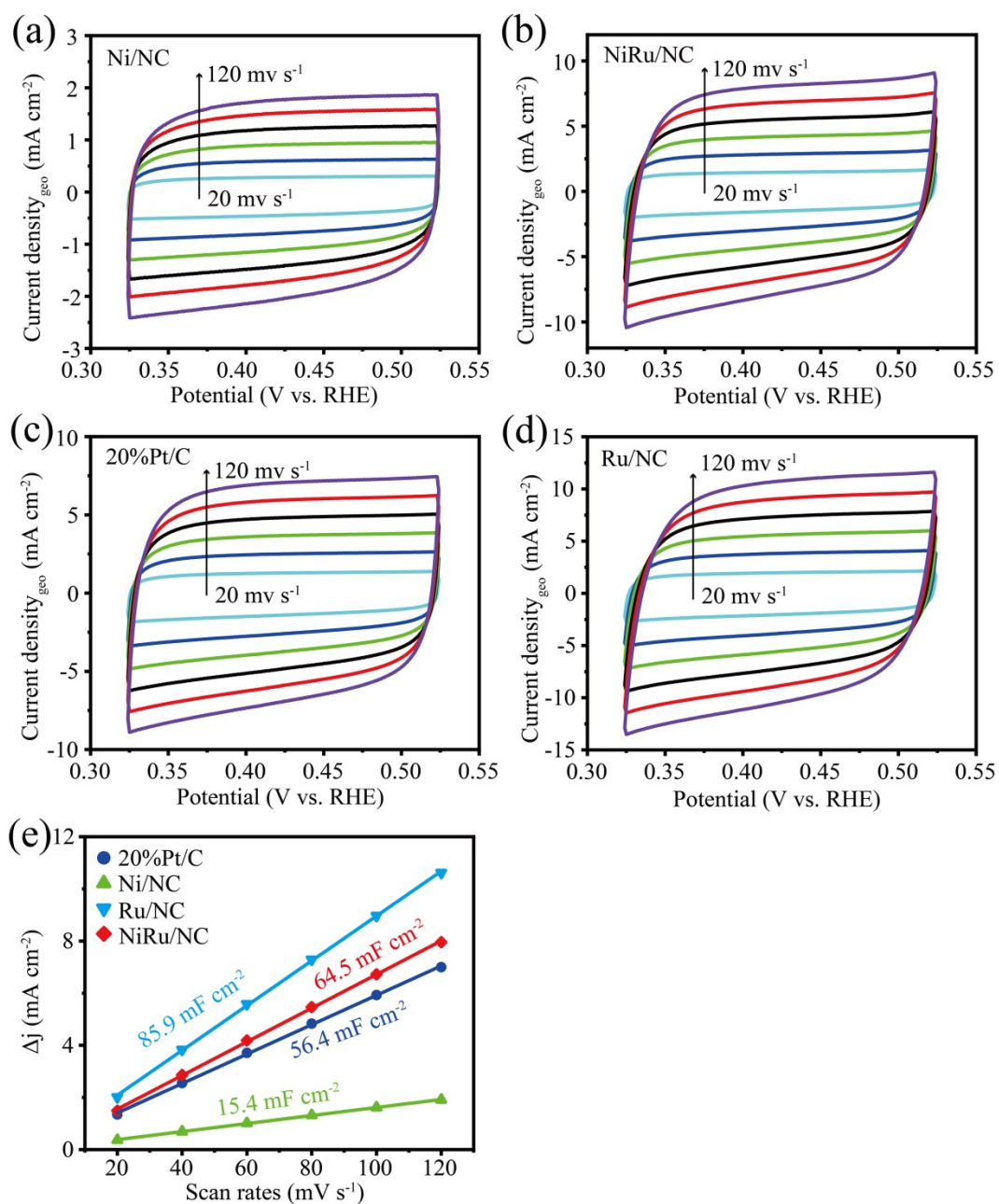


**Figure S7** The population of 4-HB-H<sub>2</sub>O, 2-HB-H<sub>2</sub>O and K<sup>+</sup>-H<sub>2</sub>O at different potentials in a) NiRu/NC , b) Ru/NC, and c) Ni/NC.

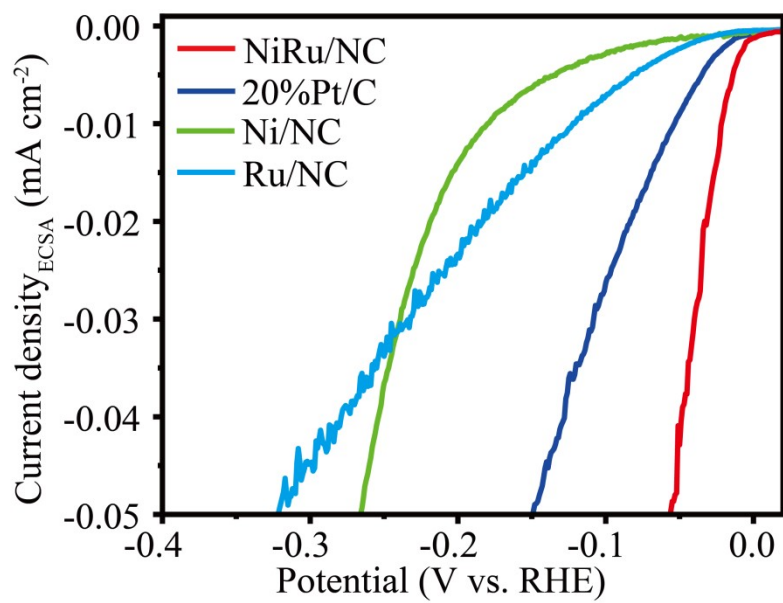


**FigureS8** LSV curves of NiRu alloys supported on nitrogen-doped carbon with Ni/Ru ratio from 1:6 to 1:2 in synthesis.

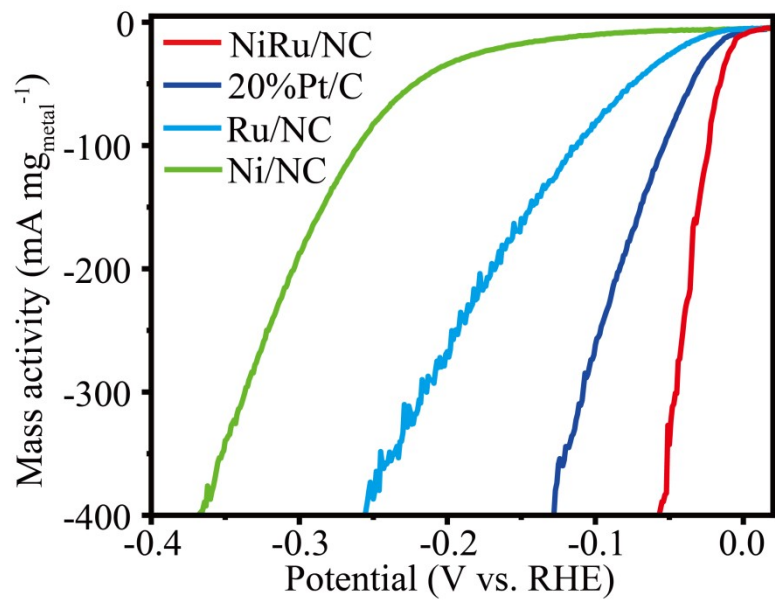




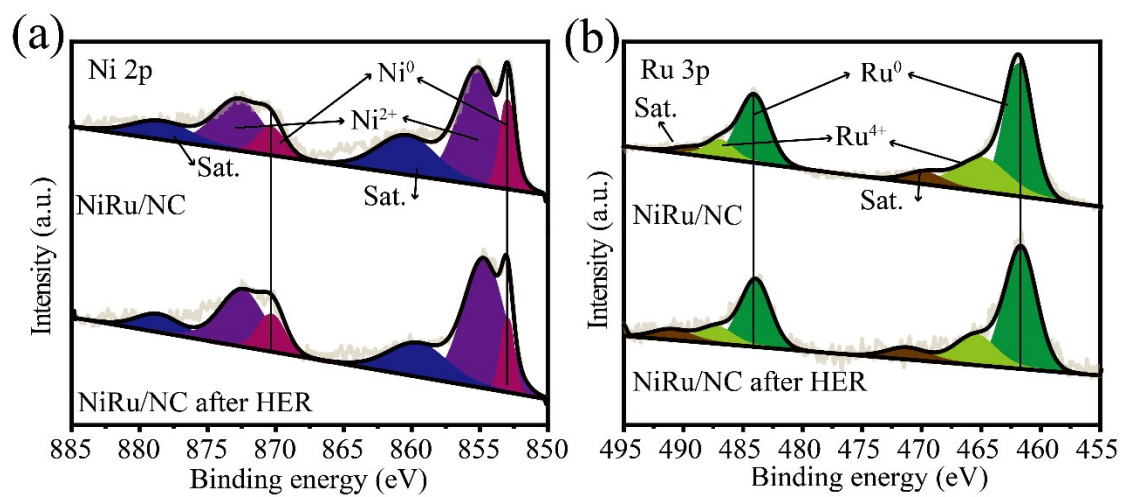
**Figure S9.** a), b), c) and d) CV curves of the Ni/NC, NiRu/NC, 20% Pt/C and Ru/NC obtained at different scan rates between 20 mV and 120 mV in 1 M KOH, respectively. e) Fitting results of double layer capacitance ( $C_{dl}$ ) among all samples.



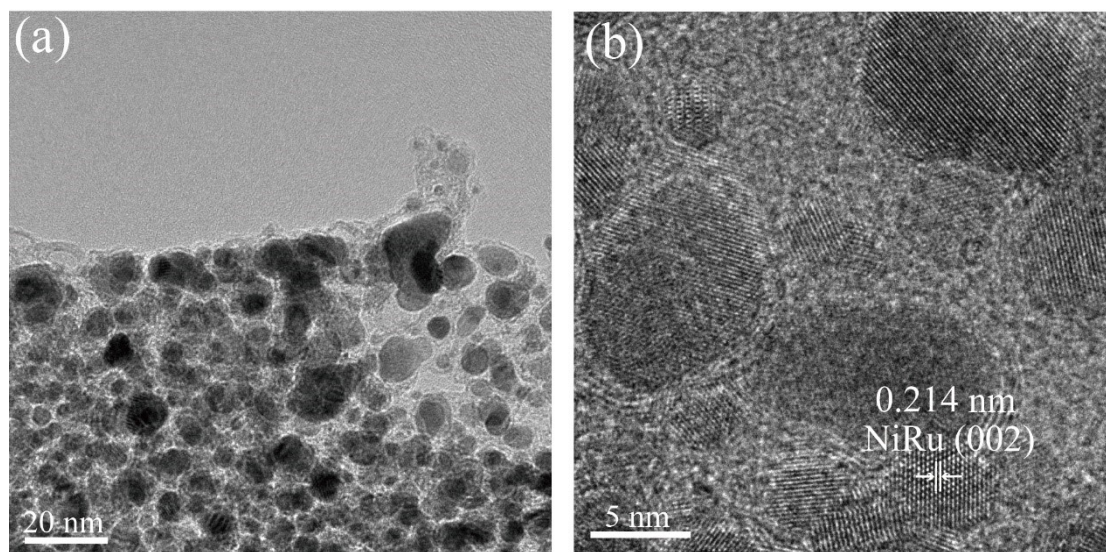
**Figure S10** LSV curves normalized by ECSA of NiRu/NC, Ru/NC, Ni/NC and 20% Pt/C.



**Figure S11** The mass activity curves of the tested catalysts.



**Figure S12** High-resolution XPS spectra for a) Ni 2p and b) Ru 3p of NiRu/NC after long-time stability test.



**Figure S13** a) and b) TEM image of NiRu/NC after long-term HER test.

**Table S1.** Comparison of HER activity data of NiRu/NC, Ni/NC and Ru/NC.

<b>Sample</b>	<b>NiRu/NC</b>	<b>Ru/NC</b>	<b>Ni/NC</b>	<b>20% Pt/C</b>
<b>geo-<math>\eta_{10}</math> (mV)</b>	16	78	228	43
<b>Tafel slope (mV dec<sup>-1</sup>)</b>	23.2	103.2	131.0	58.1
<b>C<sub>dl</sub> (mF cm<sup>-2</sup>)</b>	64.5	85.9	15.4	56.4
<b>ECSA (cm<sup>-2</sup>)</b>	113.98	151.68	27.18	99.54
<b>ECSA-<math>\eta_{0.05}</math> (mV)</b>	56	326	266	149
<b>Mass activity-<math>\eta_{10}</math> (mV)</b>	30	139	281	67
<b>R<sub>ct</sub> (<math>\Omega</math>)</b>	5.9	6.5	14.1	6.7

**Table S2.** The HER performance of NiRu/NC compared with other recently-reported HER electrocatalysts in 1 M KOH.

No.	Catalyst	$\eta_{10}$ (mV)	References
1	NiRu/NC	16	This work
2	Pt-Ru/RuO <sub>2</sub>	18	1
3	Ir@Ni-NDC	19	2
4	V-S-Ru/C	21	3
5	RhP <sub>2</sub> /Rh@NPG	21.3	4
6	P-Co/NF	23	5
7	Pt <sub>1</sub> /(Co,Ni)(OH) <sub>2</sub> /C	24	6
8	Pt-ACs/CoNC	24	7
9	Y,Co-CeO <sub>2</sub>	27	8
10	Ru@CDs	30	9
11	Ni@IrNi	33	10
12	RuBNC2000	41	11
13	PtRu/CNT@SnO <sub>2-x</sub>	53	12
14	Ru-MoCoP	55	13
15	RhPd metallene	59	14
16	Pt-V <sub>2</sub> CT <sub>x</sub>	68	15

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