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

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Supporting information

Ru single atoms and nanoclusters on highly porous N–doped carbon as hydrogen evolution catalyst in alkaline solutions with ultrahigh mass activity and turnover frequency

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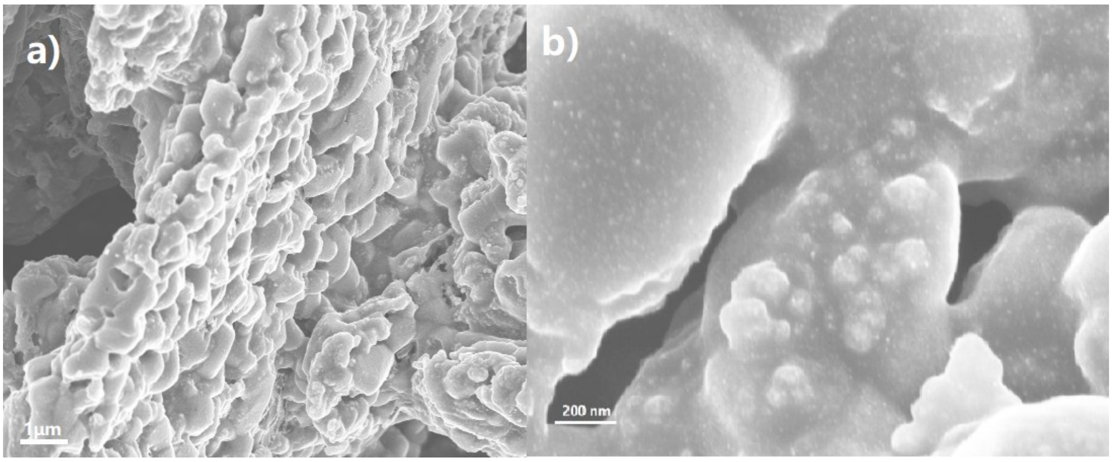

Fig. S1 SEM images of Ru/NC.

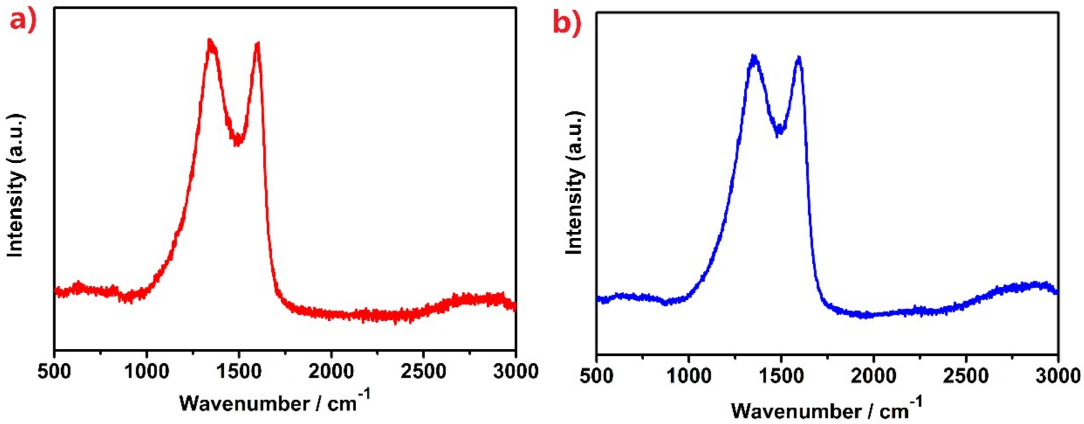

Fig. S2 Raman spectra of the catalysts. a) Ru/p-NC. b) Ru/NC.

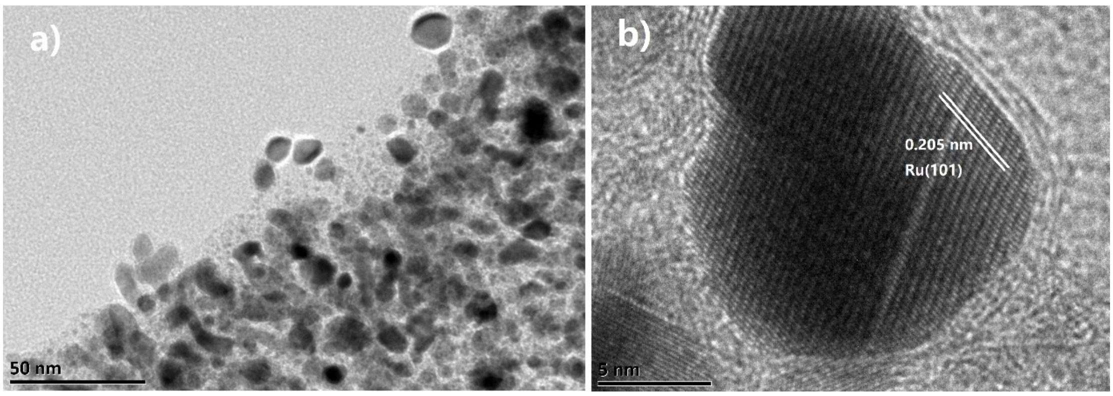

Fig. S3 a) TEM image of Ru/NC. b) HR-TEM image of Ru/NC.

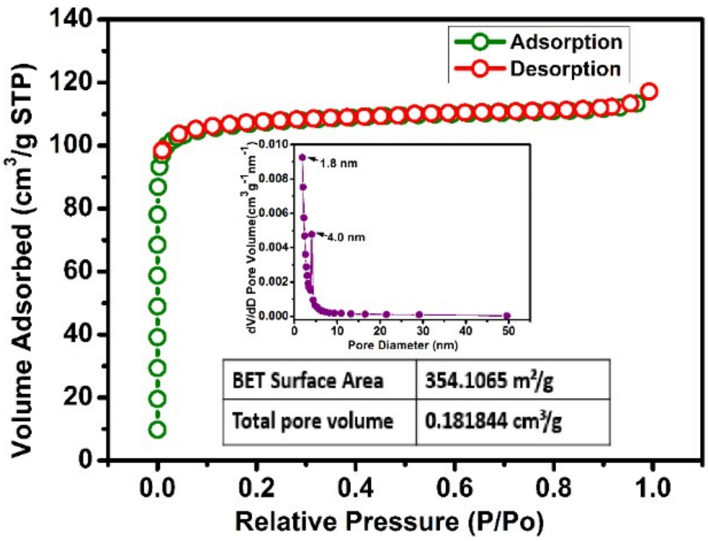

Fig. S4 N_2 adsorption/desorption isotherms of Ru/NC. Inset: corresponding pore size distribution.

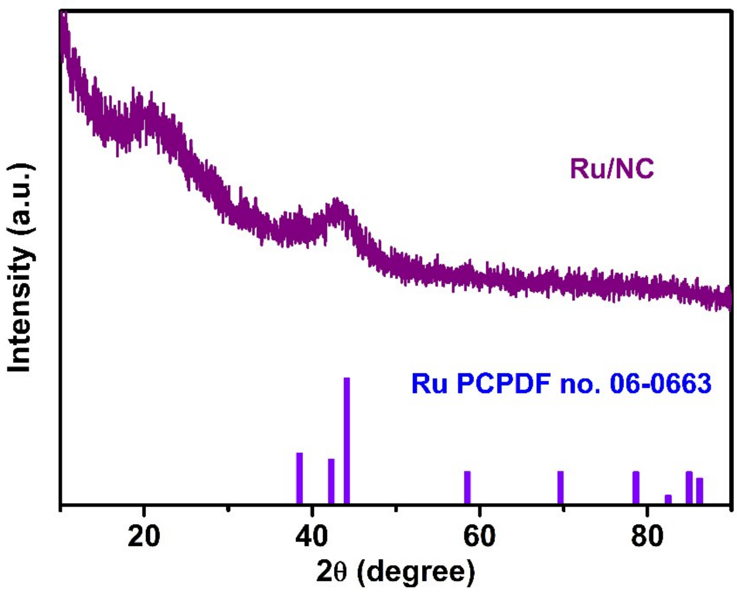

Fig. S5 XRD spectrum of Ru/NC.

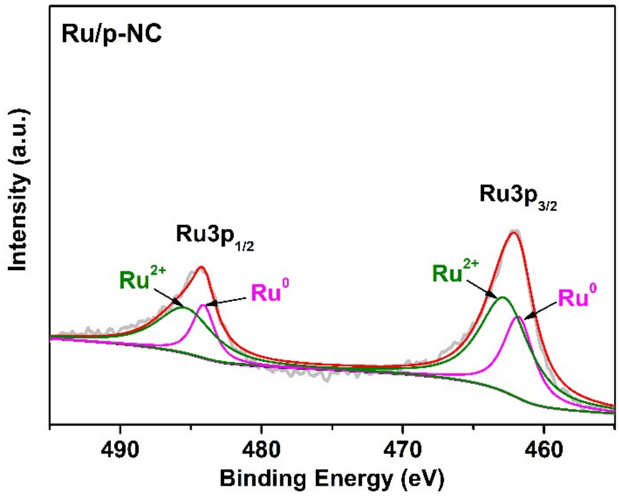

Fig. S6 High–resolution XPS spectrum of Ru 3p of Ru/p-NC.

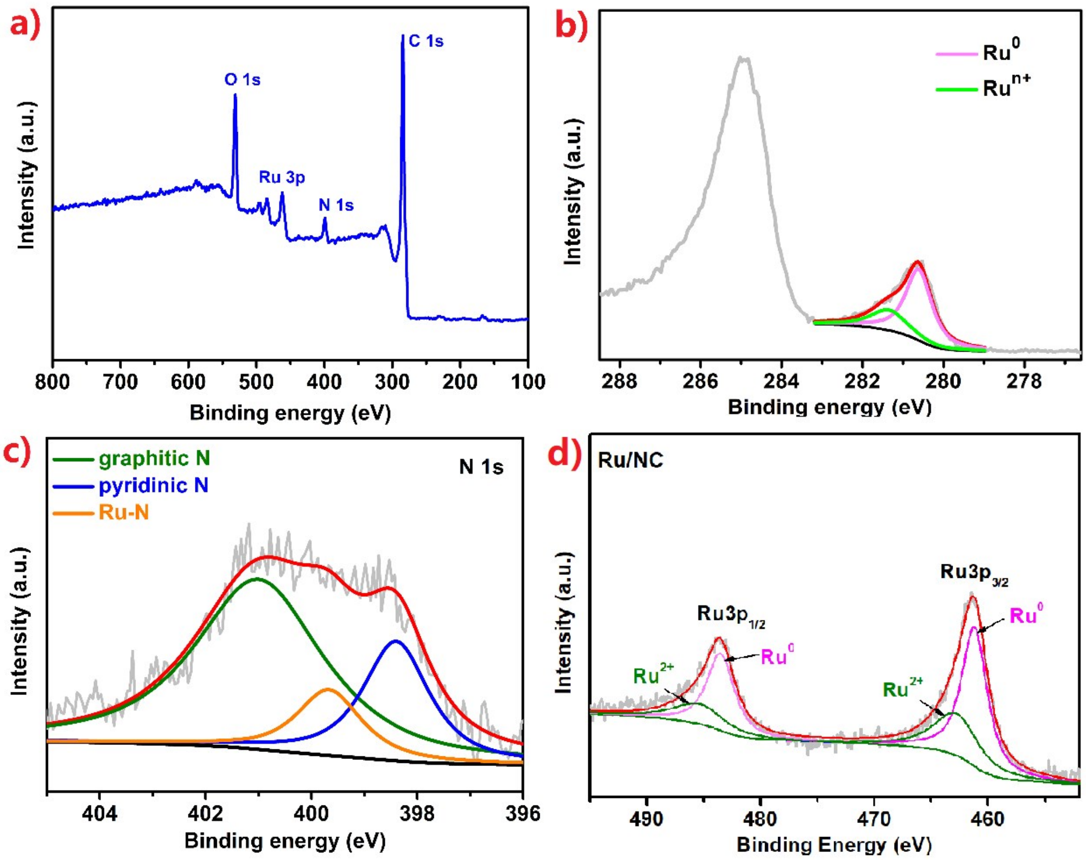

Fig. S7 a) XPS spectrum of Ru/NC. b) High–resolution XPS spectrum of C1s and Ru $3d_{5/2}$. c) High–resolution XPS spectrum of N 1s. d) High–resolution XPS spectrum of Ru 3p.

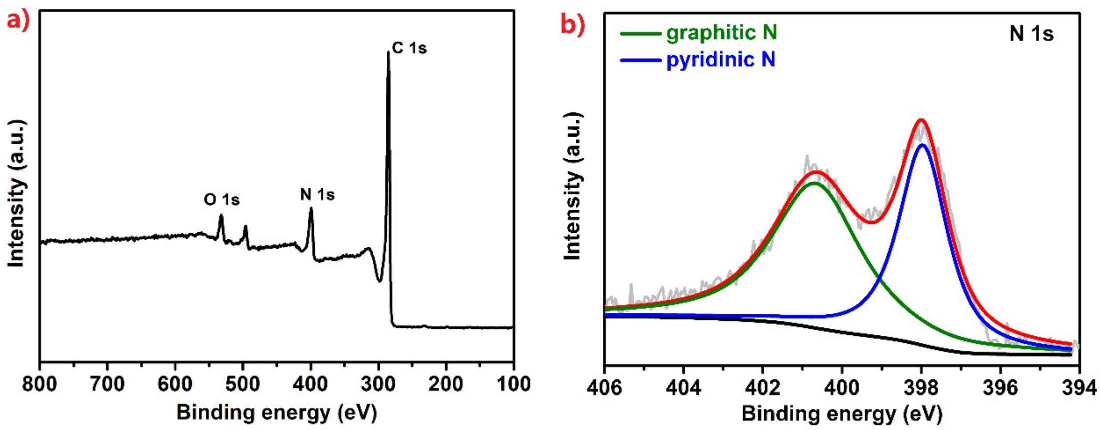

Fig. S8 a) XPS spectrum of NC. d) High–resolution XPS spectrum of N 1s.

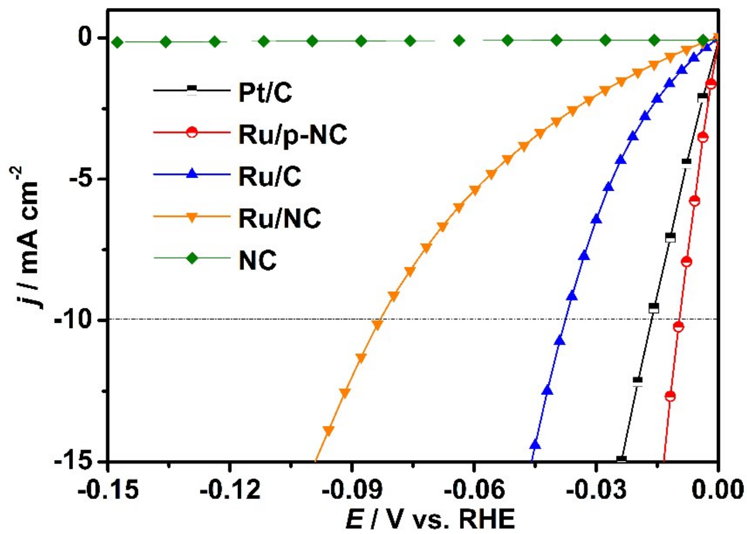

Fig. S9 A enlarged view of the HER polarization curves of Ru/p-NC, Ru/NC, Pt/C (20 wt %) and Ru/C (5 wt%) in 1.0 M KOH at a scan rate of 5 mV s^{-1}.

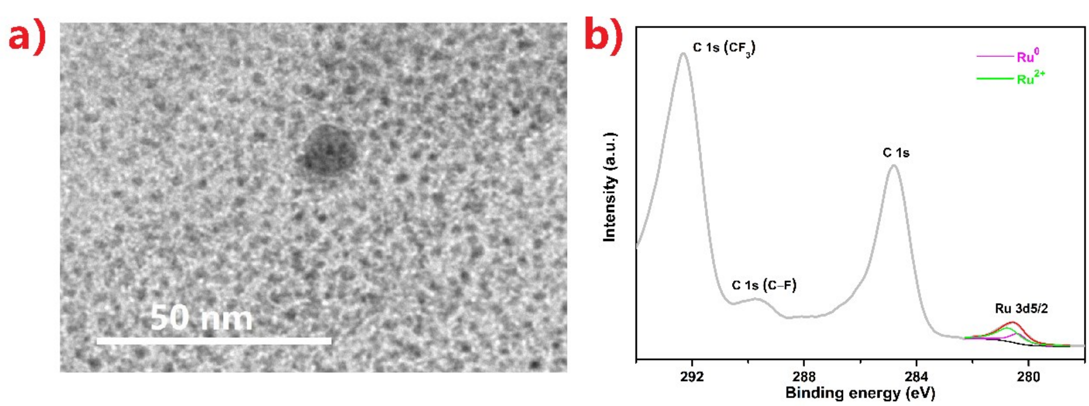

Fig. S10 a) TEM image and b) High-resolution XPS spectrum of Ru/p-NC after the test of long-term stability.

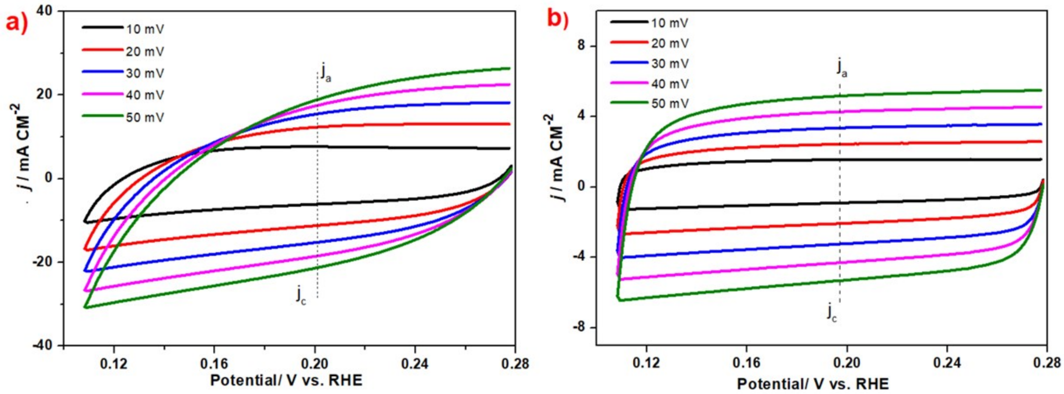

Fig. S11 Cyclic voltammetry curves of a) Ru/p-NC and b) Ru/NC.

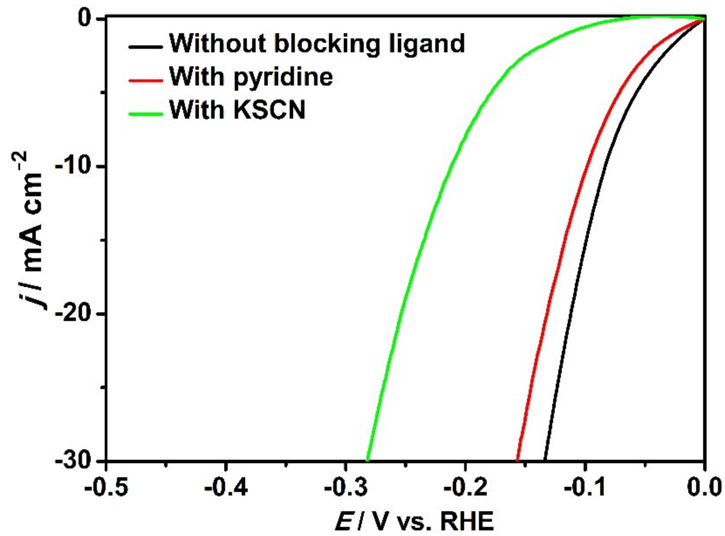

Fig. S12 HER polarization curves of the Ru/NC electrocatalyst with and without blocking ligands in 1 M KOH solution.

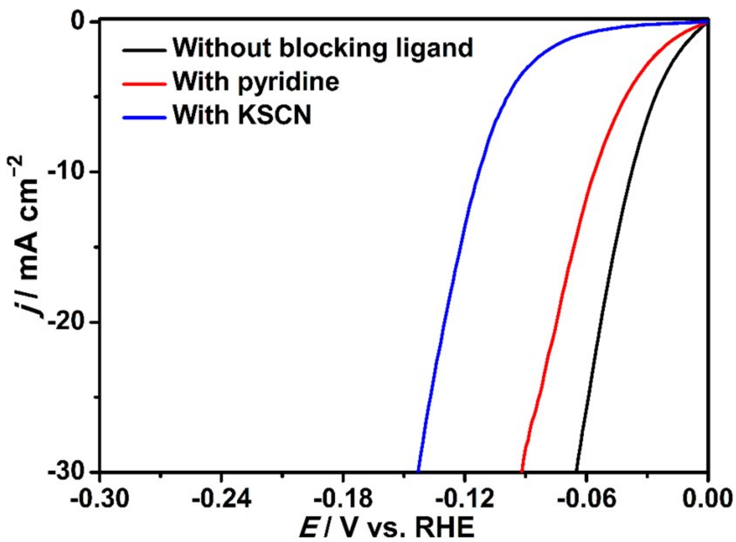

Fig. S13 HER polarization curves of the Ru/C electrocatalyst with and without blocking ligands in 1 M KOH solution.

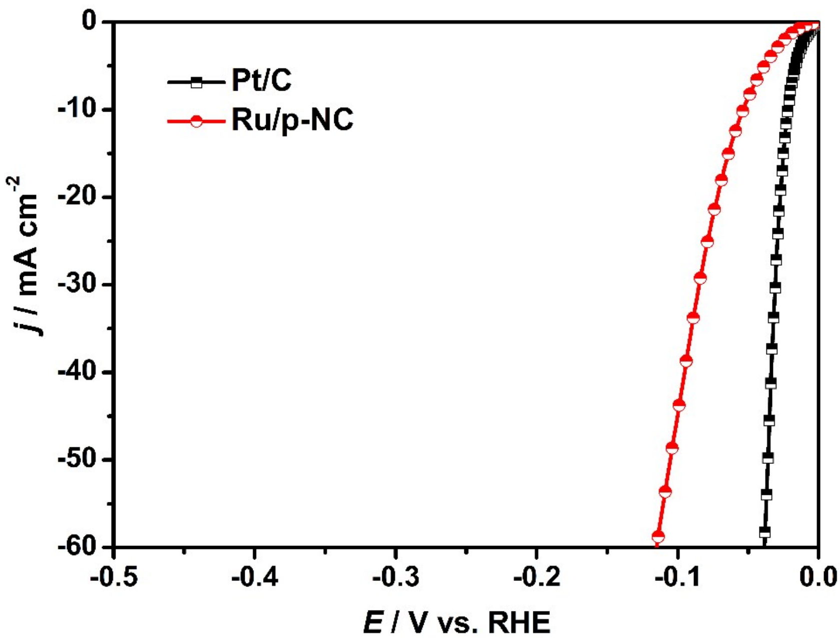

Fig. S14 HER polarization curves of the Ru/p-NC and Pt/C in 0.5 M H_2SO_4.

Table S1 Charge transfer resistances (R_{ct}) obtained by Nyquist plots in 1.0 M KOH at an applied overpotential of 10 mV.

Catalyst	R_{ct} / Ω
Ru/p-NC	4.7
Ru/NC	35.5
Ru/C	20.0
Pt/C	9.5

Table S2 Summary of HER performance of Ru-based catalysts in alkaline condition.

Catalyst	η_{10} **/ mV**	**Tafel slope / mV dec^{-1}**	**Mass activity/A mg_{Ru}^{-1}**	**TOF/ H_2 s^{-1}**	R_{ct}	**Reference**
Ru/p-NC	10	17	17 A mg_{Ru}^{-1} at 25 mV	8.9 at 25 mV	4.7 Ω	This work
Ru@C_2N	17	38	—	0.76 at 25mV, 1.66 at 50mV	43.7 Ω	1
Ru@GnP	22	28	0.23A mg_{Ru}^{-1} at 25mV	—	—	2
Ru@NC	26	36	17A mg_{Ru}^{-1} at 100 mV	10.8 at 100 mV	—	3
Ru@MW CNT	17	27	0.186 A mg_{Ru}^{-1} at 20 mV	0.4 at 25 mV	2.38Ω cm^2 at 45mV	4
Ru/NC/G F	21	31	8A mg_{Ru}^{-1} at 100 mV	4.55 at 100 mV	5Ω	5
Ru@C_4N	7	18	—	0.65 at 25 mV	0.9478 Ω	6
Ru-HPC	—	29	—	1.79 at 25 mV 9.2 at 100 mV	—	7
Ru/C-300	14	32	—	—	—	8
Ru/CN-800	14	30	—	—	13.7Ω	9
Ru@NCH NSs	28	32	0.1A mg_{Ru}^{-1} at 38.2mV	—	—	10

Ru-NC-700	12	14	—	—	20.7Ω	11
Ru-MoO_2	31	29	—	—	—	12
Ru@CN-0.16	32	53	—	—	—	13
RuCo@NC	28	31	—	—	8.58Ω	14
RuP_2@NPC	52	69	—	—	—	15
RuNi/CQDs-600	13	40	1.68A mg_{Ru}^{-1} at 13mV	—	6.45Ω	16
2DPC-RuMo	18	25	—	3.57 at 50 mV	0.9688 Ω	17

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