Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Ru@N/S/TiO_2/rGO: A High Performance HER Electrocatalyst Prepared by Dye-Sensitization

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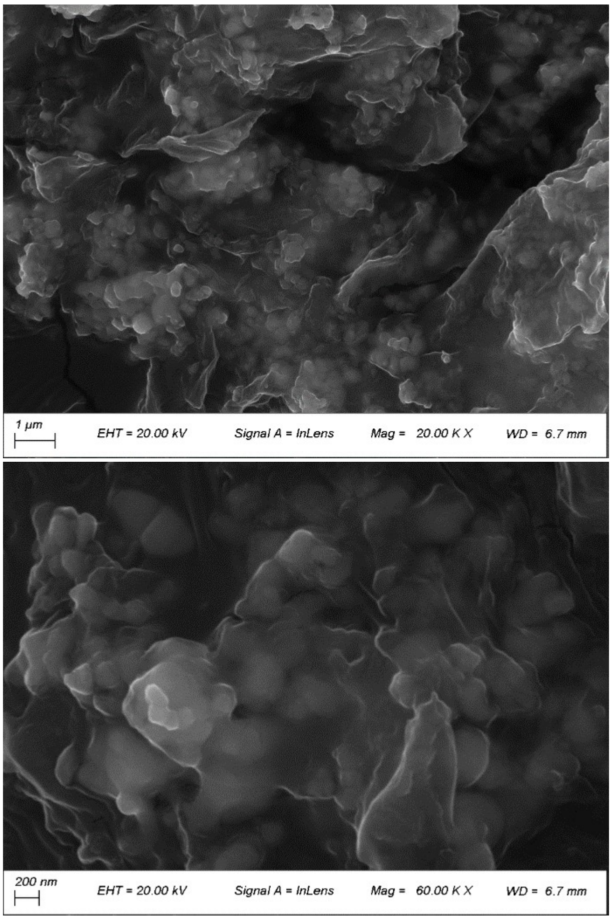


Fig. S1 SEM of Ru@N/S/TiO_2/rGO

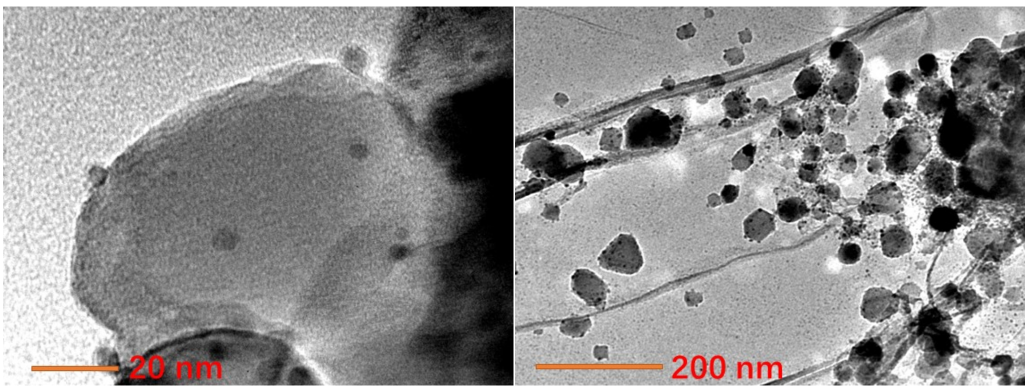


Fig. S2 TEM of Ru@N/S/TiO_2/rGO

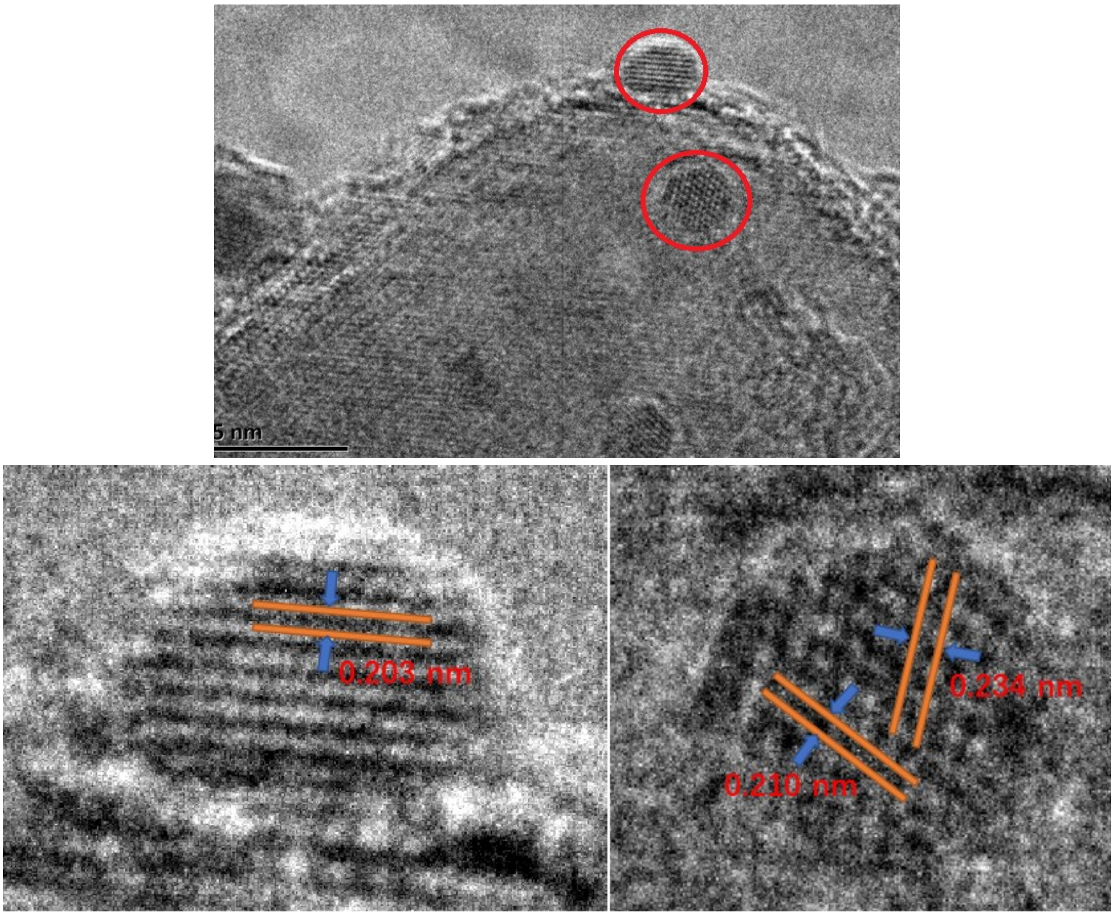


Fig. S3 HR-TEM of Ru@N/S/TiO_2/rGO

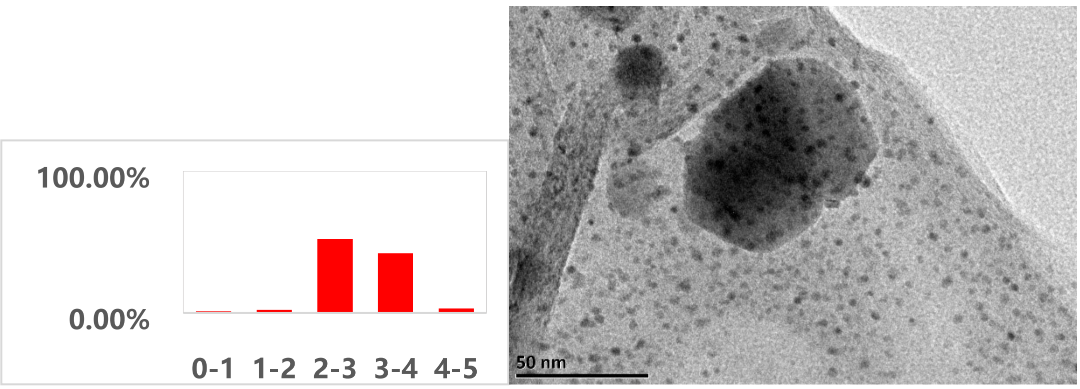


Fig. S4 Particle size distribution of Ru@N/S/TiO_2/rGO

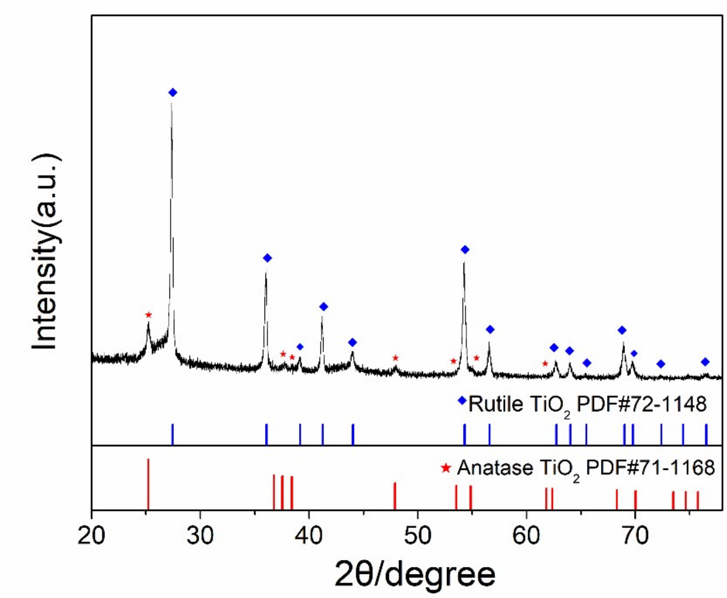


Fig. S5 XRD of Ru@N/S/TiO_2/rGO

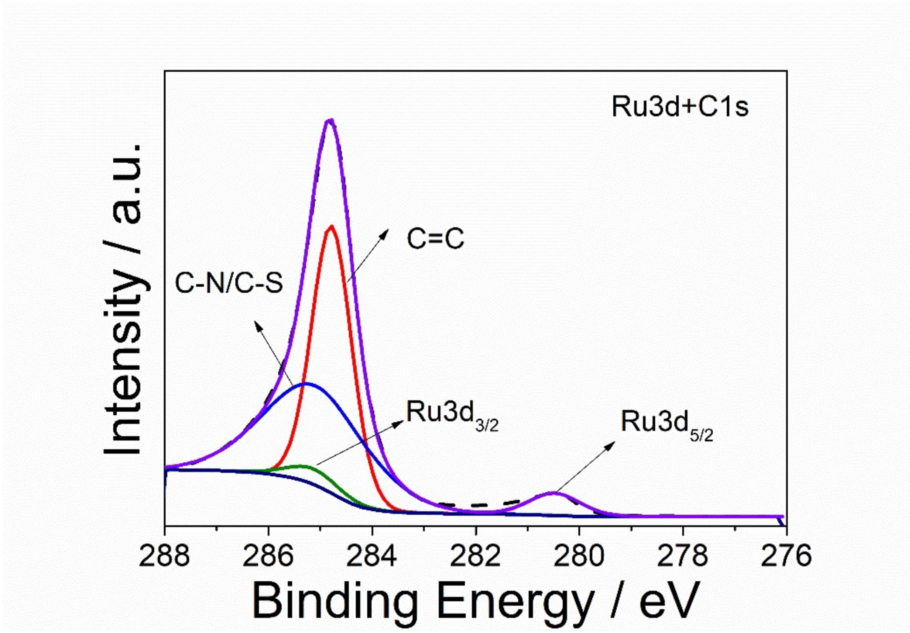


Fig. S6 High-resolution XPS spectra of Ru3d of Ru@N/S/TiO_2/rGO

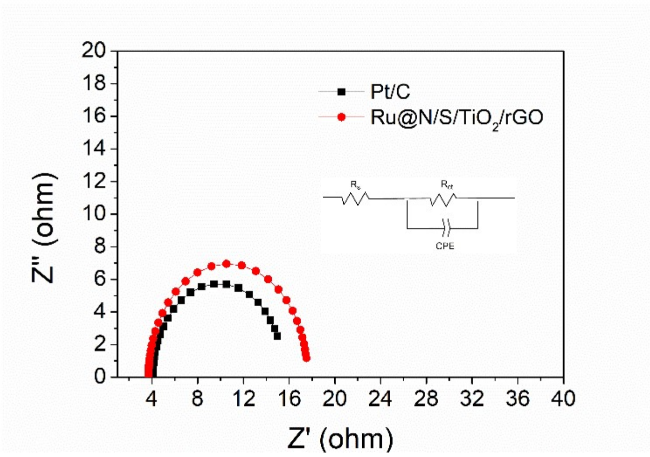


Fig. S7 EIS of Ru@N/S/TiO_2/rGO and Pt/C in 0.5 M H_2SO_4.

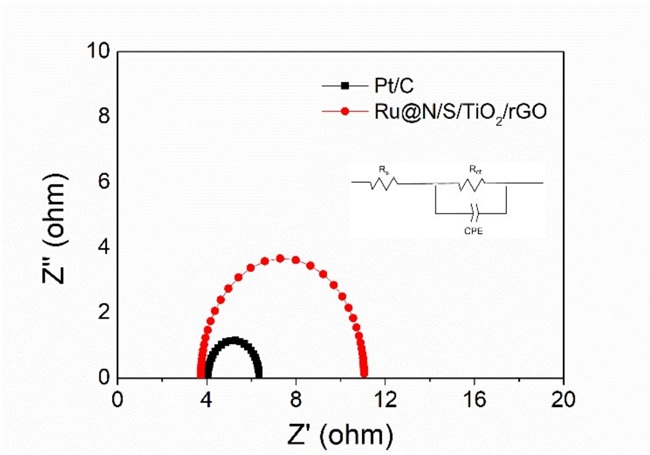


Fig. S8 EIS of Ru@N/S/TiO_2/rGO and Pt/C in 1 M KOH.

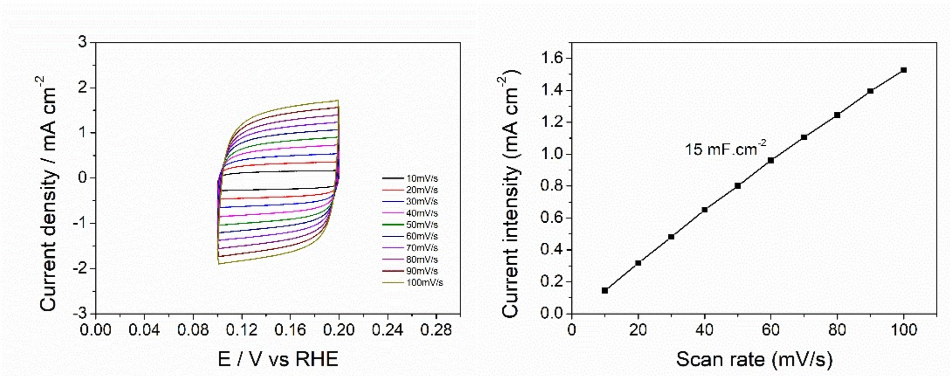


Fig. S9 CV curves of Ru@N/S/TiO_2/rGO at various scan rates in 0.5 M H_2SO_4, charging current density differences plotted against scan rates. The linear slope, equivalent to twice the double-layer capacitance, Cdl was used to represent the rECSA.

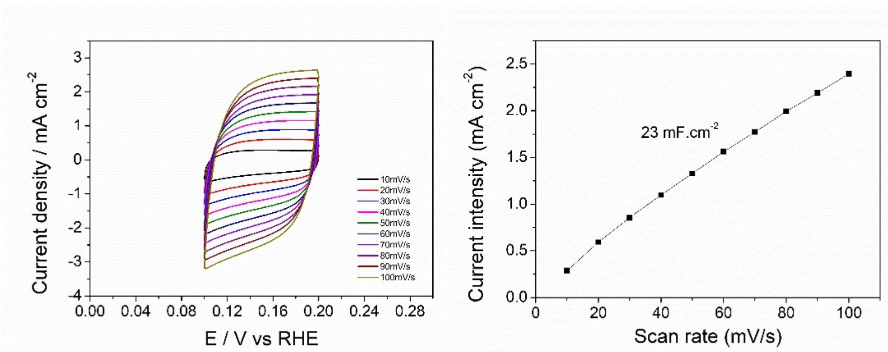


Fig. S10 CV curves of Ru@N/S/TiO_2/rGO at various scan rates in 1 M KOH, charging current density differences plotted against scan rates. The linear slope, equivalent to twice the double-layer capacitance, Cdl was used to represent the rECSA.

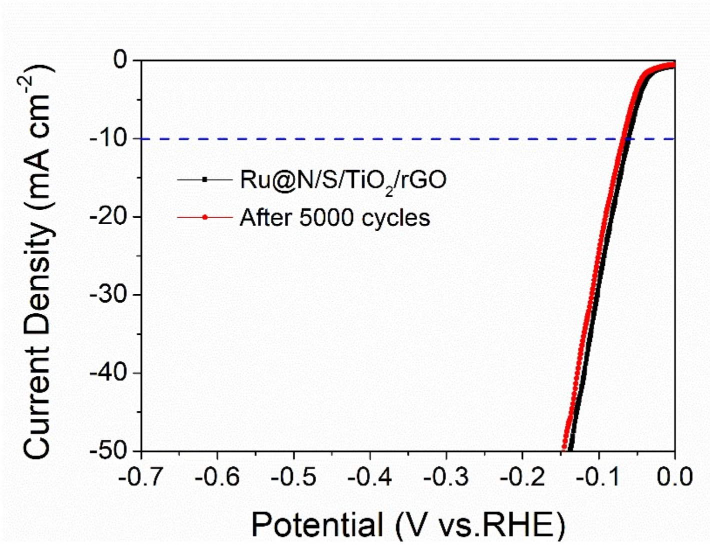


Fig. S11 LSVs of Ru@N/S/TiO_2/rGO catalysts before and after 5000 cycles in 0.5 M H_2SO_4.

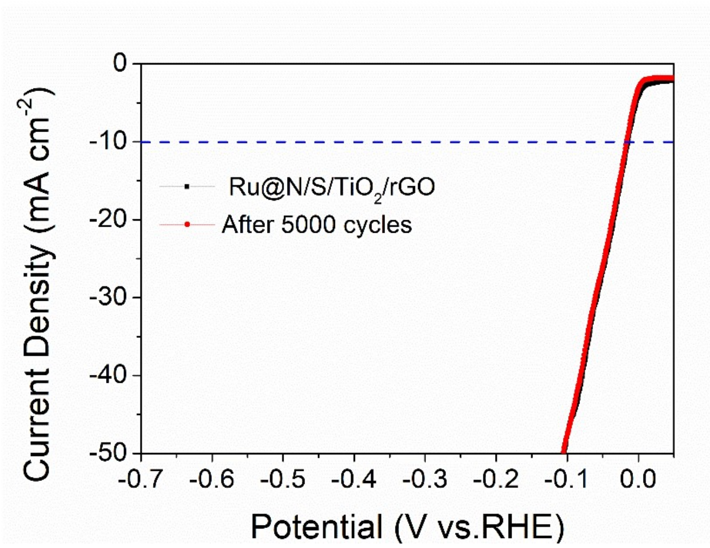


Fig. S12 LSVs of Ru@N/S/TiO_2/rGO catalysts before and after 5000 cycles in 1 M KOH.

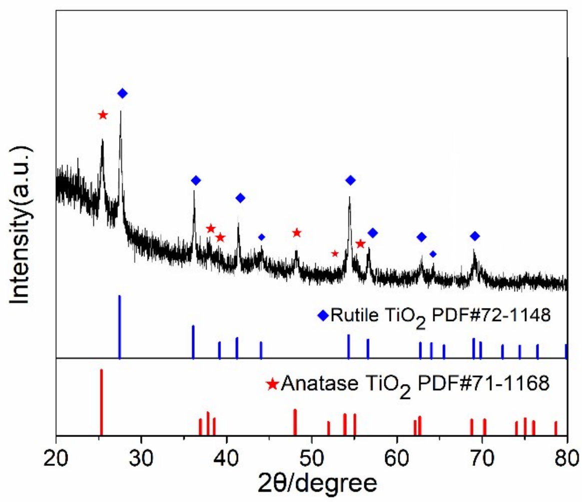
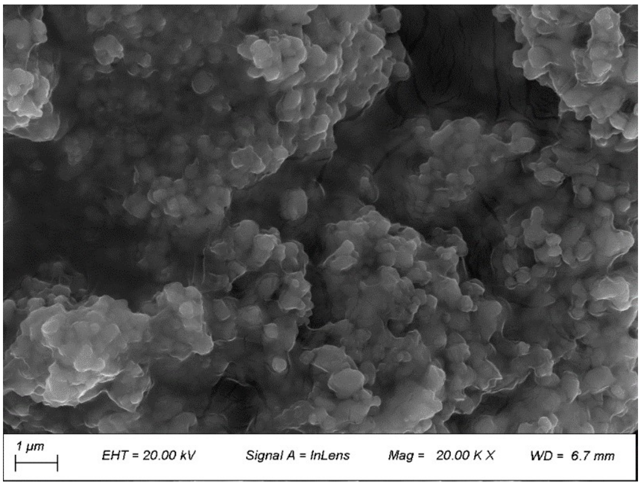


Fig. S13 XRD of Ru@N/S/TiO_2/rGO catalysts after 5000 cycles CV.



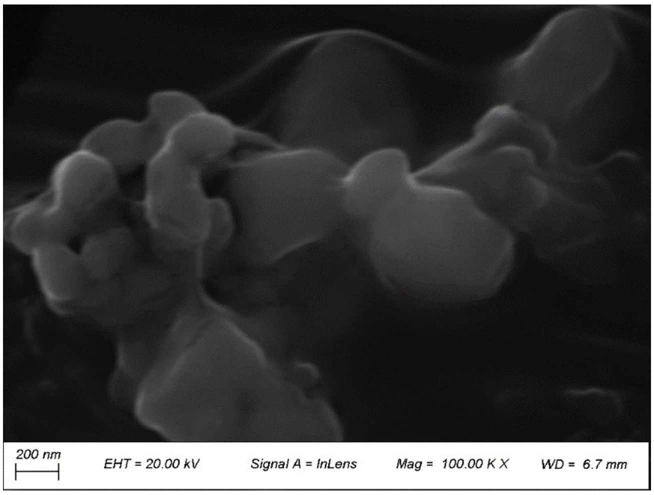


Fig. S14 SEM of Ru@N/S/TiO_2/rGO catalysts after 5000 cycles CV.

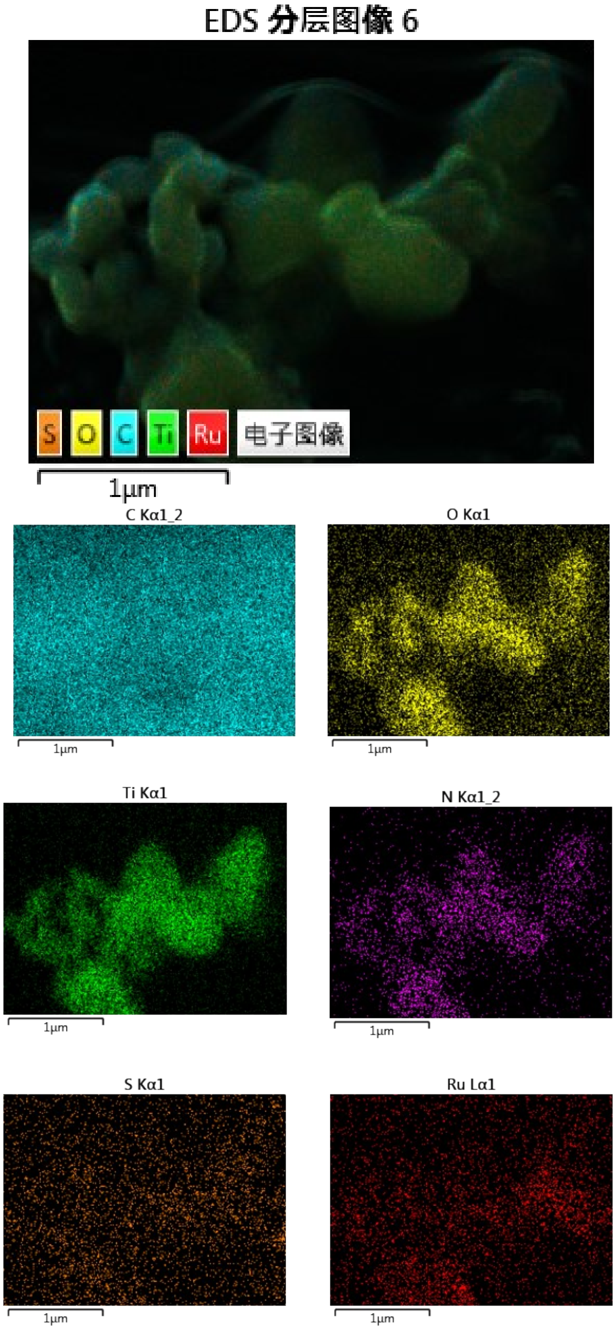


Fig. S15 EDS mapping of Ru@N/S/TiO_2/rGO catalysts after 5000 cycles CV.

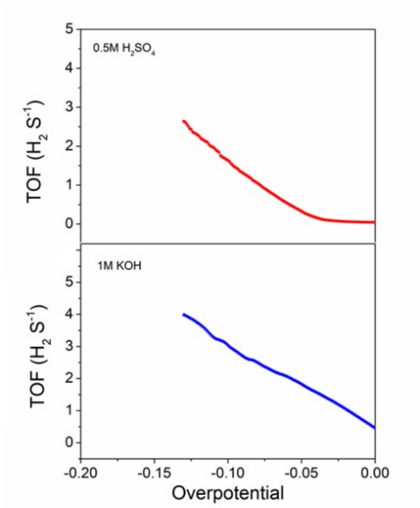


Fig. S16 TOF of Ru@N/S/TiO_2/rGO catalysts in 0.5M H_2SO_4 and 1M KOH.

Table S1. Summary of HER catalytic activities of Ru@N/S/TiO_2/rGO and some other catalysts reported in recent literatures (the potential is obtained at a current density of 10 mA cm^{-2} for HER in 0.5 M H_2SO_4).

Catalysts	HER Overpotential @10 mA cm^{-2} (mV)	Tafel Slope (mV dec^{-1})	Ref.
Ru@N/S/TiO_2/rGO	60	51	In this work
CoSAs/PTF-600	94	50	J. Mater. Chem., A, 2019, 7, 1252.
MWCNTs	17	27	Nat. Commun., 2020, 11, 1278.
MoS_2-60 s	131	48	J. Am. Chem. Soc., 2020, 142, 4298.
L-Ag	136	71	Nature Catalysis, 2020, 2, 1107.
Ru@GnP	13	30	Adv. Mater., 2018, 1803676
NPNi-MoS_2/RGO	/	71	ACS Catal., 2018, 8, 8107.
C_3N_4-Ru	140	57	J. Mater. Chem. A, 2017, 5, 18261.
Rh–Rh_2P@C	24	36	J. Mater. Chem. A, 2020 ,8, 12378.
WC1–X	247	/	ACS Appl. Energy Mater., 2020, 3, 1082.
$Fe_{40}Co_{40}P_{13}C_7$	118	46	ACS Appl. Mater. Interfaces, 2017, 9, 37, 31340.
IrO_2-CoPi-CNT	29	27	J. Mater. Chem. A, 2020, 8, 8273.
B12/G800A	115	65	J. Mater. Chem. A, 2019, 7, 7179.
FePc-MoS_2	123	32	Nanoscale, 2019, 11, 14266.
CoSAs/PTF-600	94	50	J. Mater. Chem. A, 2019, 7, 1252.
Co:WS_2	240	49	Energy Environ. Sci., 2018, 11, 2270.
D-TiO_2/Co@NCT	167	73	Nano Res., 2017, 10, 2599.
RuP_2@NPC	38	38	Angew. Chem. Int. Ed., 2017, 56, 11559.

Table S2. Summary of HER catalytic activities of Ru@N/S/TiO_2/rGO and some other catalysts reported in recent literatures (the potential is obtained at a current density of 10 mA cm^{-2} for HER in 1 M KOH).

Catalysts	HER Overpotential @10 mA cm^{-2} (mV)	Tafel Slope (mV dec^{-1})	Ref.
Ru@N/S/TiO_2/rGO	5	45	In this work
MWCNTs	16	27	Nat. Commun., 2020, 11, 1278.
Ru@GnP	22	28	Adv.Mater., 2018, 1803676.
Co_3S_4@FNC-Co3	140	103	Carbon, 2020, 160, 133.
MoS_2/NiS	244	97	Small, 2019, 15, 1803639.
MoS_2/Ni_3S_2	110	88	Angew. Chem. Int. Ed., 2016, 55, 6702.
Ni_3FeN/rGO	94	90	ACS Nano., 2018, 12, 245.
Ni-Co-P HNBs	107	76	Energy Environ. Sci., 2018, 11, 872.
Rh–Rh_2P@C	37	32	J. Mater. Chem. A, 2020, 8, 12378.
WC1–X	216		ACS Appl. Energy Mater., 2020, 3, 1082.
c-Ni@a-Ni$(OH)_2$	57	45	J. Mater. Chem. A, 2020, 8, 23323.
P-rich IrP_2@NC	28	/	Energy Environ. Sci., 2019, 12, 952.
RuP_2@NPC	52	69	Angew. Chem. Int. Ed., 2017, 56, 11559.
CoP/CC	209	129	J. Am. Chem. Soc., 2014, 136, 7587.
WP NAs/CC	150	102	ACS Appl Mater Interfaces, 2014, 6, 21874.
MoP NA/CC	80	83	Appl. Catal. B: Environ., 2016, 196, 193.
MoP_2 NPs/Mo	194	80	Nanoscale, 2016, 8, 8500.
Co-NCNT/CC	180	193	ChemSusChem, 2015, 8, 1850.