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Supporting Information for

Enhanced interaction betweeen Ru nanoparticles and N, C-modified mesoporous TiO_2 for efficient electrocatalytic hydrogen evolution at All pH Values

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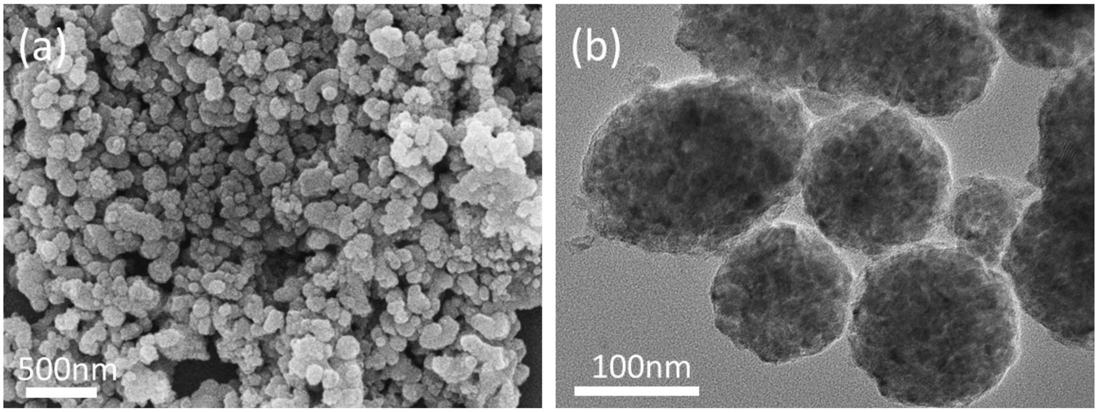

Fig. S1. (a) SEM and (b) TEM images of N-TiO_2/C nanospheres.

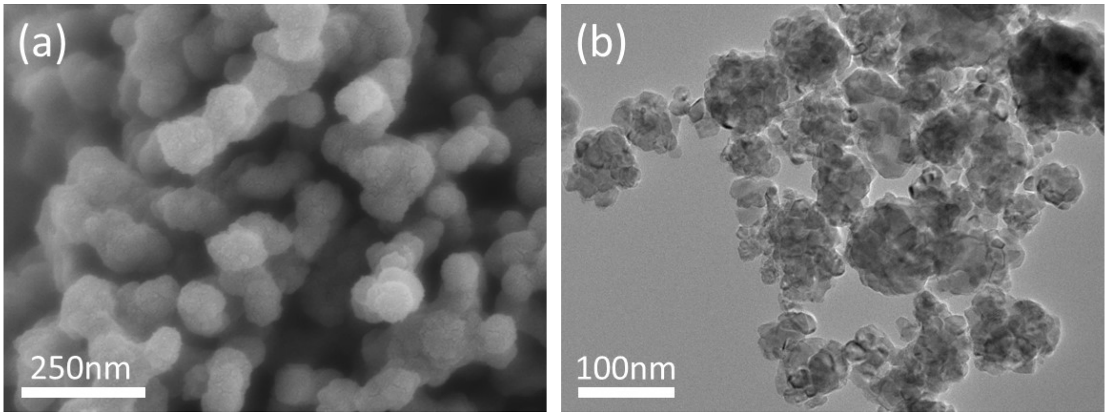

Fig. S2. (a) SEM and (b) TEM images of TiO_2 nanospheres.

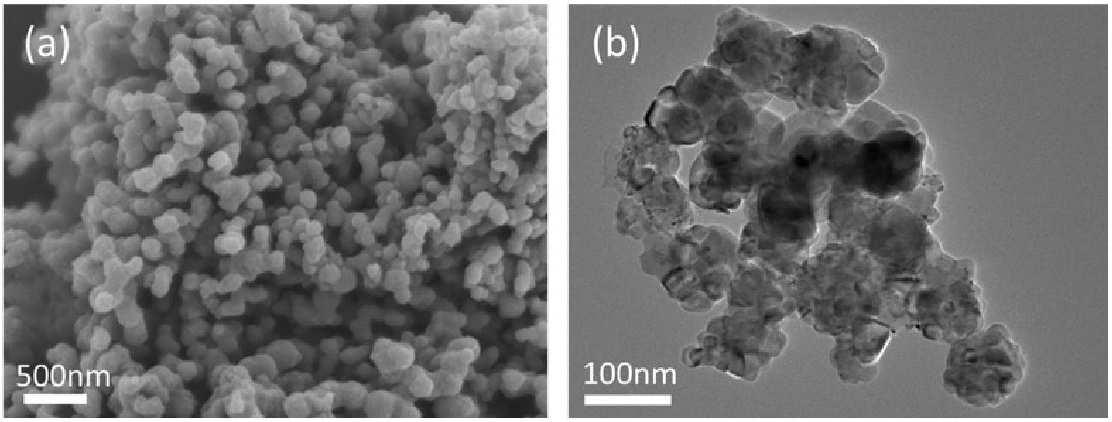

Fig. S3. (a) SEM and (b) TEM images of Ru@TiO_2 nanospheres.

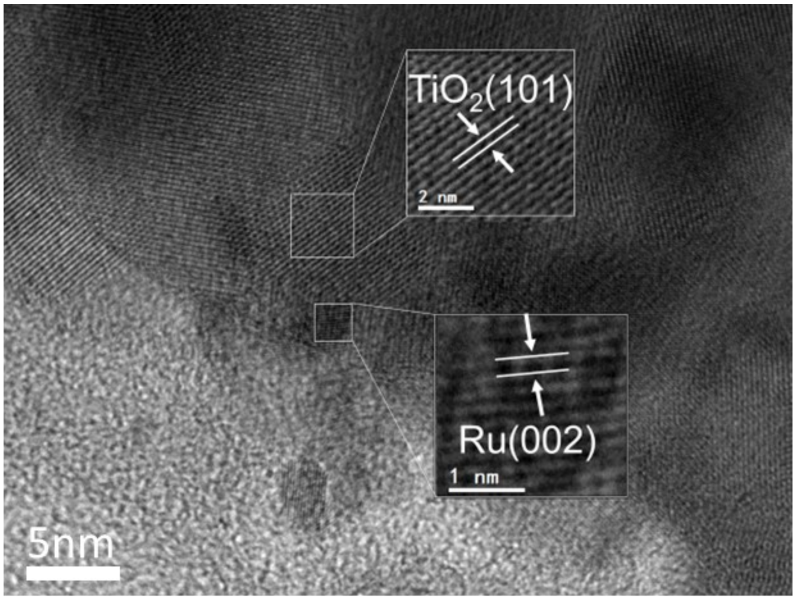

Fig. S4. HRTEM images of Ru@TiO_2 nanospheres.

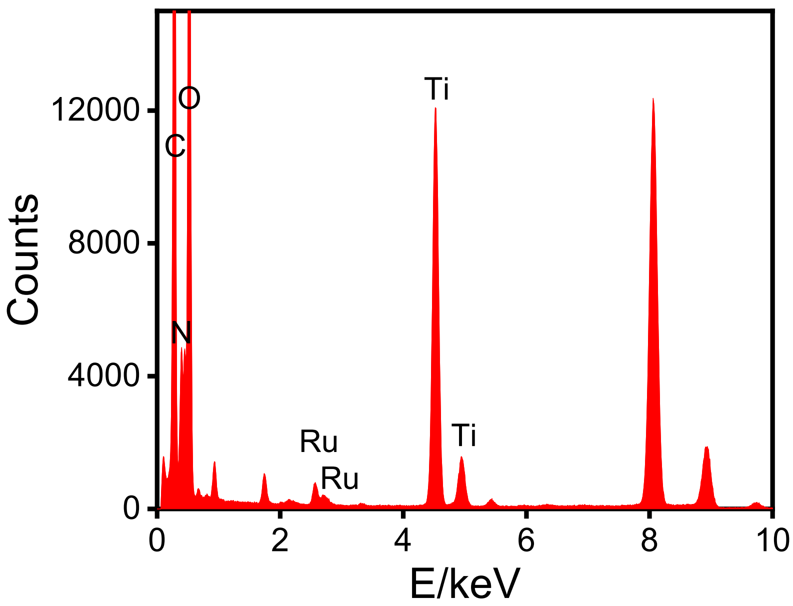

Fig. S5. The energy dispersive X-ray spectroscopy of Ru@N-TiO_2/C.

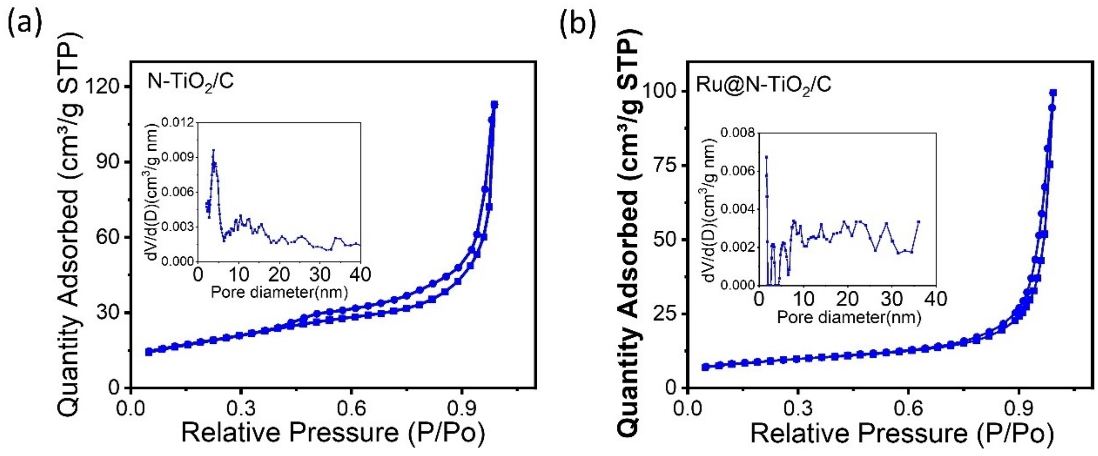

Fig. S6. Nitrogen adsorption/desorption isotherms of (a) N-TiO_2/C, (b) Ru@N-TiO_2/C composites. insert: pore size distribution of N-TiO_2/C and Ru@N-TiO_2/C composites.

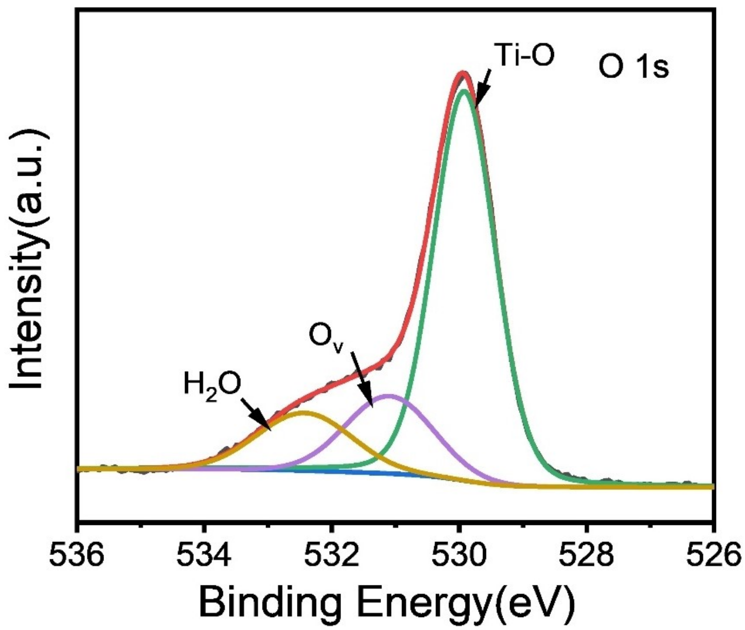

Fig. S7. High-resolution O 1s XPS spectra of Ru@N-TiO_2/C composites.

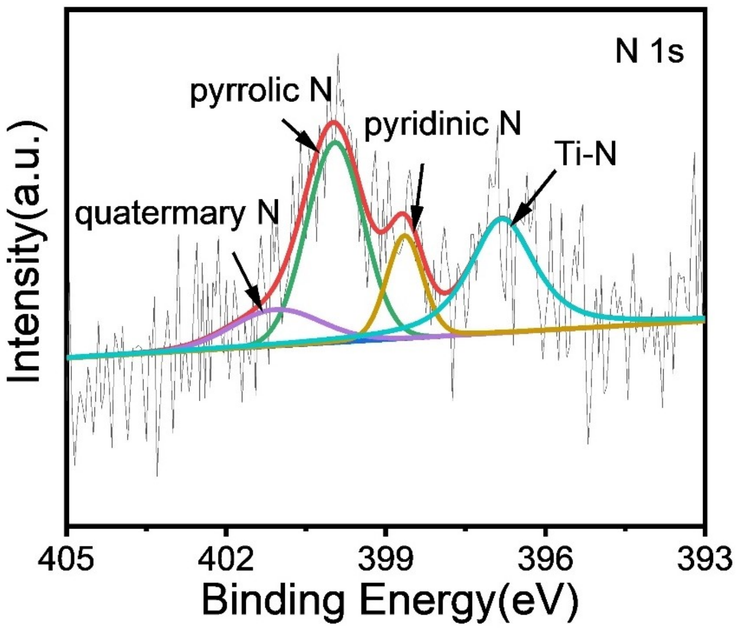

Fig. S8. High-resolution N 1s XPS spectra of Ru@N-TiO_2/C composites.

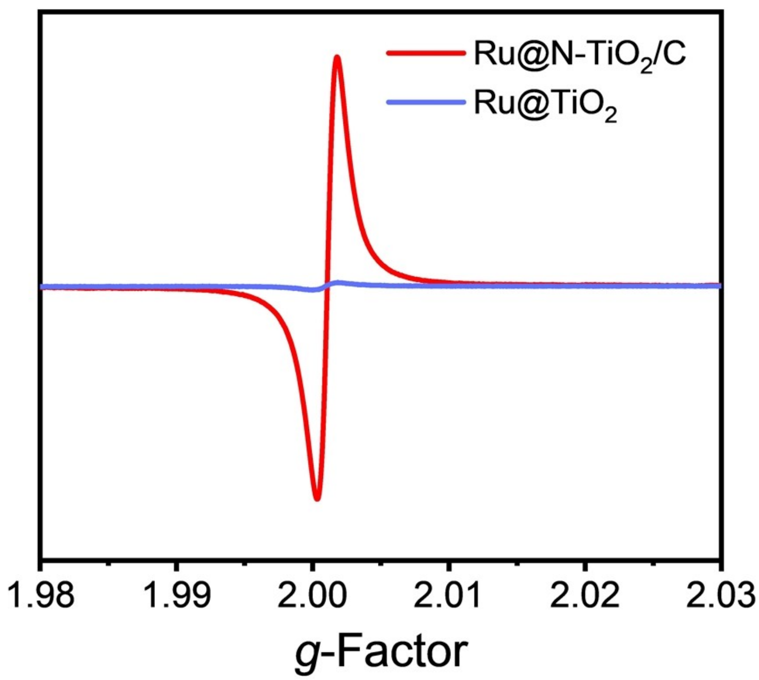

Fig. S9. EPR spectra of Ru@N-TiO_2/C and Ru@TiO_2.

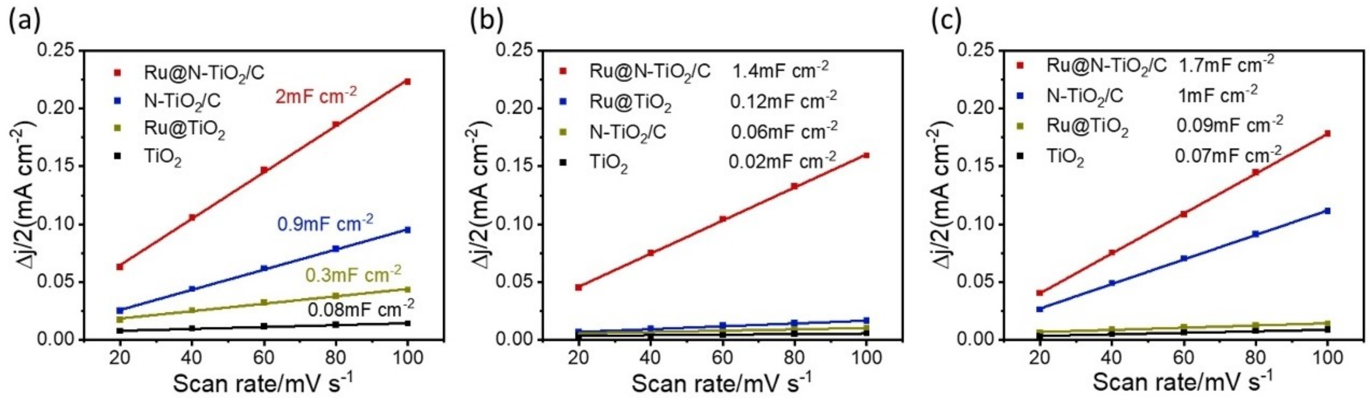

Fig. S10. Capacitive Δj/2 as a function of the scan rate for Ru@N-TiO_2/C nanospheres in (a) 1.0 M KOH, (b) 1.0 M PBS and (c) 0.5 M H_2SO_4.

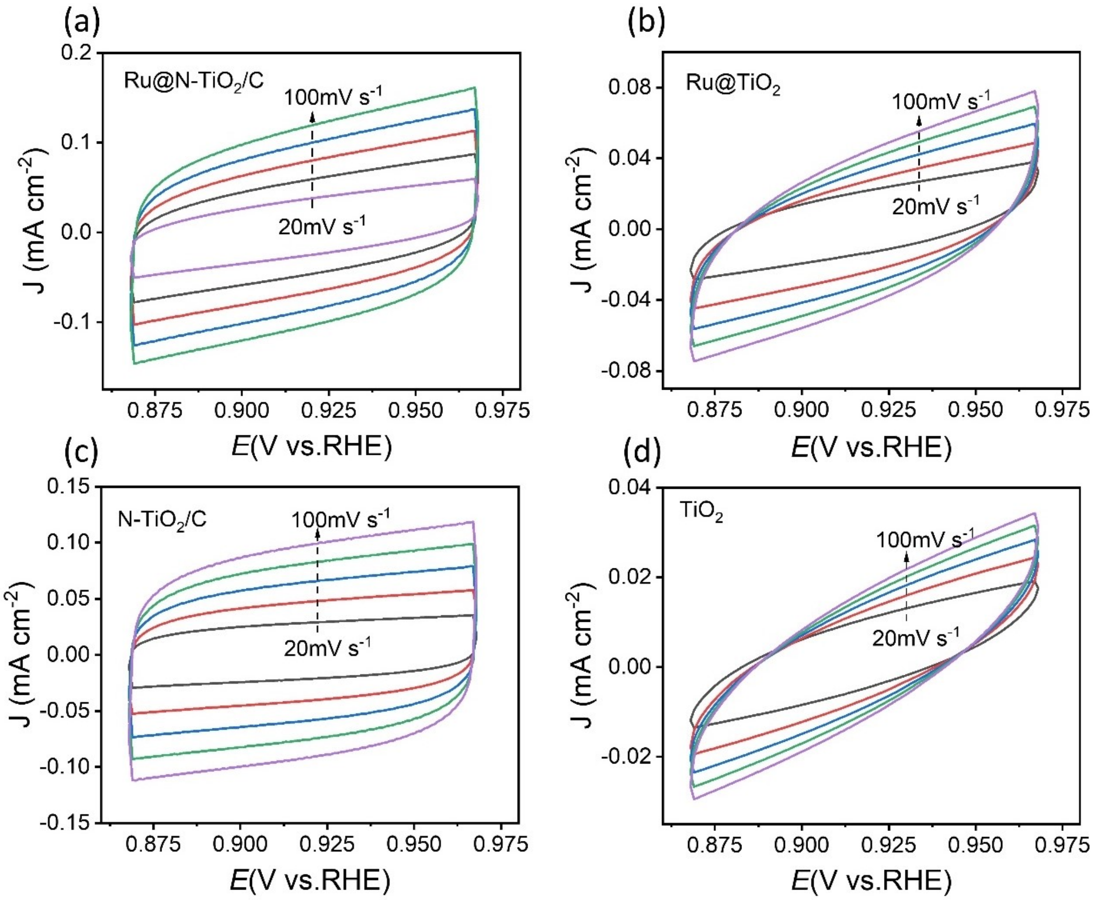

Fig. S11. Cyclic voltammetry curves of (a) Ru@N-TiO_2/C, (b) Ru@TiO_2, (c) N-TiO_2/C and (d) TiO_2, respectively. The arrow indicates the scan rate from 20 to 100 mV s^{-1}.

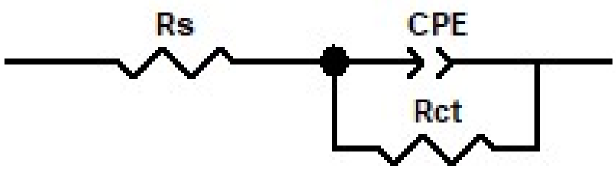

Fig. S12. Equivalent circuit model. R_{ct} and CPE represent the solution resistance, the charge transfer resistance and constant phase element, respectively.

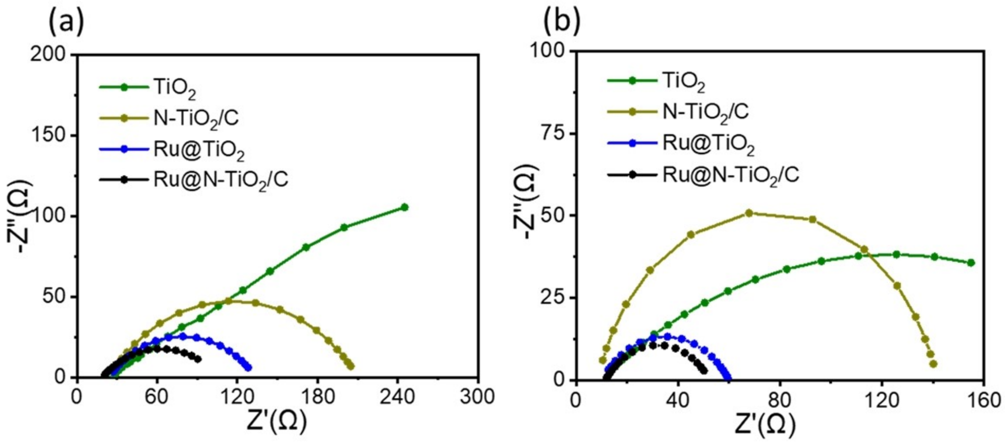

Fig. S13. Nyquist plots of Ru@N-TiO_2/C, N-TiO_2/C, Ru@TiO_2, and TiO_2 in (a) 1.0 M PBS and (b) 0.5M H_2SO_4.

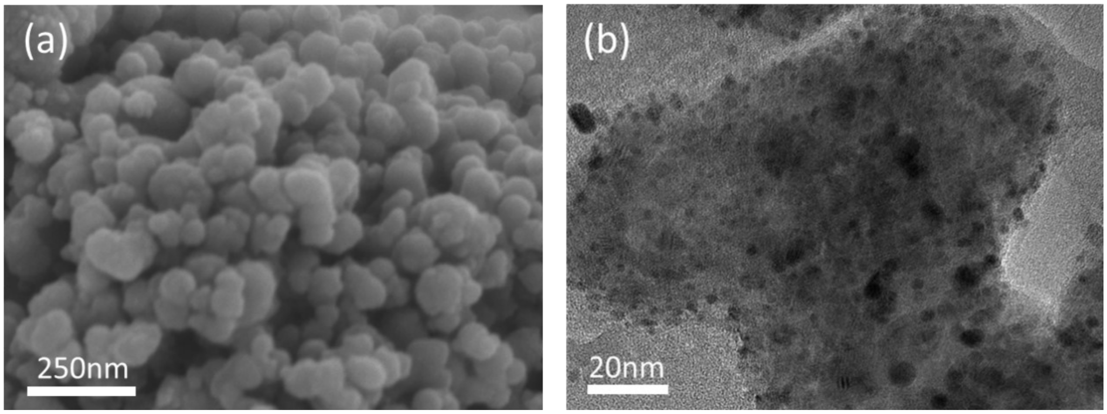

Fig. S14. (a) SEM and (b) TEM images of Ru@N-TiO_2/C nanospheres after the 1000th cycling in 1M KOH.

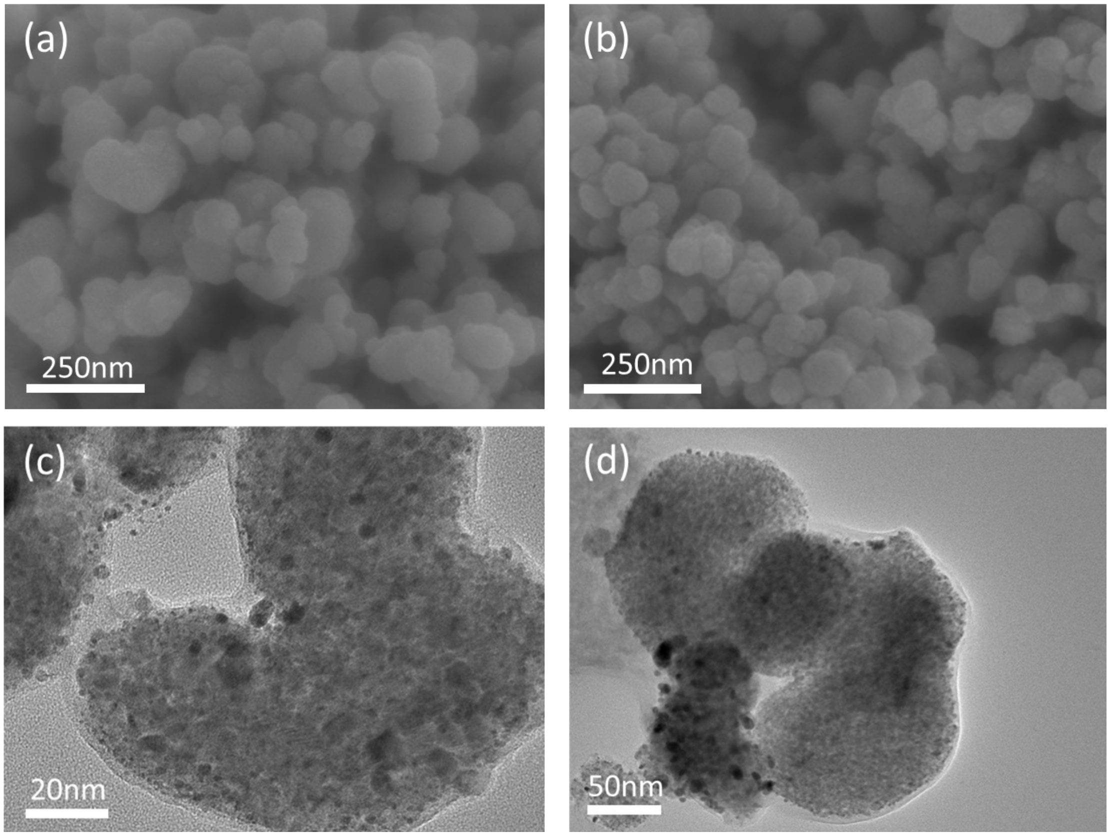

Fig. S15. (a) SEM, (c) TEM and (b) SEM, (d) TEM images of Ru@N-TiO_2/C nanospheres after the 1000th cycling in 1M PBS and 0.5M H_2SO_4, respectively.

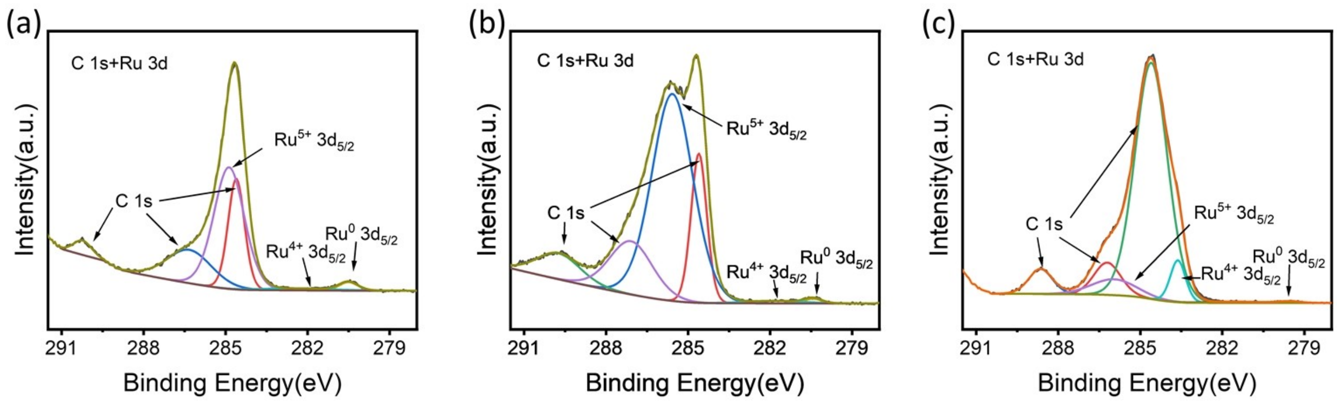

Fig. S16. High-resolution Ru 3d XPS spectra of Ru@N-TiO_2/C after stability test in (a) 1M KOH, (b) 1M PBS and (c) 0.5M H_2SO_4.

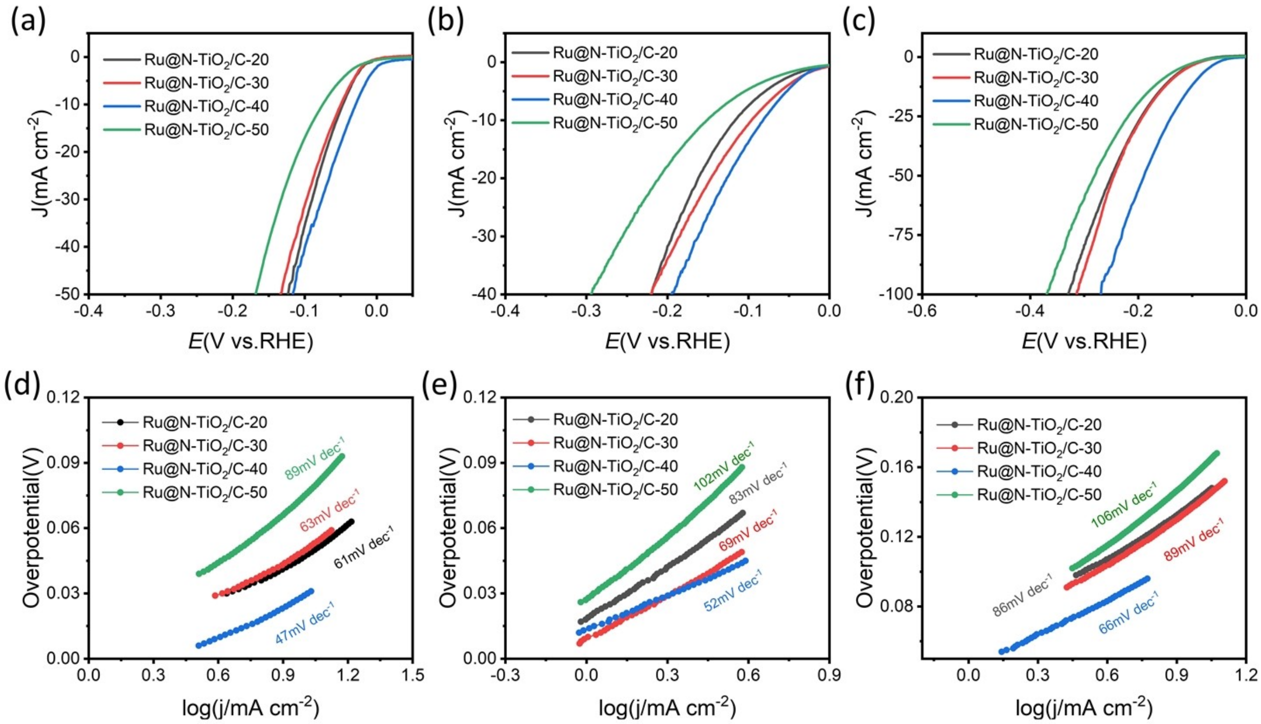

Fig. S17. LSV and Tafel plots of different loading mass Ru on Ru@N-TiO_2/C composites in (a) 1M KOH, (b) 1M PBS and (C) 0.5M H_2SO_4.

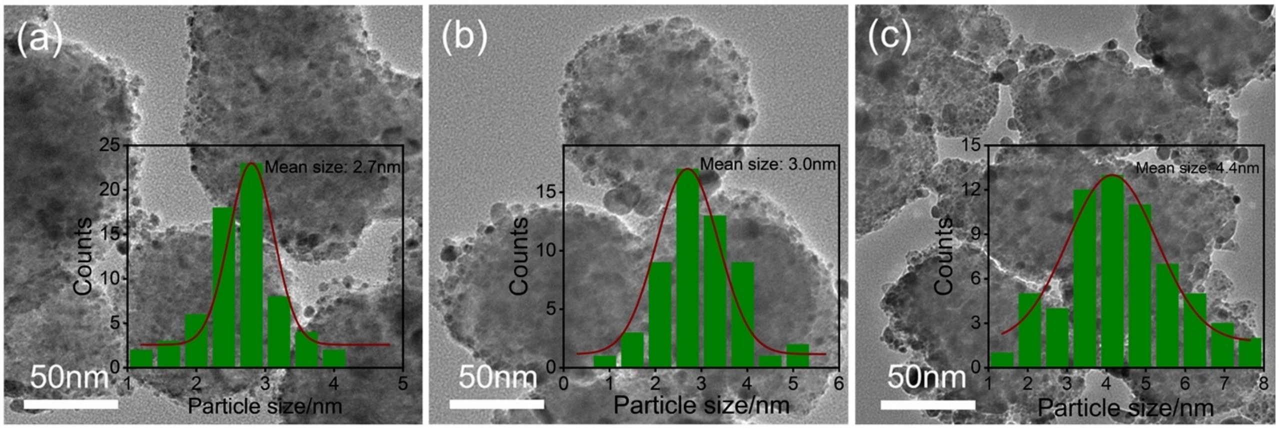

Fig. S18. TEM of different loading mass (a) Ru@N-TiO_2/C-20, (b) Ru@N-TiO_2/C-30 and (c) Ru@N-TiO_2/C-50. Inset: the corresponding size distribution of Ru.

Table S1. Summary of the recently reported HER catalysts in 1M KOH, 1.0 M PBS and 0.5 M H_2SO_4.

Catalyst	η (at 10mA cm^{-2})	Electrolyte solution	Reference
$Ru/Ni_2P@NPC$	124	1.0 M KOH	1
	132	1.0 M PBS	
	89	0.5 M H_2SO_4	
$MoP-Ru_2P/NPC$	47	1.0 M KOH	2
	126	1.0 M PBS	
	82	0.5 M H_2SO_4	
$RuP_x@NPC$	74	1.0 M KOH	3
	110	1.0 M PBS	
	51	0.5 M H_2SO_4	
CoP@BCN	215	1.0 M KOH	4
	122	1.0 M PBS	
	87	0.5 M H_2SO_4	
$Rh_{50}Ru_{50}@UiO-66-NH_2$	177	1.0 M KOH	5
	114	1.0 M PBS	
	77	0.5 M H_2SO_4	
CoRu@NG-3	62	1.0 M KOH	6
	88	1.0 M PBS	
	52	0.5 M H_2SO_4	
Ru@WNO-C	24	1.0 M KOH	7
	358	1.0 M PBS	
	172	0.5 M H_2SO_4	

Ni_2P@NC/NF	84	1.0 M KOH	8
	155	1.0 M PBS	
	68	0.5 M H_2SO_4	
W/BrN	94	1.0 M KOH	9
	190	1.0 M PBS	
	148	0.5 M H_2SO_4	
Ru@N-TiO_2/C	39	1.0 M KOH	This work
	86	1.0 M PBS	
	116	0.5 M H_2SO_4	

Table S2. Elemental values of simulated equivalent circuit for Ru@N-TiO_2/C, Ru@TiO_2, N-TiO_2/C and TiO_2 in alkaline, neutral, and acidic media.

	1M KOH		1M PBS		0.5M H_2SO_4	
	$R_s(\Omega)$	$R_{ct}(\Omega)$	$R_s(\Omega)$	$R_{ct}(\Omega)$	$R_s(\Omega)$	$R_{ct}(\Omega)$
Ru@N-TiO_2/C	10.45	52.41	19.11	87.15	11.52	40.97
Ru@TiO_2	5.579	163.9	27.96	160.3	10.23	49.75
N-TiO_2/C	8.958	194.8	23.84	186.2	8.284	138.4
TiO_2	8.034	420.1	23.54	1092	9.278	229.1

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