Supporting Information

Ruthenium Triazine Composite: A Good Match for Increasing Hydrogen Evolution Activity through Contact Electrification

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Experimental

Synthesis of Ru/triNC.

Typically, triNC is synthesized using an ionothermal method. 2.0 g tetracyanoquinodimethane (TCNQ, 0.1 mol) is mixed well with 6.7 g $ZnCl_2$ (0.5 mol) by grinding for 1 h using a mortar with a pestle until the mixture is rendered in a viscous state. The mixture is placed in a crucible and heated at 400 °C for 20 h under Ar to form CTF. After that, the CTF is directly carbonized at 700 °C for 4 h. After cooling, the black solid is collected and ground into powder. Then it is washed with 0.1 M HCl for 6 h to remove residual $ZnCl_2$; subsequently washing is done using deionized water and methanol several times. The sample is then dried at 60 °C overnight. The resulting black powder is named as triNC.

To load Ru, 0.1 g triNC is dispersed in 10 mL deionized water by ultrasonication for 1 h. After adding 1 mL Ru^{3+} solution at a concentration of 10 mg mL^{-1} into the above suspension, stirring is carried out for 1 h. This is followed by addition of 20 mL deionized water and 20 mL methanol. After evaporating solvent at 60 °C, the powder is heated at 900 °C for 2 h to reduce Ru in Ar. After cooling, the resulting powder is labeled as Ru/triNC. Ru/triNC800 and Ru/triNC1000 are synthesized using the same procedure except for changing thermal-reduction temperatures (800°C/1000°C). Ru/triNC1, Ru/triNC5 and Ru/triNC20 is synthesized using the same process as Ru/triNC, except that volume of Ru solution added is changed (0.1 mL/0.5 mL/2 mL).

Synthesis of NC, Ru/C, Ru/NC, and Pt/triNC

To synthesize N-doped Ketjen black (NC), 50 mg Ketjen black (C) was washed with 100 mL concentrated nitric acid for 10 h at 90 °C. After that excess aqueous ammonium hydroxide was added until pH reached 14. The dispersion went through a hydrothermal treatment at 180 °C for 8 h. Final product was washed with water, gathered by vacuum filtration, and dried at 60 °C overnight. Synthesis of Ru/C and Ru/NC reference materials is similar to Ru/triNC,

except for using C or NC as the support. For Pt/triNC and Rh/triNC, we used chloroplatinic acid solution and rhodium chloride solution with concentration of metal ions of 10 mg mL^{-1} instead of ruthenium chloride solution. Other process follows the synthesis of Ru/triNC mentioned above.

Electrochemical measurements. Electrochemical performance is tested using a three electrode system on a potentiostat (CHI 760C) at room temperature. The catalyst-modified glassy carbon (GC) electrode (geometric area: 0.19625 cm^2), graphite rod and saturated calomel electrode (SCE) are used as a working electrode, counter electrode (CE) and reference electrode, respectively. For preparation of catalyst ink, 5 mg catalyst is dispersed into 0.5 mL water and 0.5 mL methanol containing 20 μL 5 wt% Nafion solution. The ink is treated under ultrasonication for 1 h before test. For preparation of working electrode, 20 μL of catalyst ink is dropped on the GC electrode rotating disk electrode. The corresponding catalyst loading amount is 0.1 mg. 1M KOH solution and 0.5M H_2SO_4 solution are used as electrolyte for alkaline and acidic condition measurement, respectively. The scan rate for LSV curve is 2 mV s^{-1} and all LSV curves are corrected using the i-R compensation (the specific percentage of the correction is 90%).

Electrocatalytic hydrogen evolution process in alkaline and acidic solutions

Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are two fundamental reactions in the water splitting process. HER takes the following paths in acidic or alkaline solutions:

Volmer step:

$$H^+ + e^- + * = *H \text{ (acid)} \quad (1)$$

$$H_2O + e^- + * = *H + OH^- \text{(alkaline)} \quad (2)$$

Tafel step:

$* H + * H = H_2$

(3)

Heyrovsky step:

$H^+ + e^- + * H = H_2(acid)$ (4)

$H_2O + e^- + * H = H_2 + OH^-$ (alkaline) (5)

In the above equations, $*$ denotes an active site on surface.

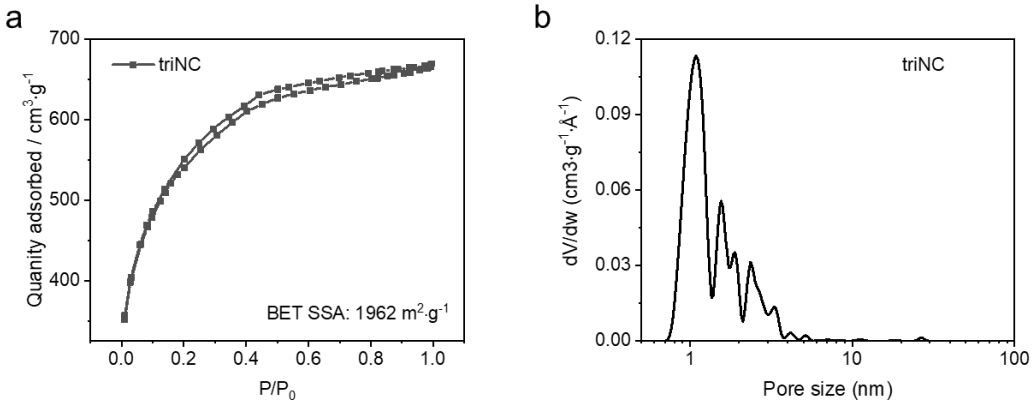
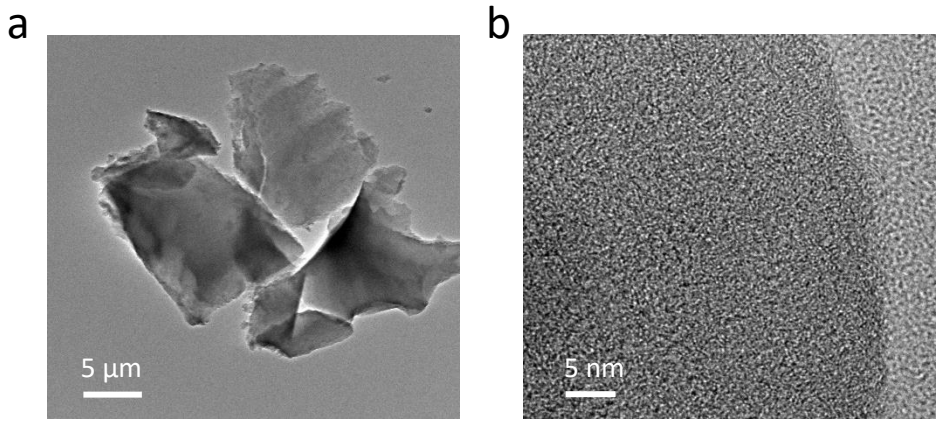


Figure S1. Nitrogen adsorption-desorption measurement of triNC. (a) Nitrogen adsorption-desorption isotherms. (b) Pore size distribution profile from NLDFT calculation.

Figure S2. (a) TEM image and (b) HRTEM image of triNC.



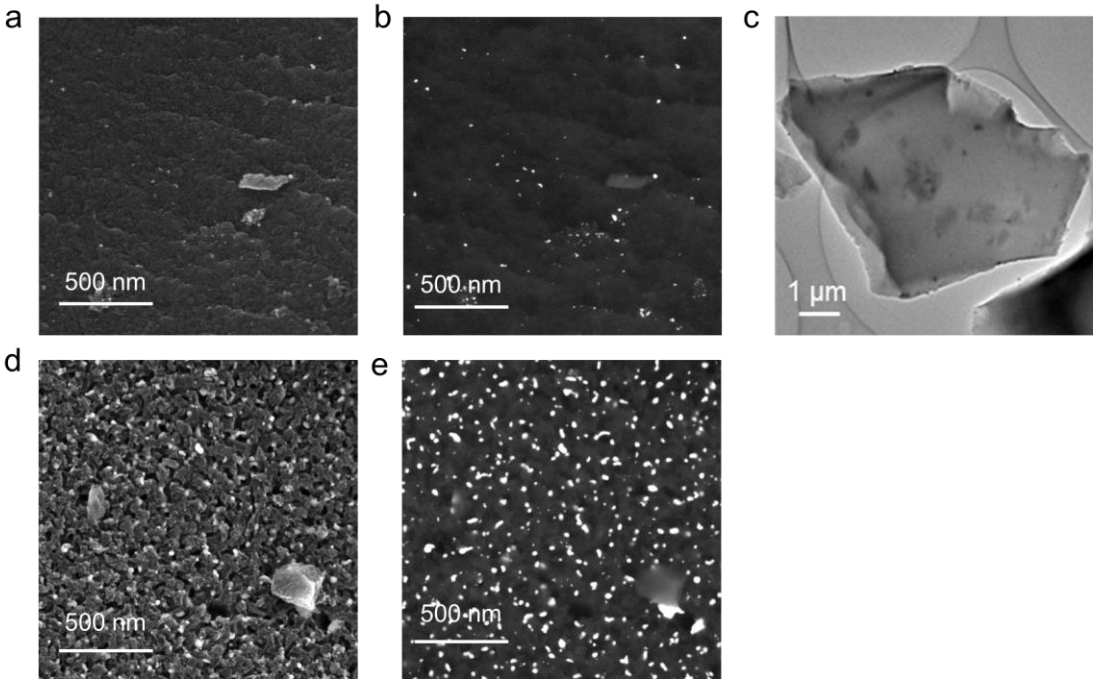


Figure S3. (a) Secondary electron image, (b) the corresponding back scattering electron image and (c) Low-magnification TEM image of Ru/triNC. (d) Secondary electron image and (e) the corresponding back scattering electron image of Ru/triNC20.

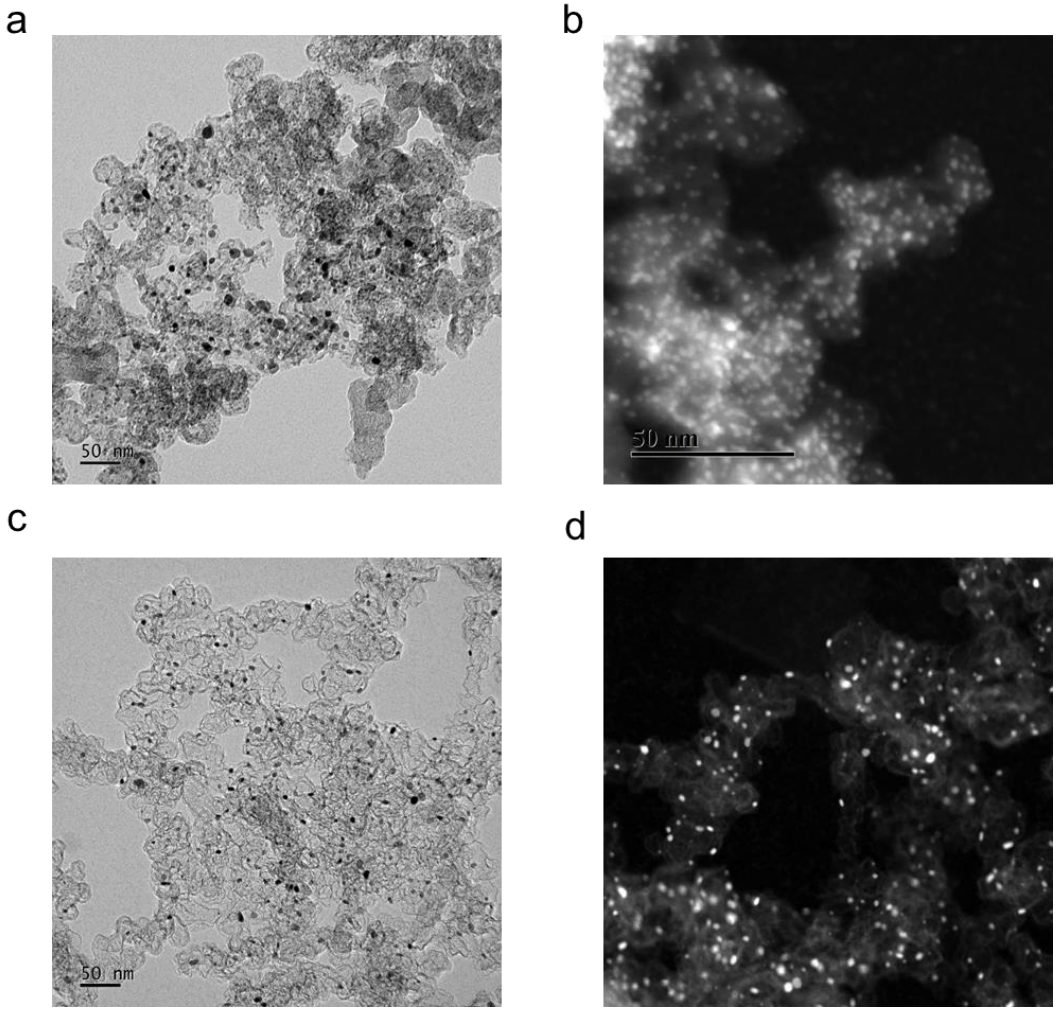


Figure S4. TEM and corresponding HADDF-STEM images of (a, b) Ru/C and (c, d) Ru/NC.

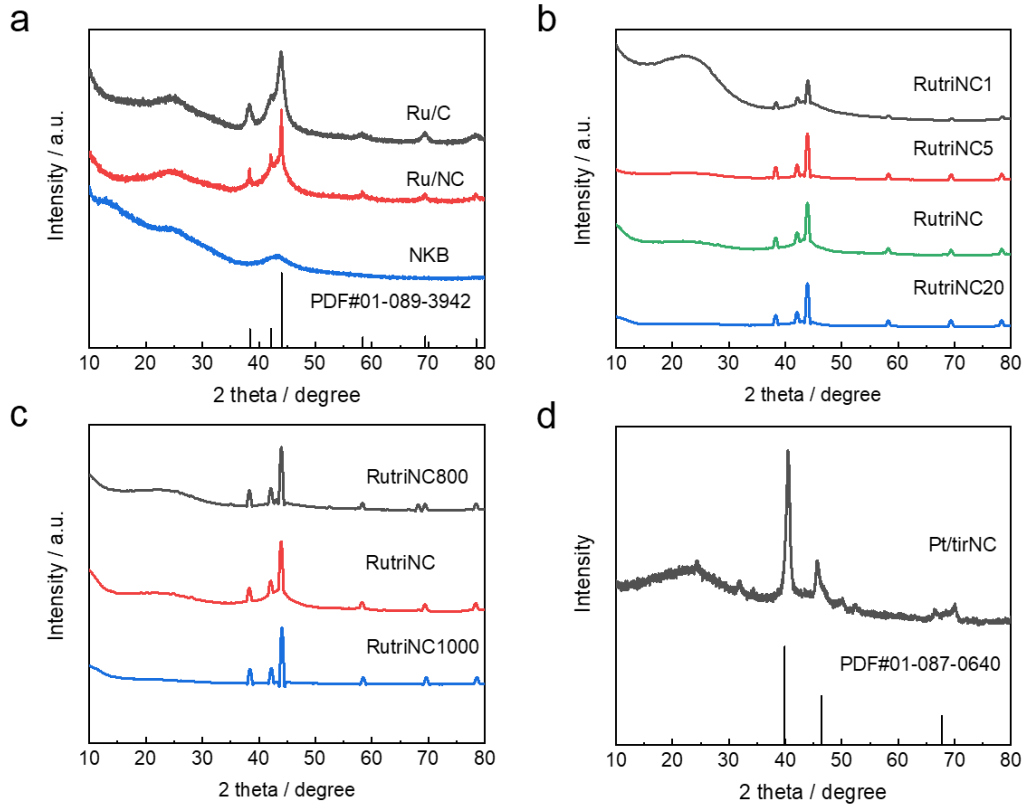


Figure S5. XRD patterns of (a) Ru/C, Ru/NC and N-doped Ketjen black (NC). (b) Ru/triNC1, Ru/triNC5, Ru/triNC and Ru/triNC20. (c) Ru/triNC800, Ru/triNC and Ru/triNC1000. (d) Pt/triNC.

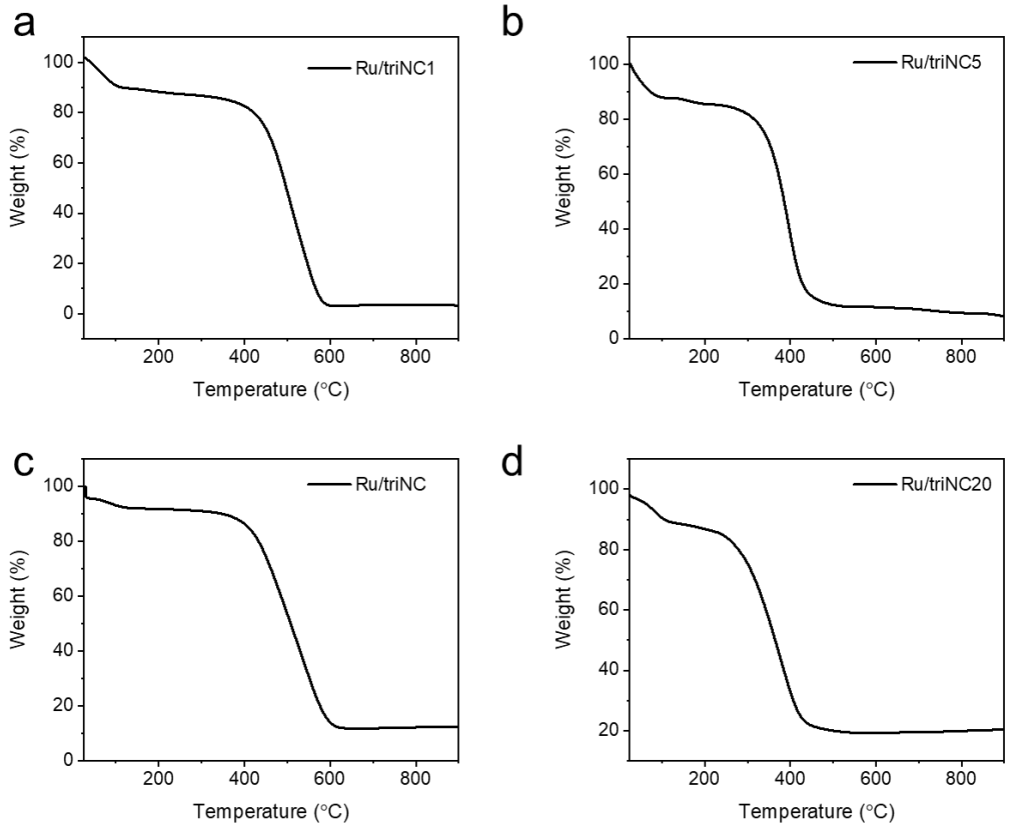


Figure S6. TG curves of (a) Ru/triNC1, (b) Ru/triNC5, (c) Ru/triNC and (d) Ru/triNC20.

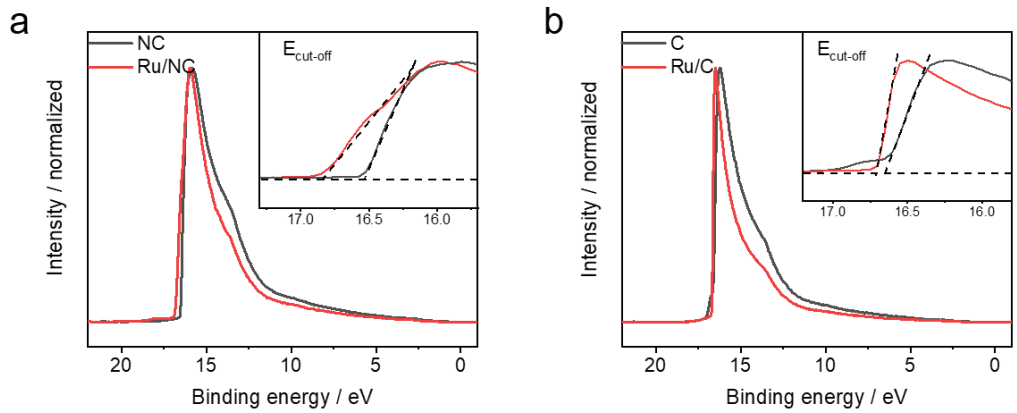


Figure S7. UPS spectra of C and NC before and after Ru loading.

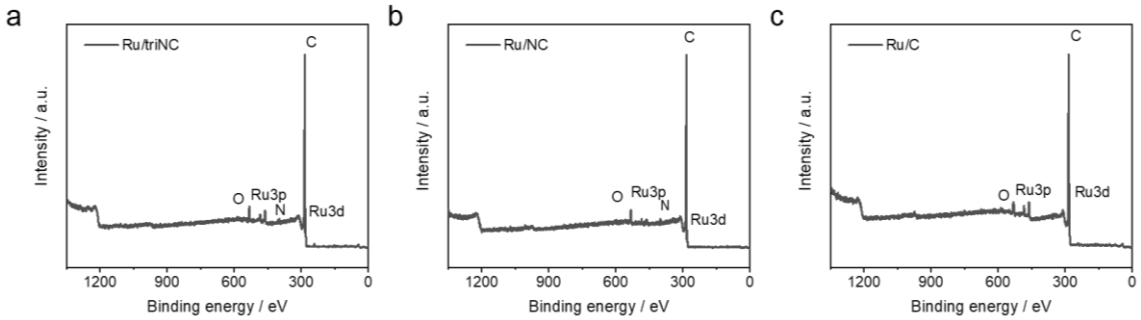


Figure S8. XPS spectra of (a) Ru/triNC, (b) Ru/NC, and (c) Ru/C.

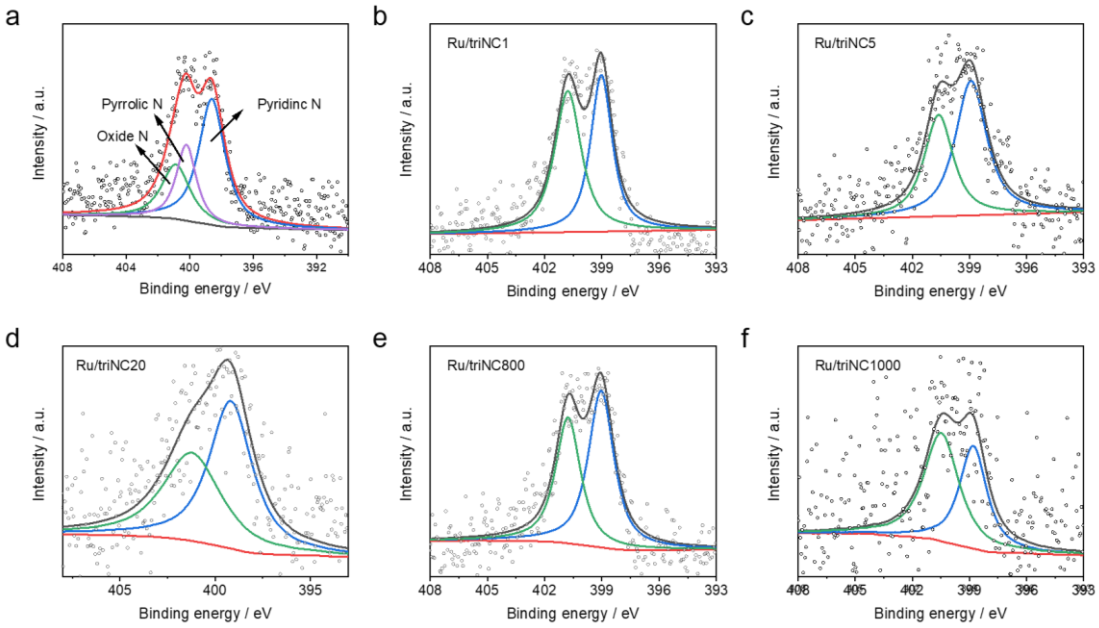


Figure S9. XPS spectra of N1s of Ru/NC and Ru/triNC with different annealing temperature and Ru loading amounts.

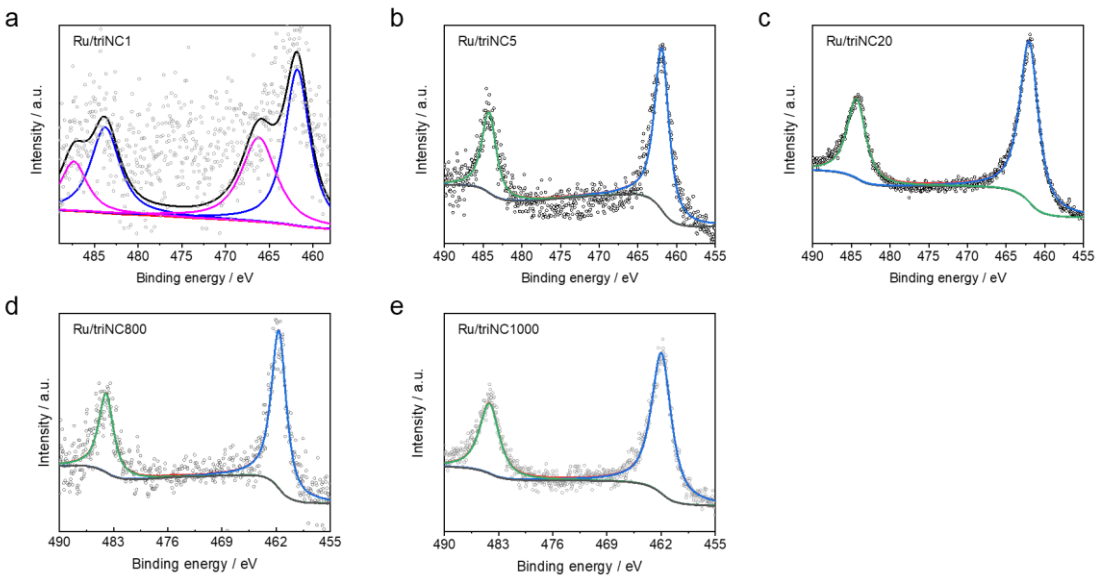


Figure S10. XPS spectra of Ru 3p of Ru/triNC with different annealing temperatures and Ru loading amounts.

As shown in Figure S10, Ru/triNC1 reveals a different peak pattern compared with other samples. Ru shows two peaks at higher binding energy which is corresponding to Ru^{4+}, even this spectrum was obtained after Ar etching to remove surface oxide. Due to low loading amount and high dispersion, Ru cannot reach a good degree of crystallinity and its oxidation degree is much higher than other samples.

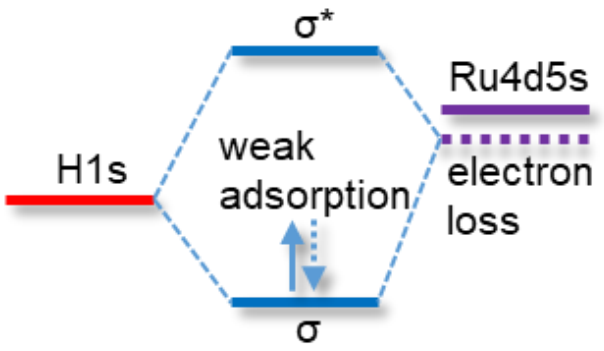


Figure S11. Illustration of hydrogen bonding adjustment in Ru surface by contact electrification and charge transfer process.

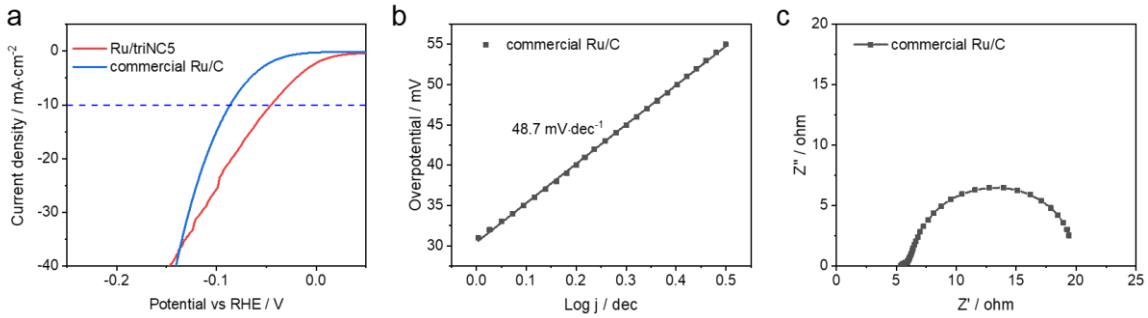


Figure S12. Comparison of HER catalytic activities of commercial Ru/C (5 wt%) and Ru/triNC5 in 1 M KOH solution.

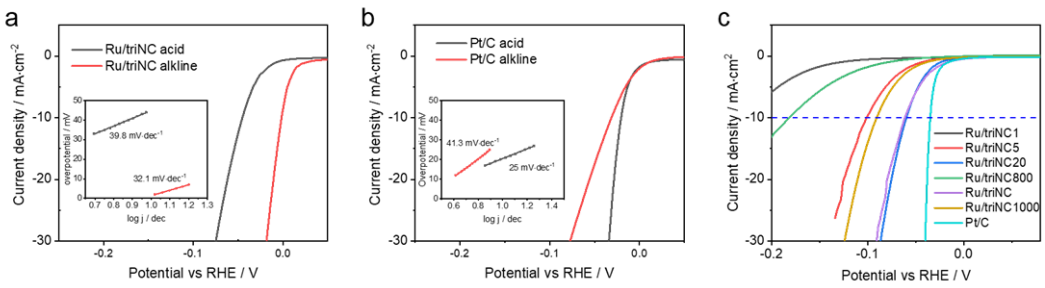


Figure S13. (a-b) Comparison of HER catalytic activities in acid (0.5 M H_2SO_4) and alkaline (1 M KOH) condition. Insert graph is the corresponding Tafel slope. (c) LSV curves of all samples in acidic condition.

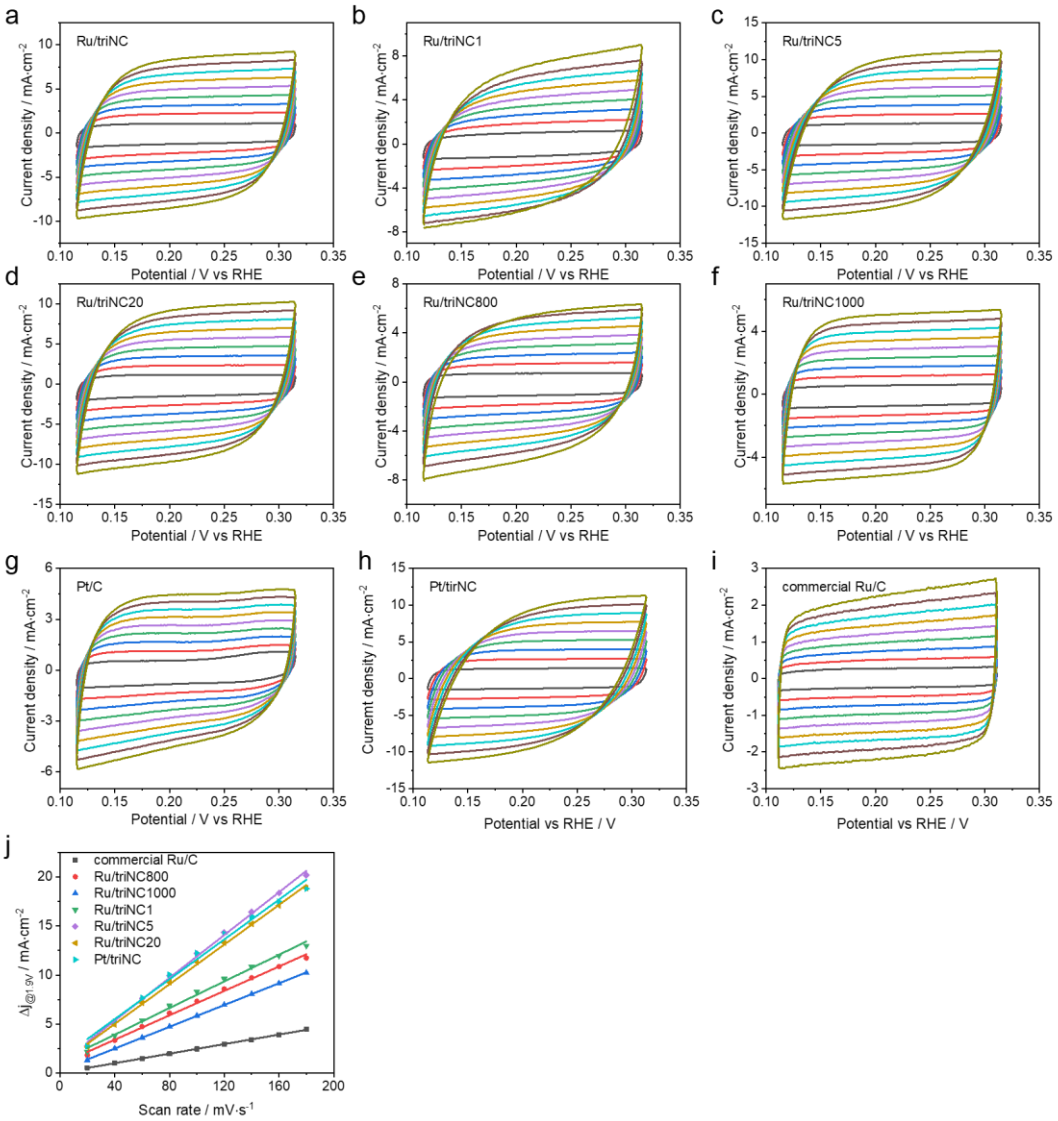


Figure S14. ECSA measurements. CV scan at different scan rate (from 20 to 180 mV s^{-1}) of (a) Ru/triNC, (b) Ru/triNC1, (c) Ru/triNC5, (d) Ru/triNC20, (e) Ru/triNC800, (f) Ru/triNC1000, (g) Pt/C, (h) Pt/triNC, (i) commercial Ru/C and (j) corresponding C_{dl}.

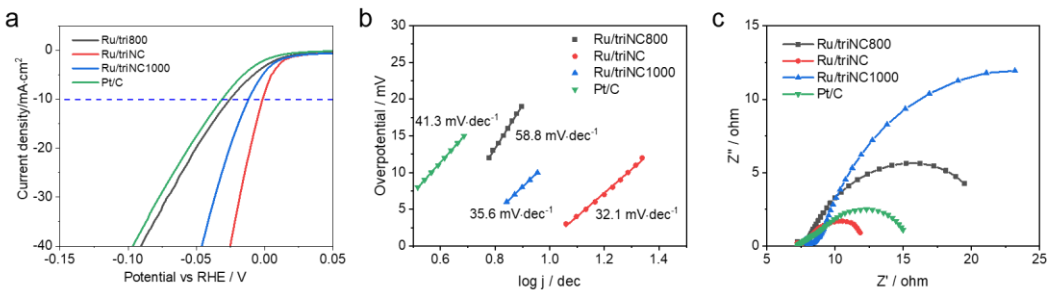


Figure S15. Comparison of HER catalytic activities of different Ru/triNC samples with different annealing temperatures.

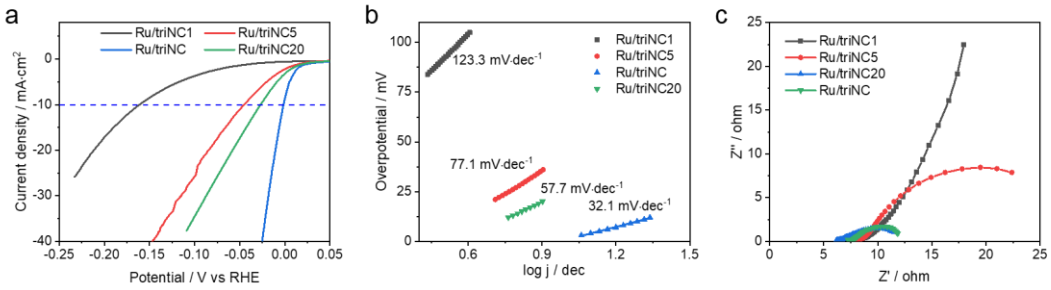


Figure S16. Comparison of HER catalytic activities of Ru/triNC with different Ru loading amounts.

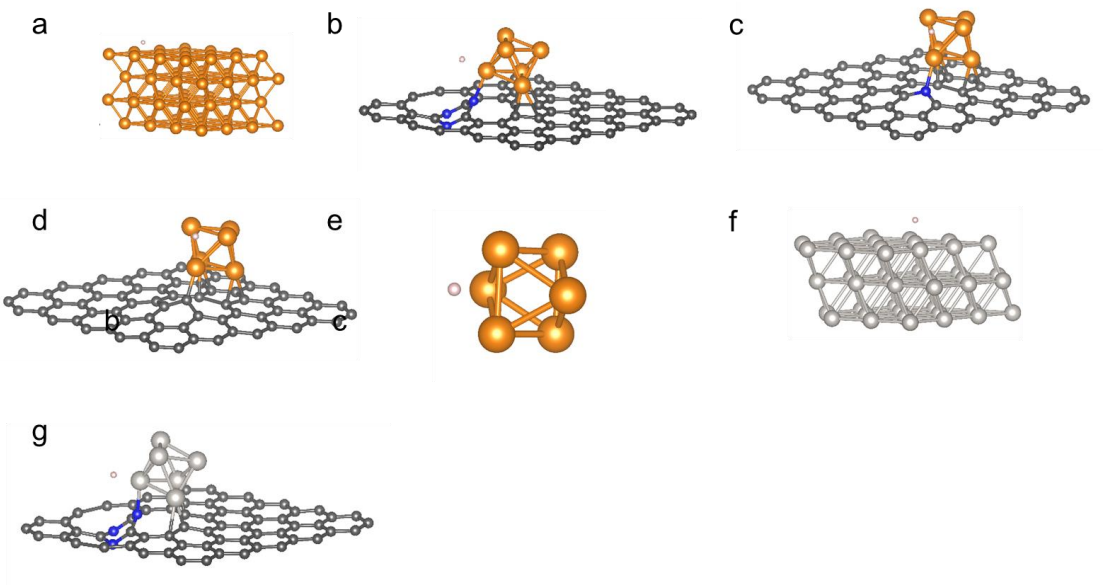


Figure S17. Structure models of hydrogen adsorption for (a) Ru (001), (b) Ru/triNC, (c) Ru/NC, (d) Ru/C (e) Ru cluster, (f) Pt (111) and (g) Pt/triNC (after structure relaxation). Orange, silver, grey, blue and white sphere are corresponding to Ru, Pt, C, N and H atoms, respectively.

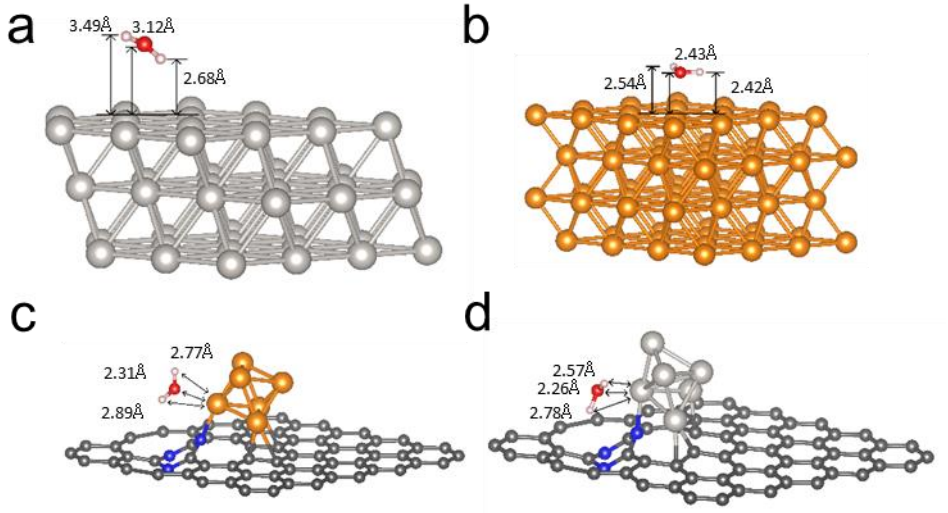


Figure S18. Structure models of water adsorption for (a) Ru (001), (b) Pt (111), (c) Pt/triNC, (d) Ru/triNC Orange, silver, grey, blue and white sphere are corresponding to Ru, Pt, C, N and H atoms, respectively. The number in the graph represent the corresponding atomic distance.

Table S1. Nitrogen content (at%) and triazine doped occupancy of Ru/triNC with different annealing temperature and Ru loading amount.

	Ru/triNC1	Ru/triNC5	Ru/triNC20	Ru/triNC800	Ru/triNC	Ru/triNC1000	triNC
N content at%	2.39	1.63	1.24	2.03	1.32	1	5.2
Trazine content at%	48	59	55	56	47	43	55

Table S2. Calculated work functions of C, NC and triNC and corresponding Fermi levels and vacuum levels.

	E_f	E_{vac}	Work function	Work function experimental
C	-2.24 eV	2.02 eV	4.26 eV	4.52 eV
NC	-2.76 eV	1.98 eV	4.74 eV	4.70 eV
triNC	-3.06 eV	1.89 eV	4.95 eV	5.01 eV

Table S3. C_{dl} of Ru/triNC, Ru/triNC800, Ru/triNC1000, Ru/triNC1, Ru/triNC5, Ru/triNC20, and Pt/triNC.

Sample	C_{dl} / mF cm^{-2}
Ru/triNC	89.9
Ru/triNC800	62.3
Ru/triNC1000	55.6
Ru/triNC1	68.3
Ru/triNC5	109.3
Ru/triNC20	101.3
Pt/triNC	101.7
Commercial Ru/C	24.3

Table S4. Comparison of HER catalytic performance for some typical HER electrocatalyst works based on Ru. Ru content, overpotential at 10 mA cm^{-2} and Tafel slope were compared.

Catalyst	Ru content/wt%	Overpotential@10 $mA \cdot cm^{-2}$/mV	Tafel slope/$mV \cdot dec^{-1}$	Reference
Ru/CQD	-	10	47	Adv. Mater. 2018, 30, 1800676
Ru-NC	-	27.5	34	ACS Catal. 2018, 8, 5714-5720
Ru/CoP	40	23	31	Energy Environ. Sci., 2018, 11, 1819-1827
Ru/C_2N	28.7	17	38	Nature Nanotech., 2017, 12, 441-446
$Ru/C_3N_4/C$*	20	79	69	J. Am. Chem. Soc. 2016, 138, 16174
Co-doped Ru	-	13	29	Nature Communications, 2018, 9, 4958
Ru/NC(0.2)	2	26	36	Angew. Chem. Int. Ed., 2018, 57, 5848-5852

RuSi	-	19	28.9	Angew. Chem. Int. Ed., 2019, 58, 11409-11413
Ni/NiP-Ru	-	31	41	J. Am. Chem. Soc., 2018, 140, 2731-2734
Ru/triNC	**10**	**2**	**32.1**	**This work**

* denoting that the HER measurement was conducted in 0.1 M KOH while that of other works were conducted in 1 M KOH.