

Supporting information

Optimizing the Hydrogen Adsorption Strength on Interfacial Ru sites with WN for High-Efficiency Hydrogen Evolution

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1. Calculation of the total turnover frequency (TOF):

The TOF (in s^{-1}) reported in this work is an apparent TOF value based on the number of metal atoms in catalyst, which was calculated with the following equation:

$$TOF = I/2NF$$

I: current (A) during the linear sweep voltammetry (LSV) tests in 1 M KOH

N: Number of active sites (in mol)

F: Faraday constant (96485.3 C/mol)

The factor 1/2 arrives by taking into account that two electrons are required to form one hydrogen molecule from two protons. The CV measurements of the freshly prepared Ru NP-WN/CC and Pt/C electrodes were carried out in PBS electrolyte (pH 7) to quantify the number of active sites. Assuming a one-electron redox process, the number of active sites (n) of these catalysts was calculated from the following equation: $n = Q/2F$, where F and Q are the Faraday constant and the whole charge of the CV curve, respectively. The factor 1/2 arrives by taking into account that two electrons are required to form one hydrogen molecule from two protons.

2. Calculations:

The present first principle DFT calculations are performed by Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method. The exchange-functional is treated using the generalized gradient approximation (GGA) of Perdew-Burke-Emzerhof (PBE) functional. The energy cutoff for the plane wave basis expansion was set to 450 eV and the force on each atom less than 0.05 eV/Å was set for convergence criterion of geometry relaxation. Grimme's DFT-D3 methodology was used to describe the dispersion interactions. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The Brillouin zone was sampled with Monkhorst mesh $2 \times 2 \times 1$ through all the computational process. The self-consistent calculations apply a convergence energy threshold of 10^{-5} eV. A 15 Å vacuum space was added to avoid the interaction between the two neighboring images.

The free energy (ΔG) on those catalysts was defined as

$$\Delta G = E_{DFT} + E_{ZPE} - T \times S$$

where E_{DFT} , E_{ZPE} , T and S are the calculation total energy of intermediate on catalysts surface, the zero-point energy, temperature and entropy.



Fig. S1 XRD pattern of WO₃ Precursor

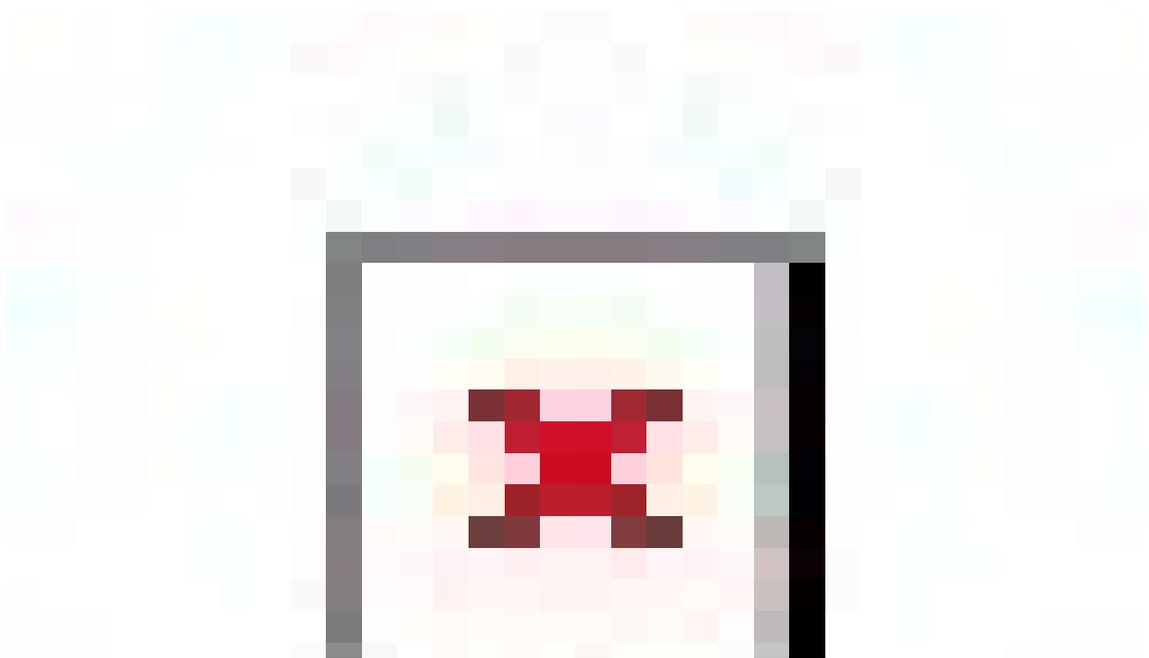


Fig. S2 SEM images of WO₃ precursor.

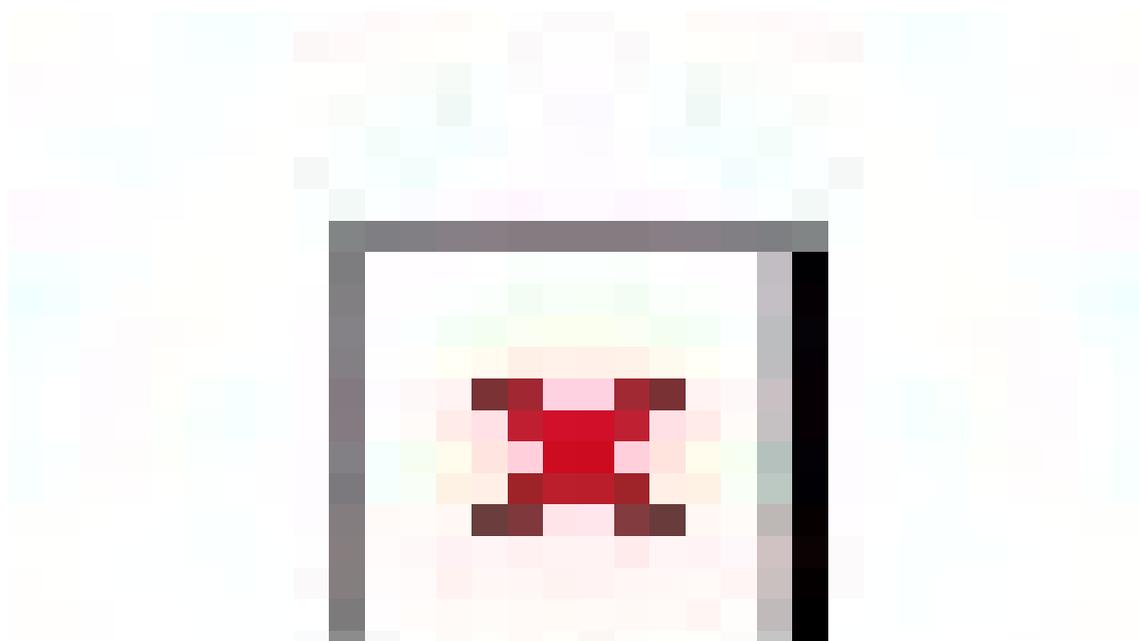


Fig. S3 (a, b) SEM images of WN/CC, and corresponding element mapping of (c) W, (d) N.

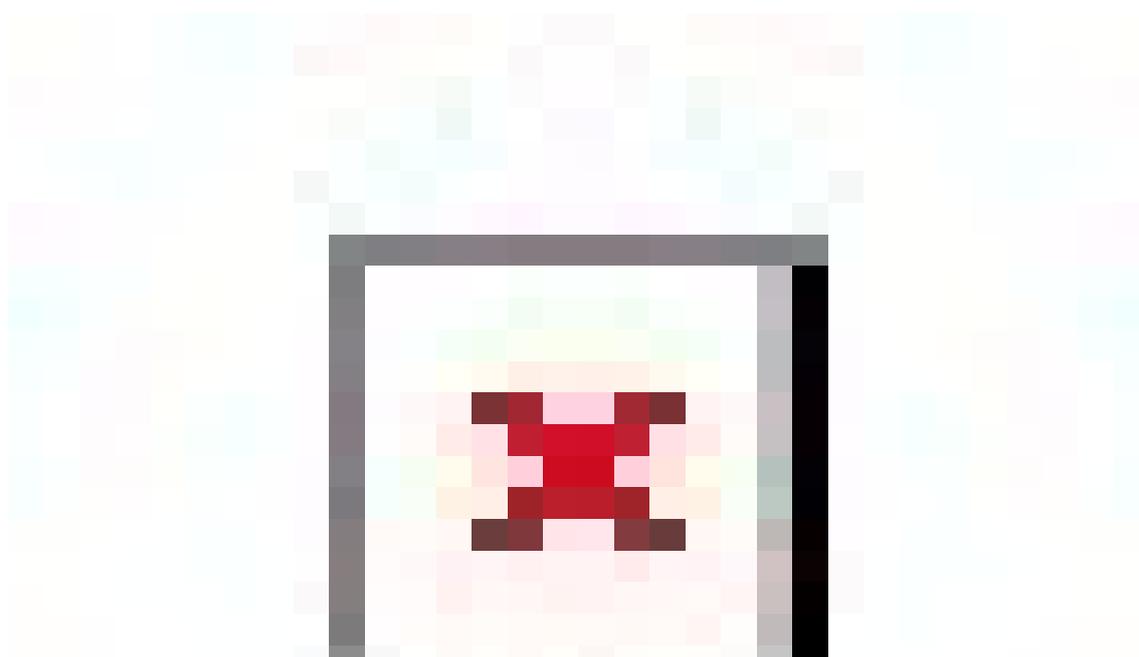


Fig. S4 (a, d) HR-TEM images of WN/CC, and (b, c) corresponding elemental distribution maps of N and W.

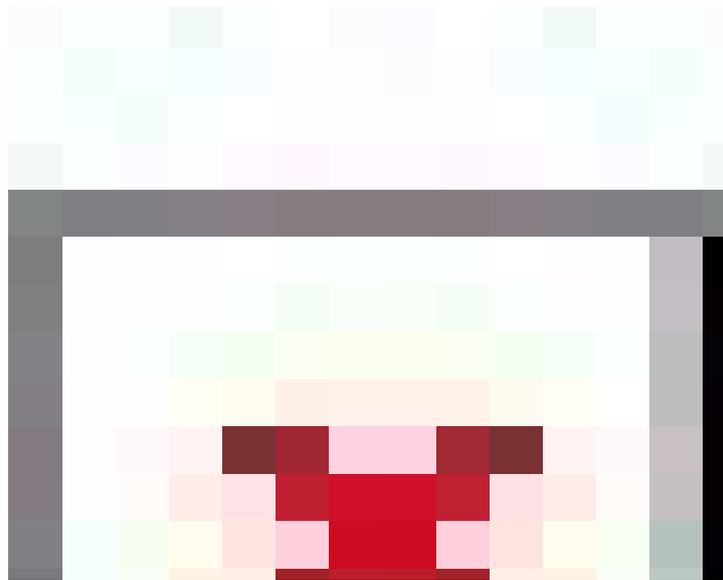


Fig. S5 XPS survey scan spectra of the WN/CC

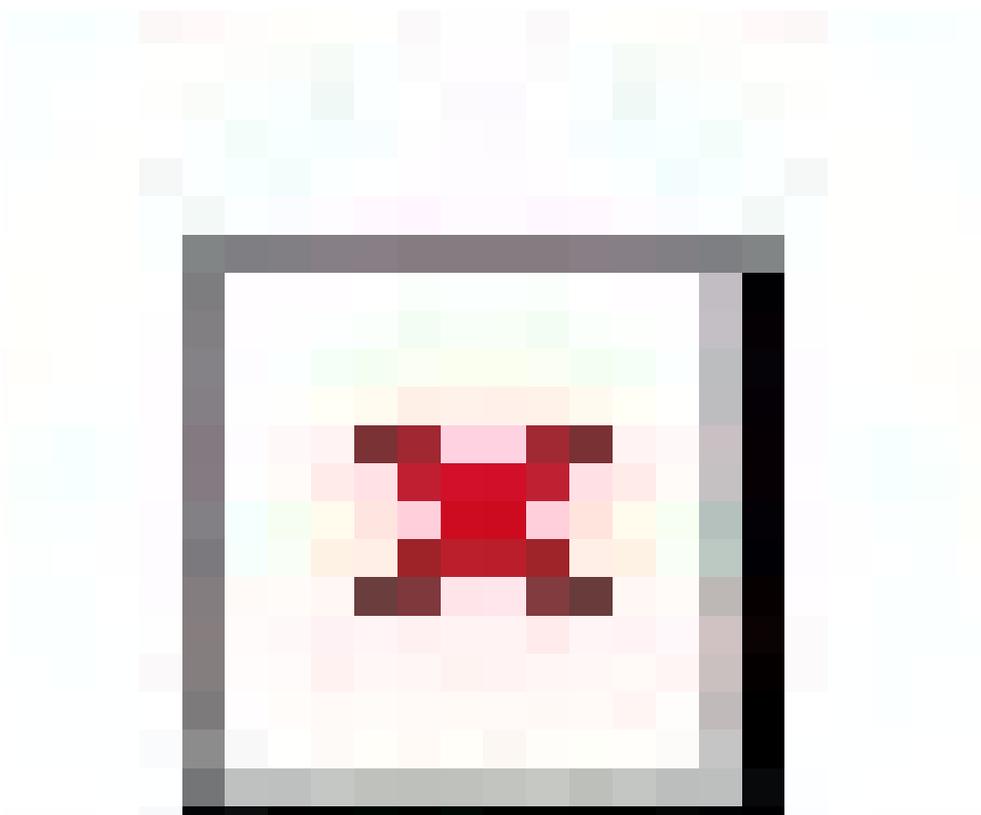


Fig. S6 (a) The exchange current densities of Ru NP-WN/CC, Pt/C and Ru/C. Cyclic voltammetry curves at different scan rates (mV s^{-1}) for (b) WN/CC, (c) Ru NP-WN/CC. (d) The current density differences vs. scan rates and corresponding yielded C_{dl} .



Fig. S7 SEM images of Ru NP-WN/CC after durability test.

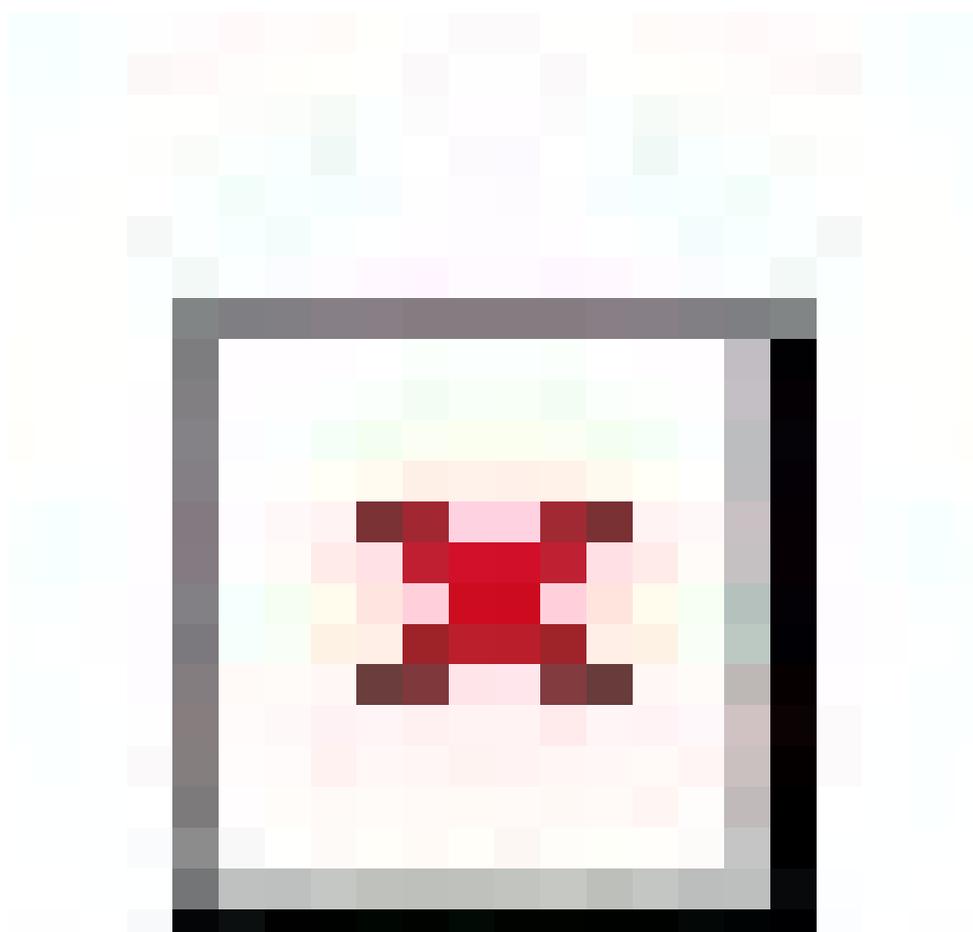


Fig. S8 XPS spectra of the Ru NP-WN/CC after stability test: (a) Survey scan spectrum, (b) N 1s, (c) Ru 3p, (d) W 4f.

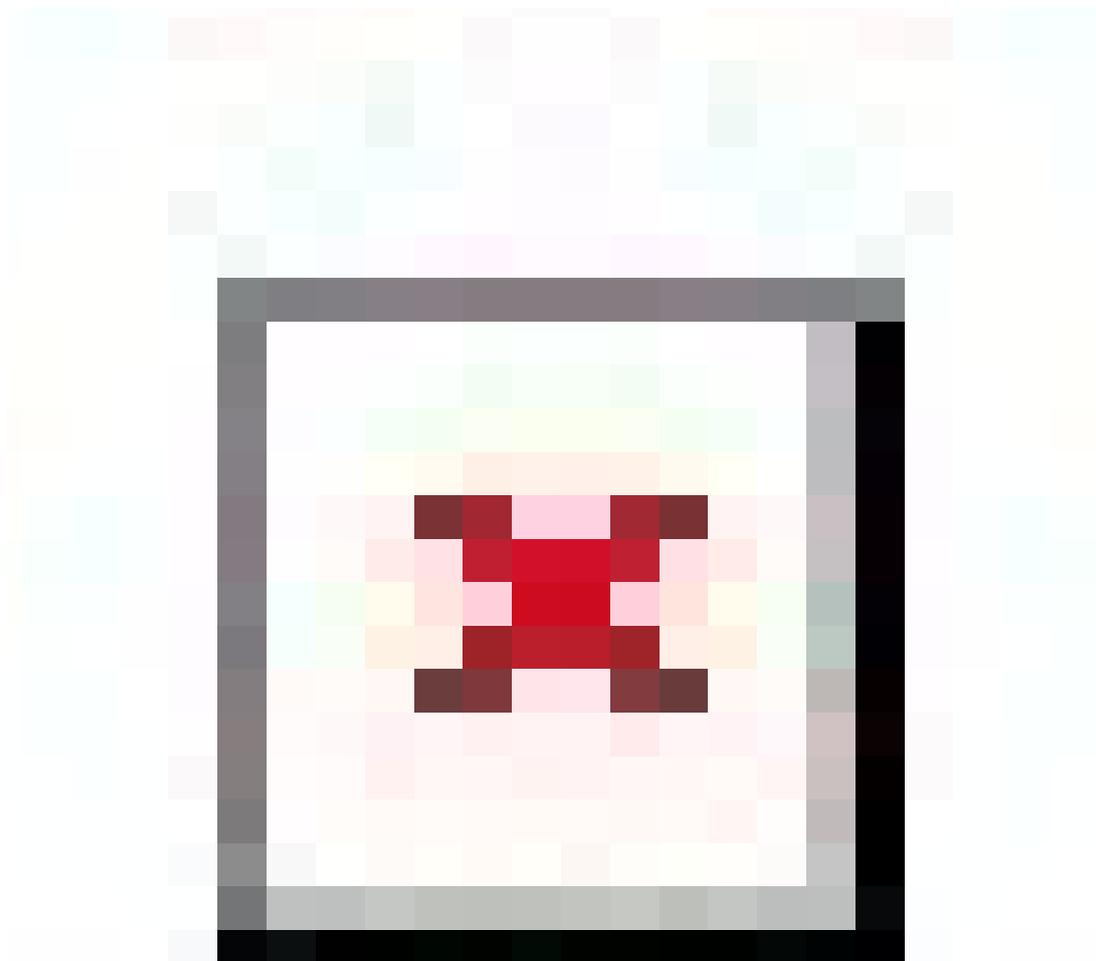


Fig. S9 (a) Device diagram for measuring Faraday efficiency. (b) Diagram of the amount of H₂ released over time in 1.0 M KOH.

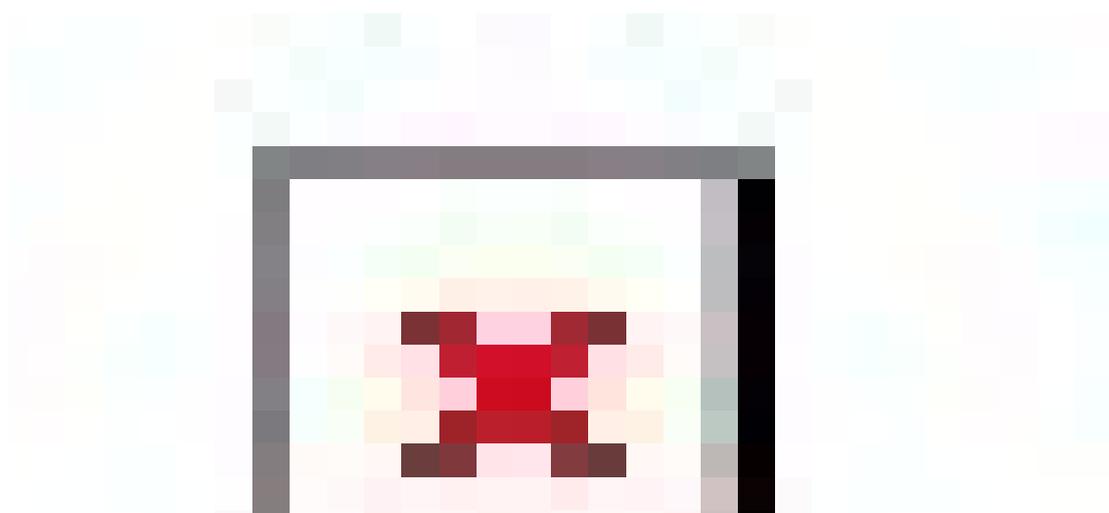


Fig. S10 (a) Theoretical model of Ru NP-WN/CC system. (b) Bader charge analysis of Ru₁, Ru₂, Ru₃, and Ru₄.

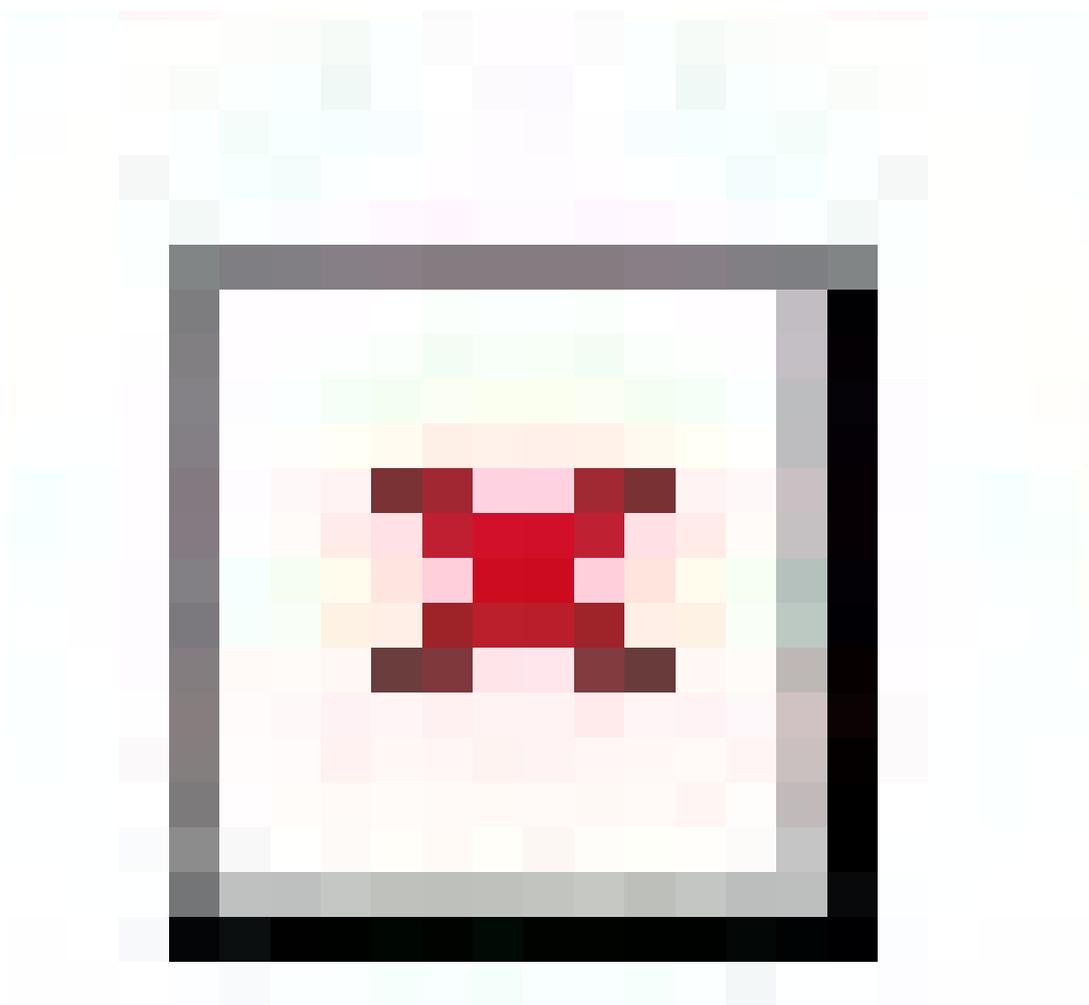


Fig. S11 Simulation models and Bader charge analysis corresponding of (a) Ru₁-H, (b) Ru₂-H, (c) Ru₃-H and (d) Ru₄-H.

Table S1. Ru wt.% determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Sample	Ru wt.%
Ru NP-WN/CC	1.1

Table S2. Comparison of HER performance with recently reported HER catalysts in 1.0 M KOH.

Catalysts	Overpotential /mV @ 10 mA cm ⁻²	Tafel slope / mV dec ⁻¹	Reference
Ru NP-WN/CC	9	29	This work
NS-Ru@NiHO/Ni ₅ P ₄	16	35	<i>Adv. Funct. Mater.</i> 2023, 2212321
Ru/Mo ₂ CT _x	78	49	<i>Adv. Funct. Mater.</i> 2023, 2214375
Ru/np-MoS ₂	30	31	<i>Nat. Commun.</i> 2021, 12, 1687
CoRu _{0.5} /CQDs	18	39	<i>Angew. Chem. Int. Ed.</i> 2021, 60, 3290
RuNi/CQDs	13	40	<i>Angew. Chem. Int. Ed.</i> 2020, 59, 1718
Ru@N-CNFs	16	32	<i>Small</i> , 2022, 2206781
NiRu _{0.13} -BDC	36	32	<i>Nat. Commun.</i> 2021, 12, 1369
Pt/RuCeO _x -PA	41	31	<i>Angew. Chem. Int. Ed.</i> 2020, 59, 20423
R-NiRu	16	40	<i>Adv. Mater.</i> 2021, 33, 2104764
PtSe ₂ /Pt	42	53	<i>Angew. Chem. Int. Ed.</i> 2021, 60, 23388
Dr-Pt	26	52	<i>Adv. Mater.</i> 2022, 34, 2106973
RuNP-RuSA@CFN-800	33	37	<i>Adv. Funct. Mater.</i> 2023, 33, 2213058
RuCuO _x /NC	29	58	<i>Appl. Catal. B.</i> 2023, 324, 122169
Ni ₅ P ₄ -Ru	54	52	<i>Adv. Mater.</i> 2020, 32, 1906972