Supporting Information

Active ruthenium (101) crystal plane selectively exposed by in-situ metal hyperaccumulation on living plant for overall water splitting

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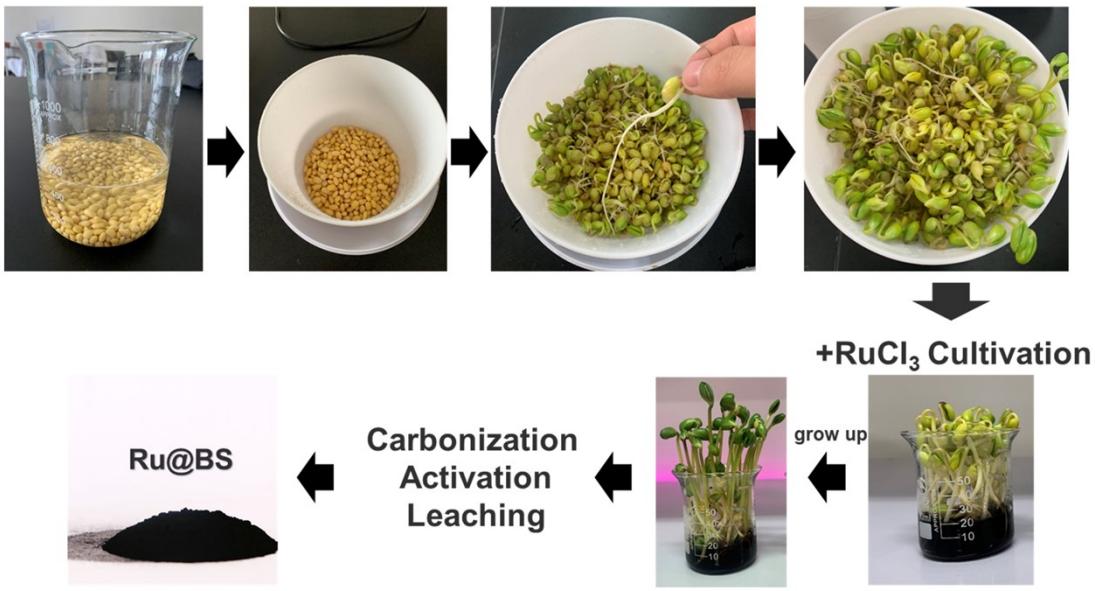

Fig S1. Digital photograph of the in-situ biosynthesis preparation of Ru@BS.

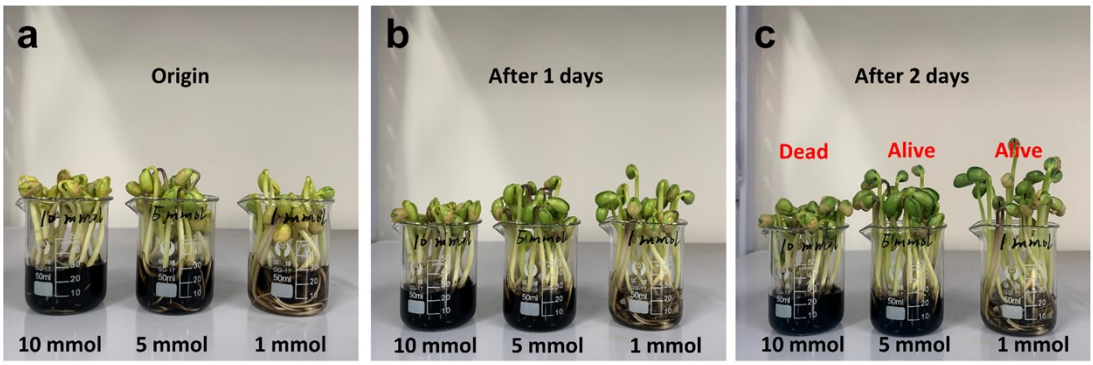

Fig S2. Digital photograph of enrichment process.

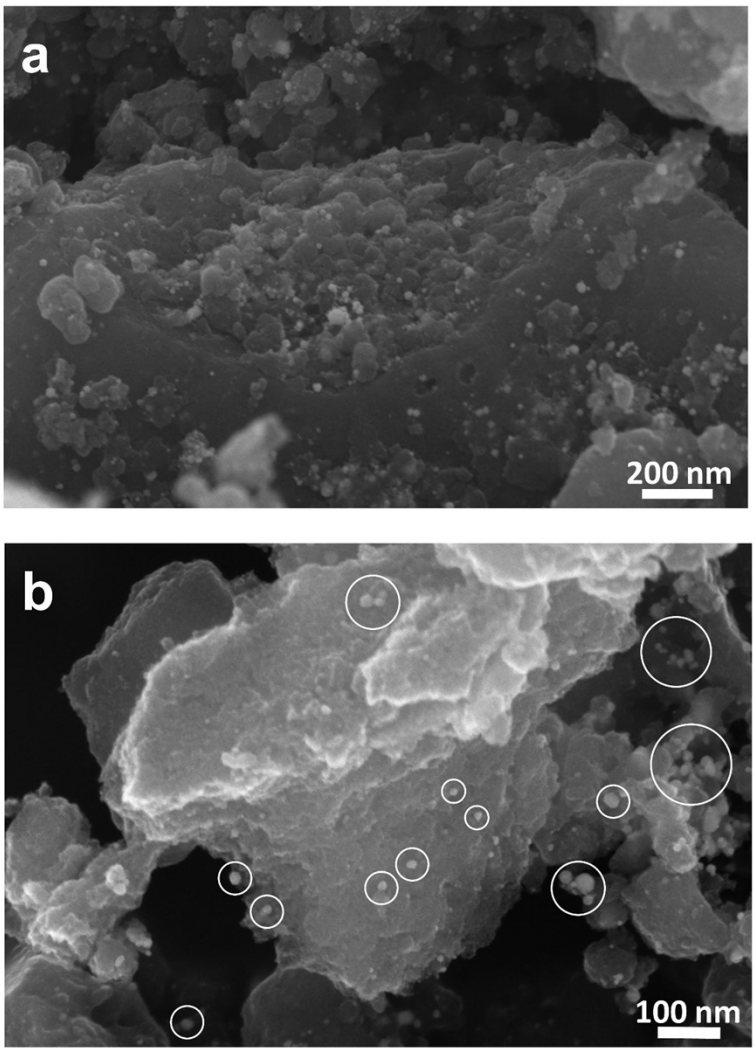

Fig S3. The SEM images of Ru@BS-5 at different resolution.

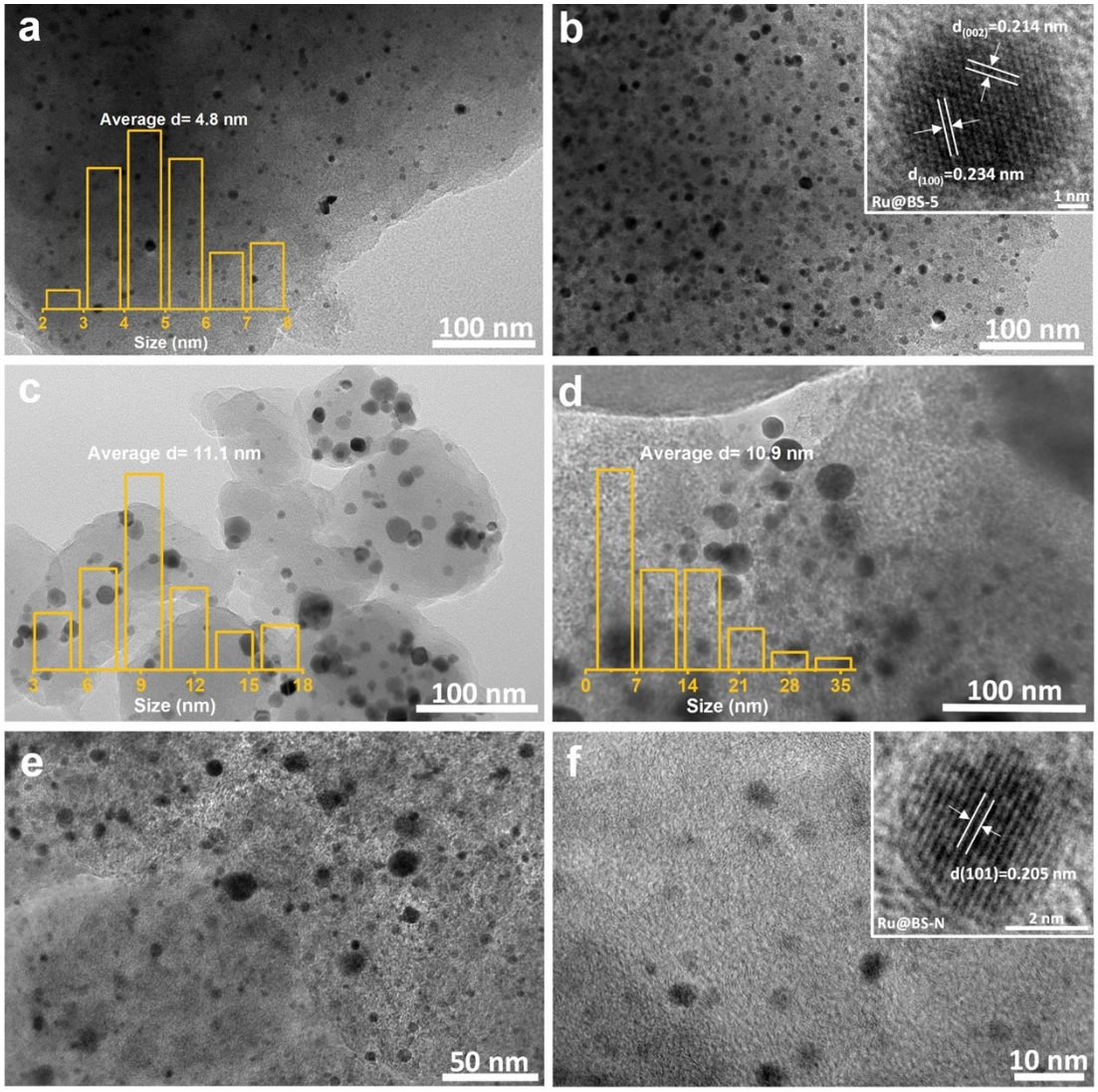

Fig S4. (a-d) The TEM images of Ru@BS-1 (a), Ru@BS-5 (b), Ru@BS-10 (c), and Ru@BS-N (d). (e-f) The high-resolution TEM images of Ru@BS-N.

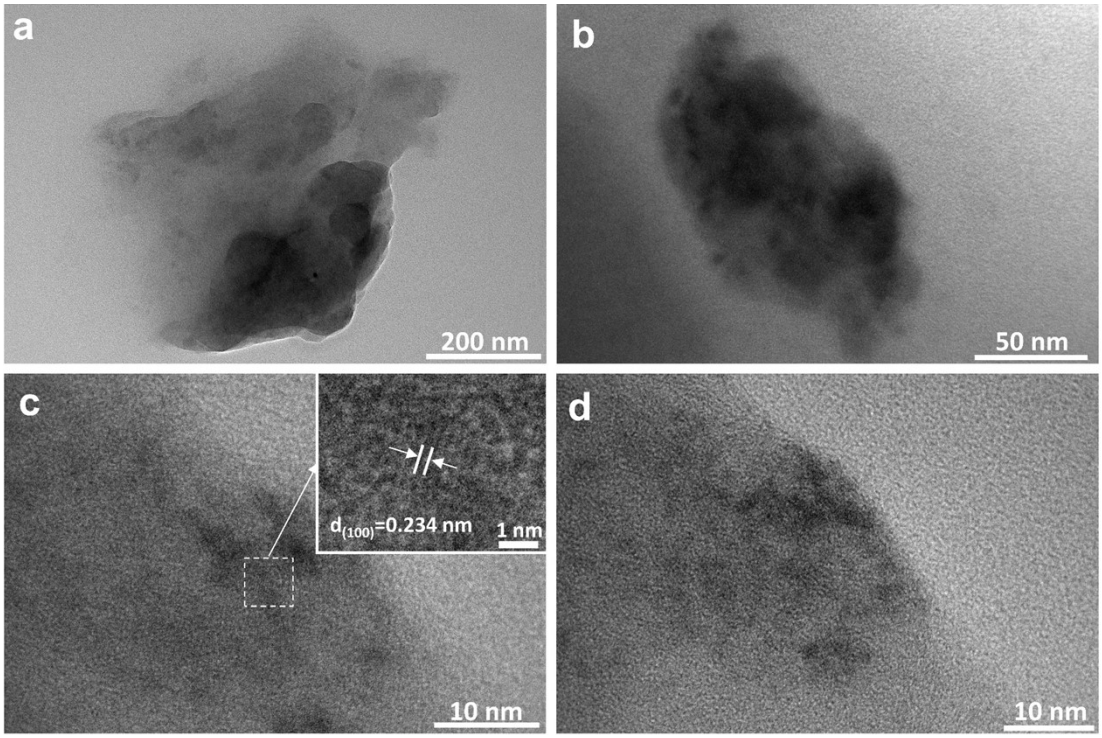

Fig S5. The TEM images of Ru@BS-Raw at different resolution.

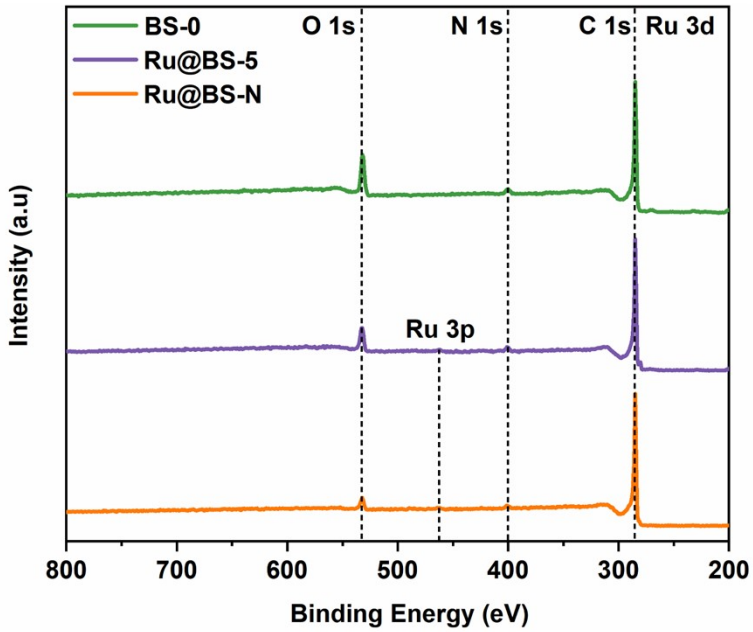

Fig S6. The XPS survey of BS-0, Ru@BS-5, and Ru@BS-N.

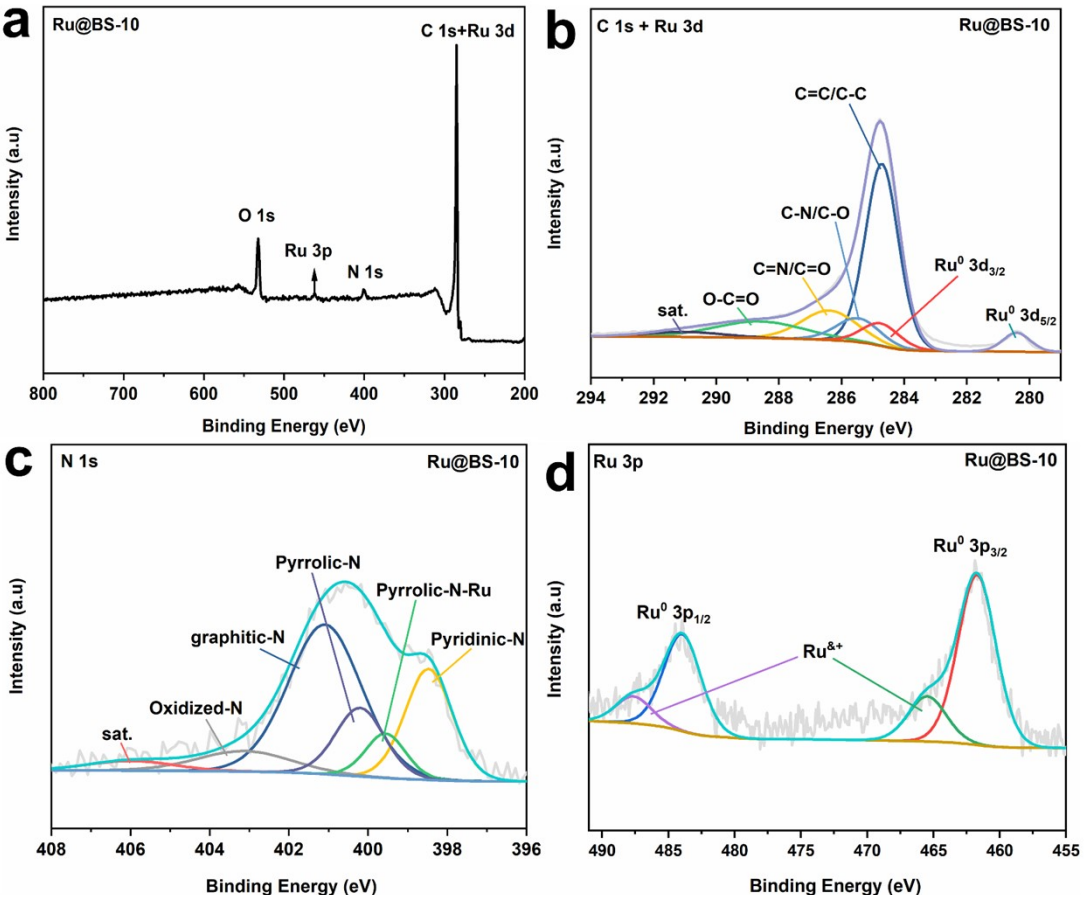

Fig S7. (a) The XPS survey of Ru@BS-10. (b-d) The high-resolution XPS spectra of (b) C 1s + Ru 3d, (c) N 1s, and (d) Ru 3p for the prepared Ru@BS-10.

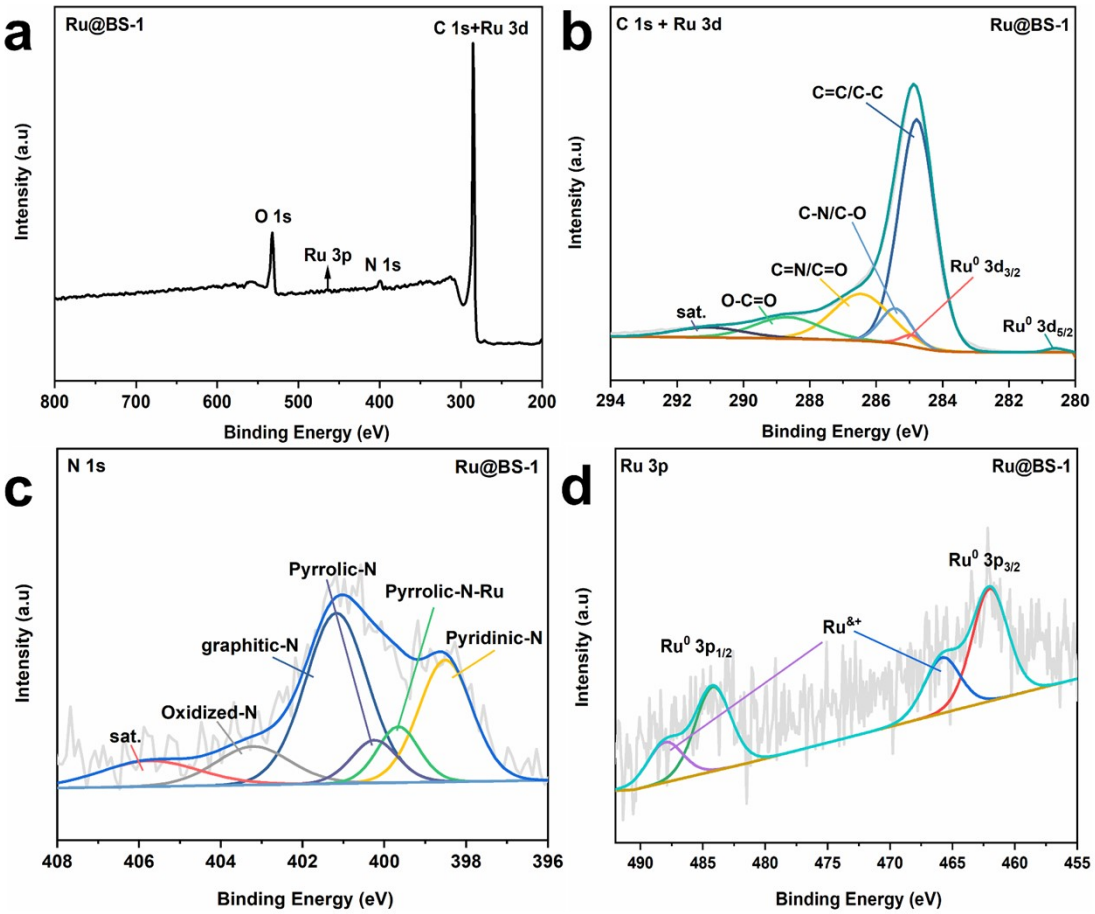

Fig S8. (a) The XPS survey of Ru@BS-1. (b-d) The high-resolution XPS spectra of (b) C 1s + Ru 3d, (c) N 1s, and (d) Ru 3p for the prepared Ru@BS-1.

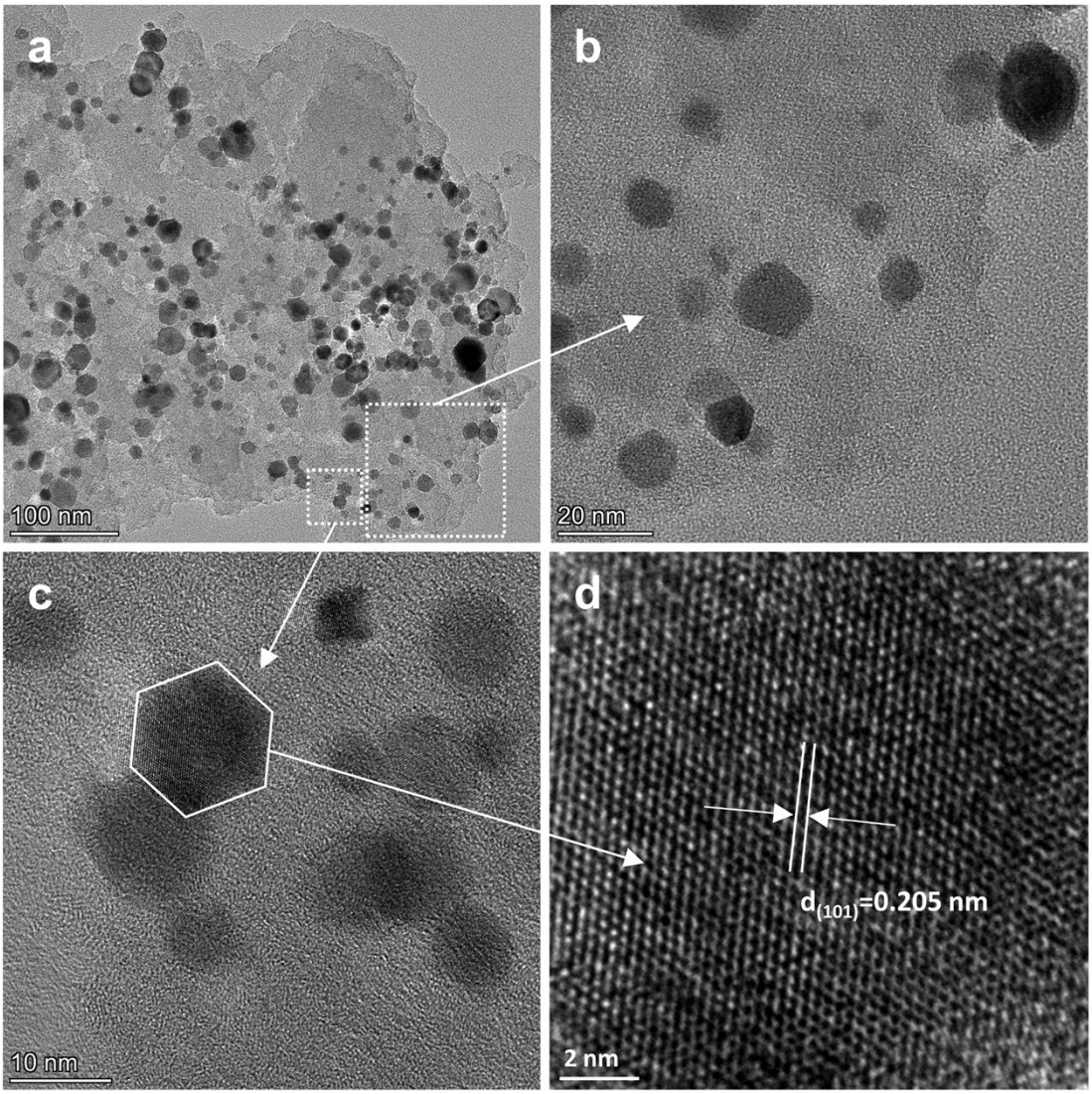

Fig S9. The TEM images of Ru@BS-5 after OER polarization test at different resolution.

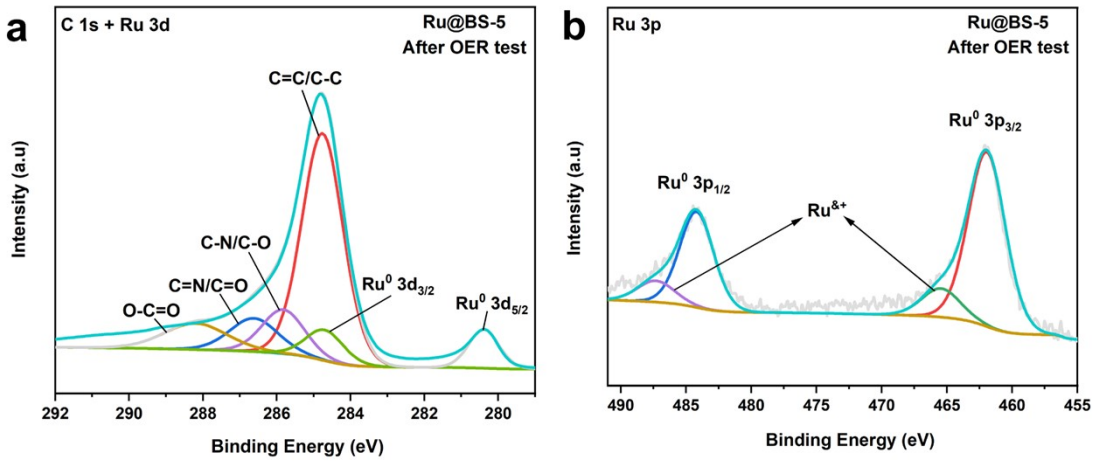

Fig S10. The high-resolution XPS spectra of (a) C 1s + Ru 3d and (b) Ru 3p for the Ru@BS-5 after OER polarization test.

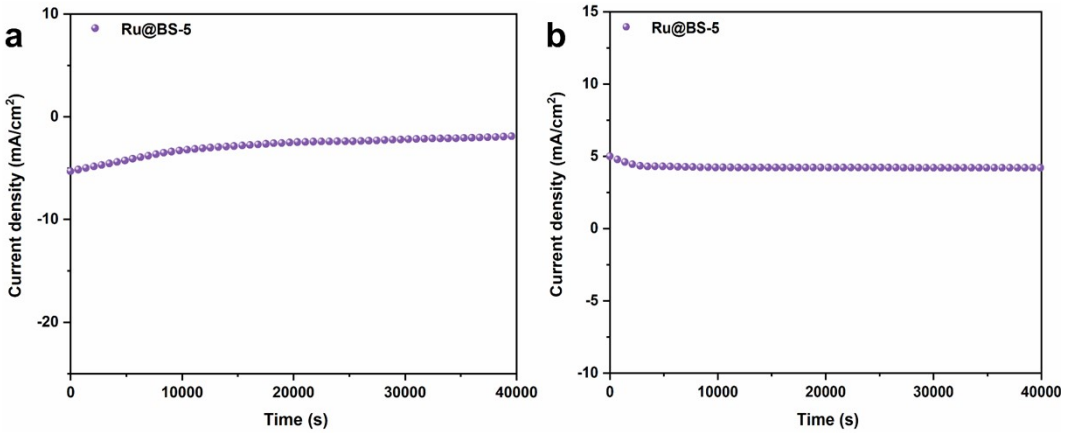

Fig S11. Chronoampermetry curves of Ru@BS-5 in 1 M KOH at a constant current density of 5 mA cm^{-2} in HER (a) and OER (b).

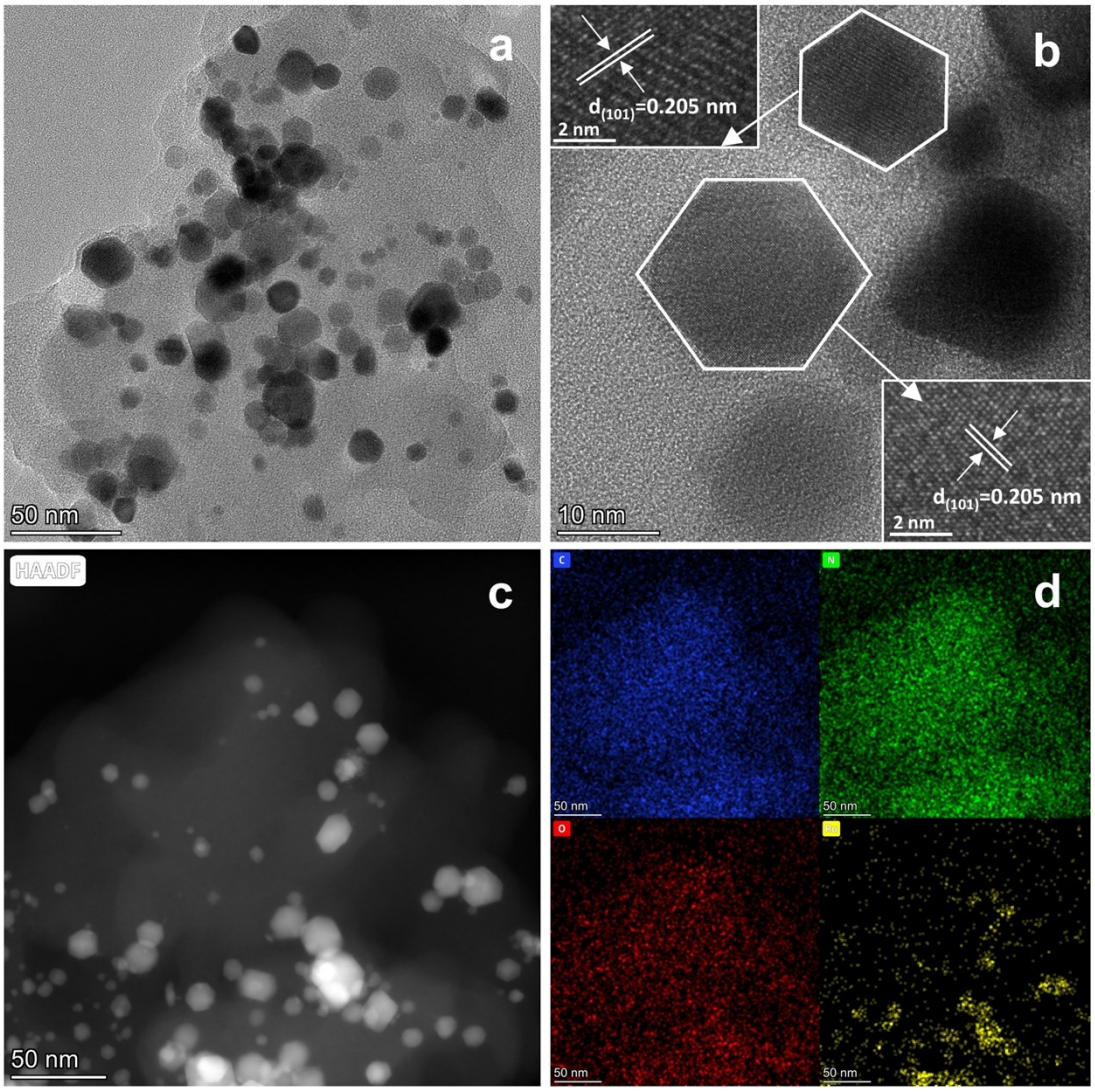

Fig S12. (a-b) The TEM images of Ru@BS-5 after HER stability test at different resolution. (c-d) The HAADF-STEM image of Ru@BS-5 after HER stability test and corresponding EDS mapping for C, N, O and Ru.

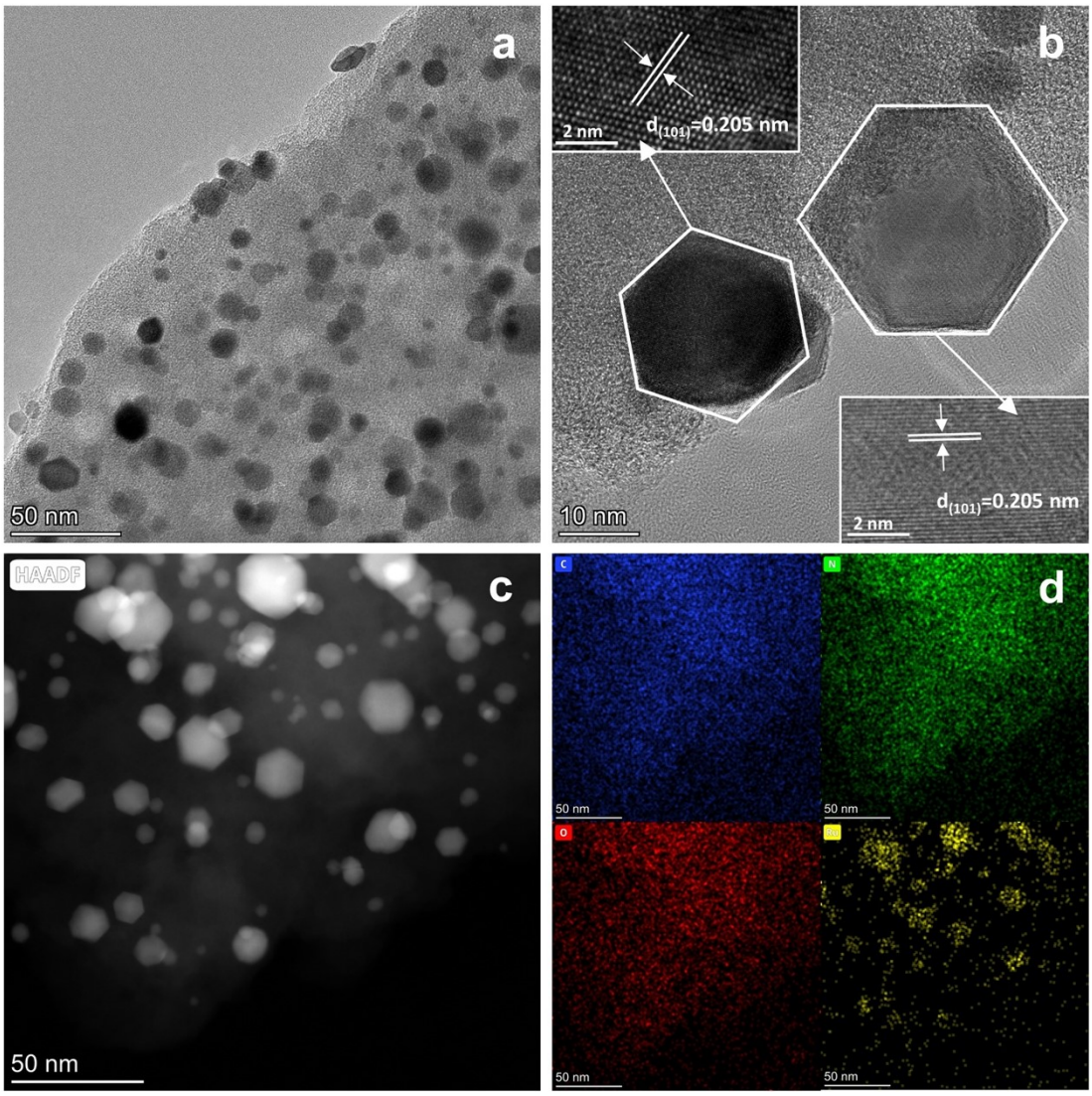

Fig S13. The TEM images of Ru@BS-5 after OER stability test at different resolution. (c-d) The HAADF-STEM image of Ru@BS-5 after OER stability test and corresponding EDS mapping for C, N, O and Ru.

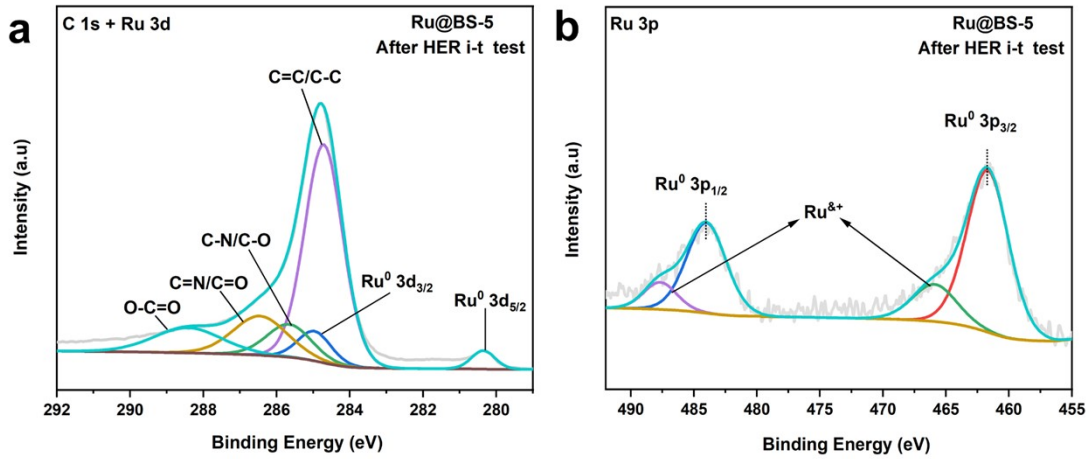

Fig S14. The high-resolution XPS spectra of (a) C 1s + Ru 3d and (b) Ru 3p for the Ru@BS-5 after HER stability test.

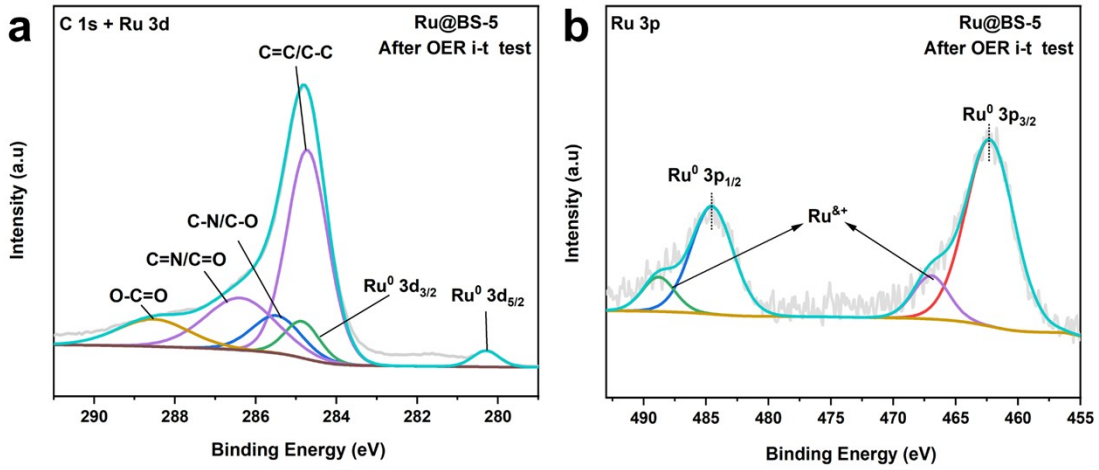

Fig S15. The high-resolution XPS spectra of (a) C 1s + Ru 3d and (b) Ru 3p for the Ru@BS-5 after OER stability test.

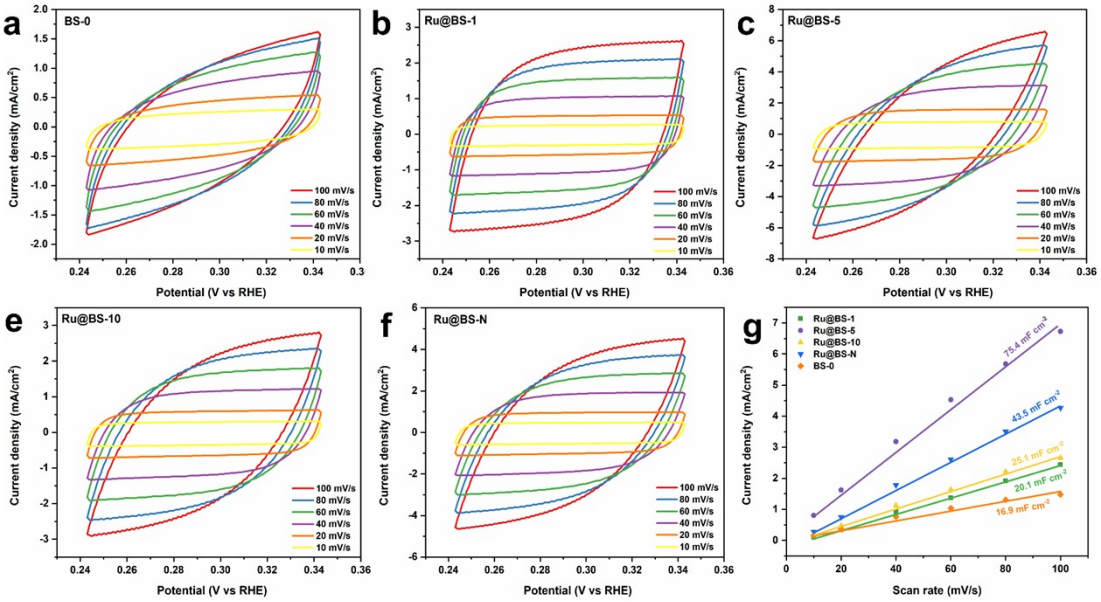

Fig S16. (a-f) CV conducted at potential from 0.24 V to 0.34 V vs RHE at scan rates of 10 mV/s, 20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s and 100 mV/s. (g) Electrochemical surface area plots showing the extraction from the C_{dl} of all studied electrocatalysts.

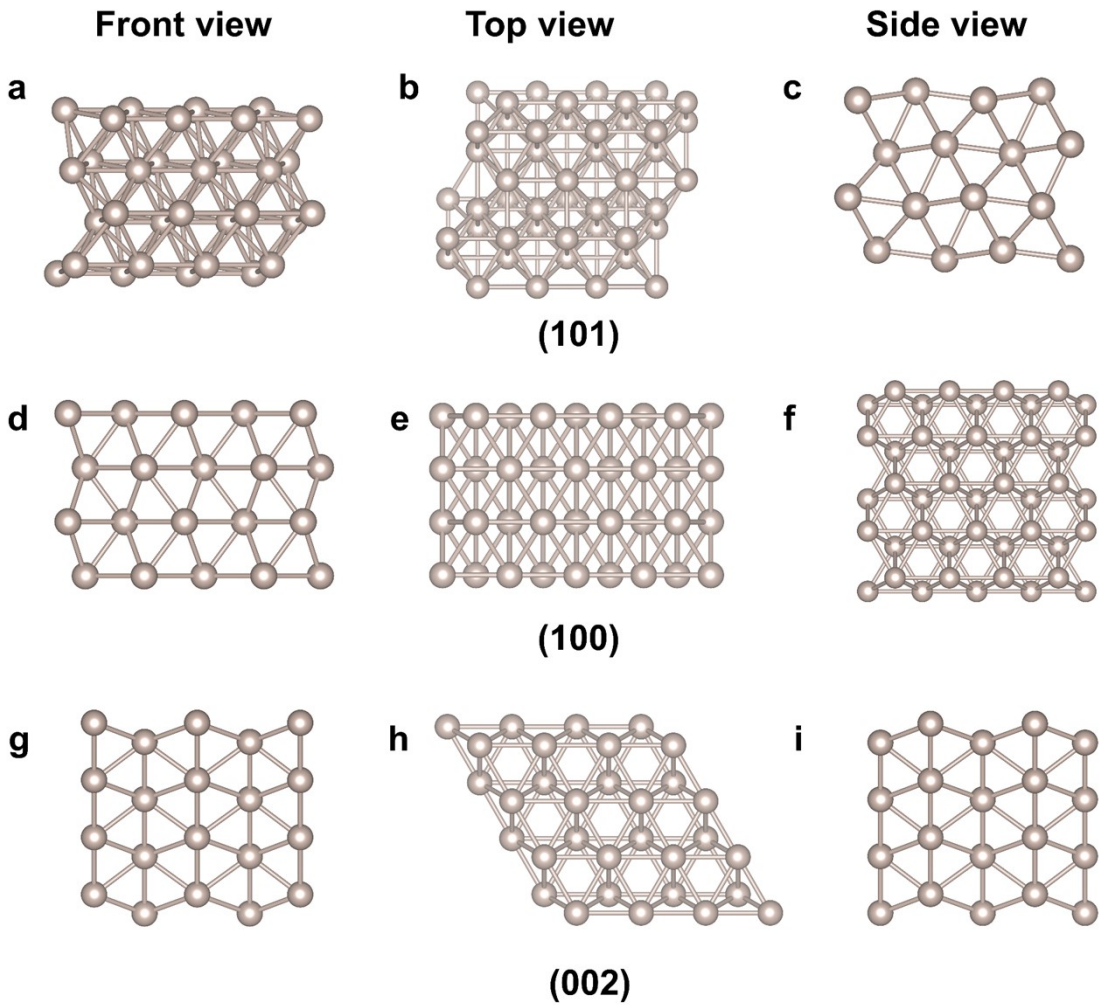

Fig S17. Front view, top view, and side view of the DFT calculation model of different Ru particle crystal planes.

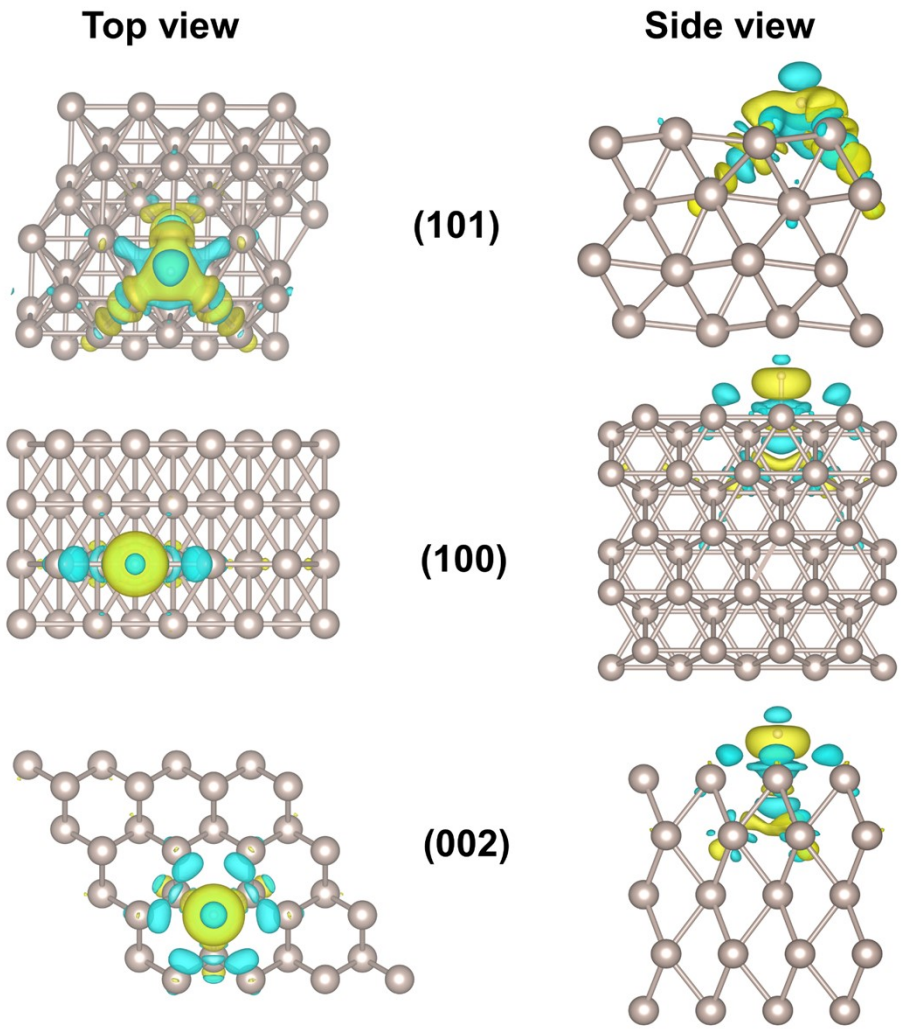

Fig S18. The charge distribution diagrams of the Ru (101), (100) and (002) crystal planes with the adsorption of hydrogen atoms by top view and side view.

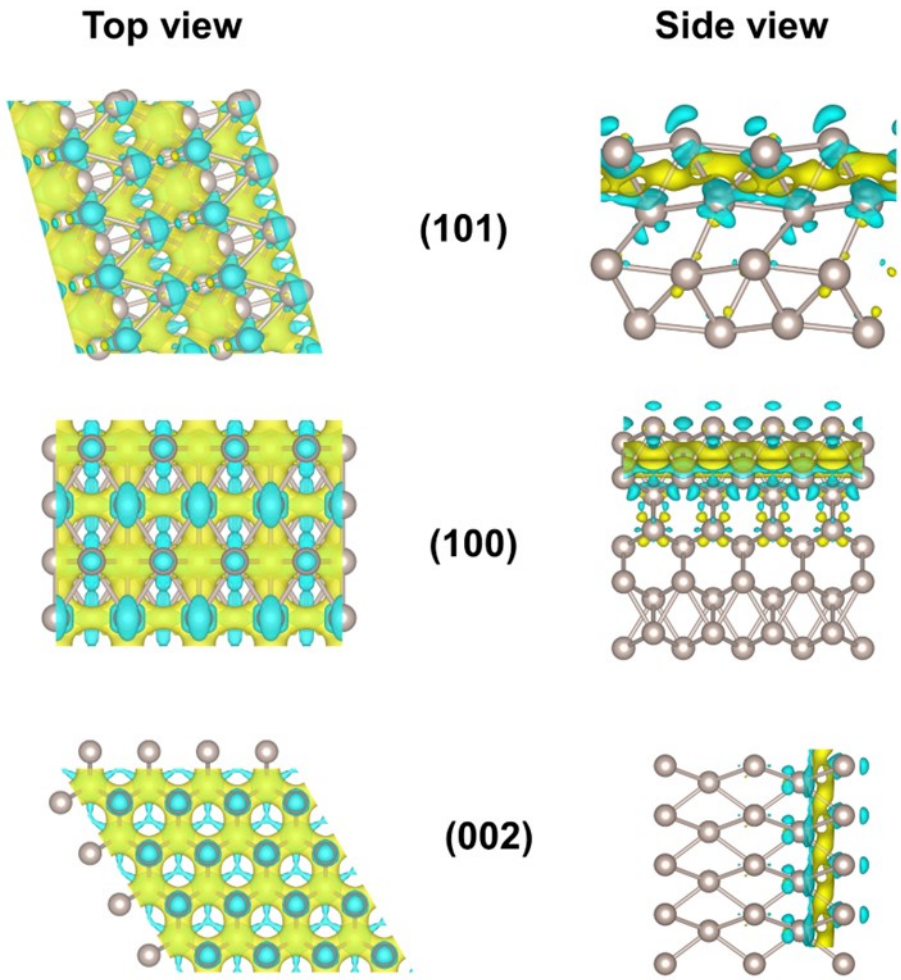

Fig S19. The charge distribution diagrams of the Ru (101), (100) and (002) crystal planes by top view and side view.

Combining the experimental results and the conclusions of previous work[1], the (101), (002) and (100) facets of Ru nanosheets have excellent catalytic performance. Then, the structural models are established to explore their catalytic performances for the hydrogen evolution reaction (HER).

At the temperature of 298K and the atmospheric pressure of 1 atm, the Gibbs free energy was described by Eq (1) [2]:

$$\Delta G = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \quad (1)$$

Where the ΔG is the Gibbs free energy of the HER, ΔE_H is the differential hydrogen adsorption energy, ΔE_{ZPE} is the zero-point energy of adsorbed hydrogens on the Ru nanosheets, and ΔS_H is the entropy between adsorption and hydrogen in the gas phase.

Table S1. The atomic percentage of Ru and N in XPS survey.

Sample	Ru (at %)	N (at %)
Ru@BS-10	0.88 %	4.35 %
Ru@BS-5	0.84 %	3.59 %
Ru@BS-1	0.47 %	3.16 %
Ru@BS-N	0.86 %	1.58 %

References

1. P. Jiang, Y. Yang, R. Shi, G. Xia, J. Chen, J. Su and Q. Chen, *J. Mater. Chem. A*, 2017, **5**, 5475-5485.
2. J. Su, Y. Yang, G. Xia, J. Chen, P. Jiang and Q. Chen, *Nat. Commun.*, 2017, **8**, 1-12.