

Supporting Information for

Highly Dispersed Ru Nanoclusters Anchored on B, N Co-doped Carbon Nanotubes for Water Splitting

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Chemicals and Reagents

Ruthenium trichloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) and carboxylated multi walled carbon nanotubes were purchased from Aladdin Chemistry Co., Ltd. Boric acid (H_3BO_3) and urea ($\text{CH}_4\text{N}_2\text{O}$) were obtained from Beijing Chemical Factory. Platinum on graphitized carbon (20 wt% Pt/C) and Nafion perfluorinated resin solution were bought from Alfa Aesar Chemicals Co., Ltd. Ethanol, isopropanol and sulfuric acid (H_2SO_4) were purchased from Beijing Chemical Factory. Highly purified water ($>18 \text{ M}\Omega \text{ cm}$ resistivity) was provided by a PALL PURELAB Plus system.

Material Characterizations

The powder X-ray diffraction (XRD) patterns of the materials were obtained with X-ray diffractometer (Rigaku D/Max 2550) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology and structure of the as-prepared materials were characterized using a scanning electron microscope (SEM) (JSM-6701F, JEOL) that was operating at 5 kV and a transmission electron microscope (TEM) (JEM-2010, JEOL) that was operating at 200 kV. X-ray photoemission spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific ESCALAB 250Xi with photoelectron spectroscopy system using a monochromatic $\text{Al K}\alpha$ (1486.6 eV) X-ray source. The surface area of catalyst was calculated by the Brunauer-Emmett-Teller (BET) method by a Micromeritics SSA-4300 system of Beijing BIOD Electronic Technology Co., Ltd. H_2 temperature-programmed reduction characterizations (H_2 -TPR) were performed using a Micromeritics AutoChem 2920 II system. Raman analysis was carried out on LabRAM HR Raman spectrometer of Bergson Beijing Co., Ltd

Electrochemical Measurements

Electrochemical impedance spectroscopic (EIS) measurements were performed in KOH solution (1 M) to investigate the interfacial electron transfer dynamics of Ru@B,N-CNTs. The electrochemically active surface area (ECSA) was estimated by determining the double-layer capacitance of the system from CV.[1] Measurement of current in a selected non-Faradaic potential range was assumed to double-layer charging. C_{dl} was tested by a series of cyclic voltammetry (CV) measurements with various scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/s) in $-0.2 - -0.1 \text{ V versus SCE}$. The sweep segments were set to 10 to ensure consistency in the measurements. The charging current, i_c , is equal to the product of the electrochemical double layer capacitance, C_{dl} , and the scan rate, ν ,

$$i_c = \nu C_{\text{dl}} \quad \text{Eqn. 1}$$

Subsequently, the C_{dl} was estimated by the half of the slope of the fitting line by plotting the difference of currents (i) between the anodic and cathodic sweeps ($i_{\text{anodic}} - i_{\text{cathodic}}$) at $-0.15 \text{ V versus SCE}$ against the scan rate. The electrochemically active surface area (ECSA) of the catalyst can be calculated by dividing C_{dl} by the specific capacitance of the sample. The twice of C_{dl} value is proportional to the ECSA of the catalyst. The ECSA of catalyst on GCE is estimated according to Eqn. 2:

$$\text{ECSA} = \frac{C_{dl}}{C_s} \quad \text{Eqn. 2}$$

where C_s is the specific capacitance of the sample. In this work, the value of C_s is estimated to be 0.06 mF/cm² according to previous reports[2].

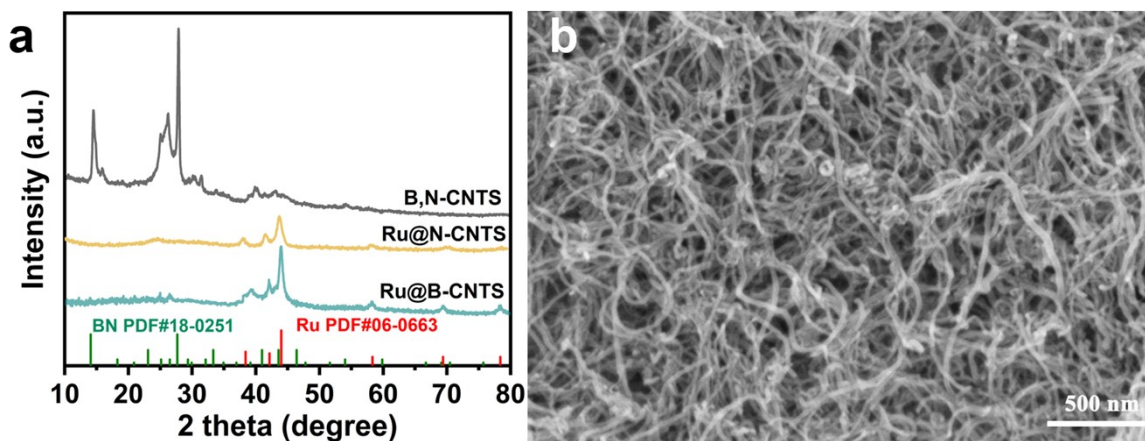


Figure S1 (a) XRD patterns of B,N-CNTs, Ru@N-CNTs and Ru@B-CNTs. (b) SEM image of CNTs-COOH.

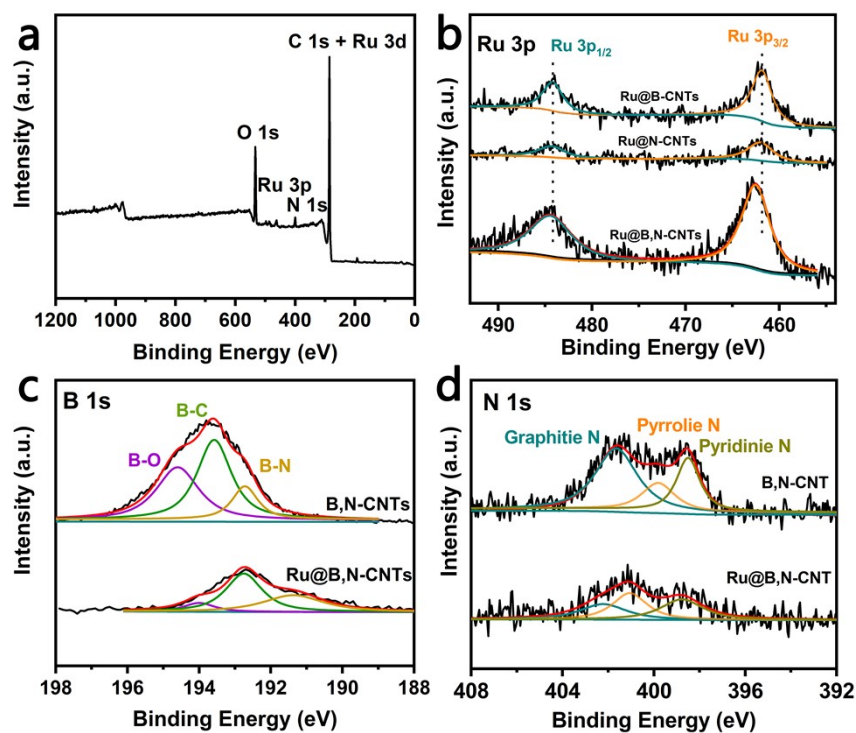


Figure S2 (a) Survey of the as-prepared Ru@B,N-CNTs. (b) Ru 3p XPS spectra of Ru@B-CNTs, Ru@N-CNTs and Ru@B,N-CNTs. (c, d) B 1s and N 1s XPS spectra of B,N-CNTs and Ru@B,N-CNTs.

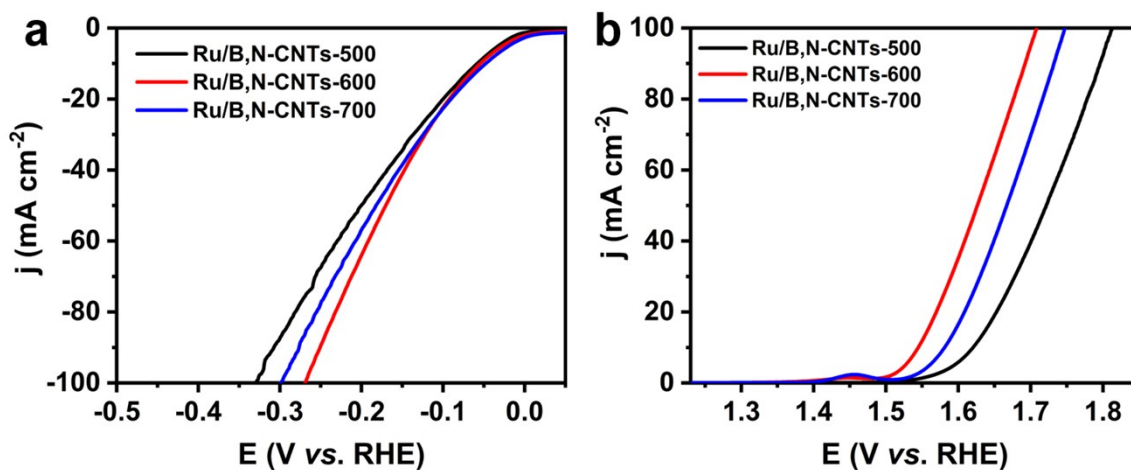


Figure S3 LSV curves of calcinated at 500 °C, 600 °C and 700 °C toward HER (a) and OER (b).

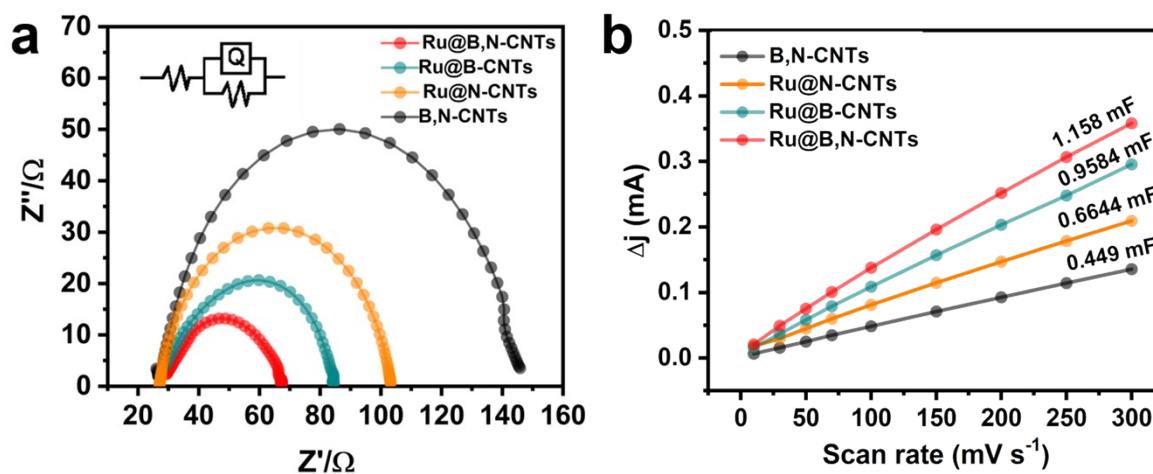


Figure S4 (a) Electrochemical impedance spectroscopy (EIS) impedance spectrum of B,N-CNTs, Ru@B-CNTs, Ru@N-CNTs and Ru@B,N-CNTs in 1 M KOH solution. (b) C_{dl} values calculated based on the plots of the difference in current density (J) between the anodic and cathodic sweeps (Janodic–Jcathodic) at 0.12 V vs. RHE against the scan rate.

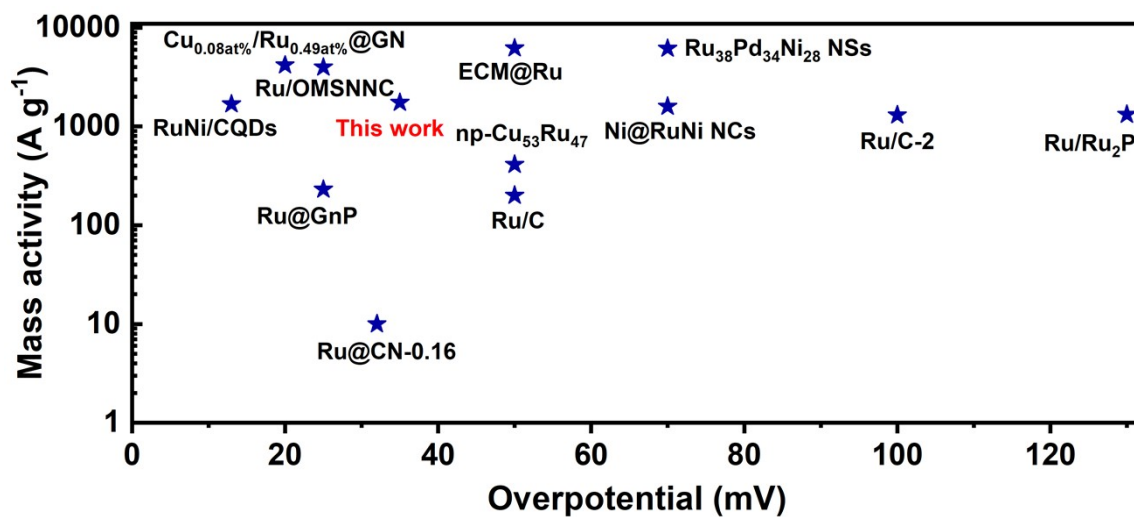


Figure S5 Comparison of ruthenium mass activities (j_{Ru}) of ruthenium-based catalysts.

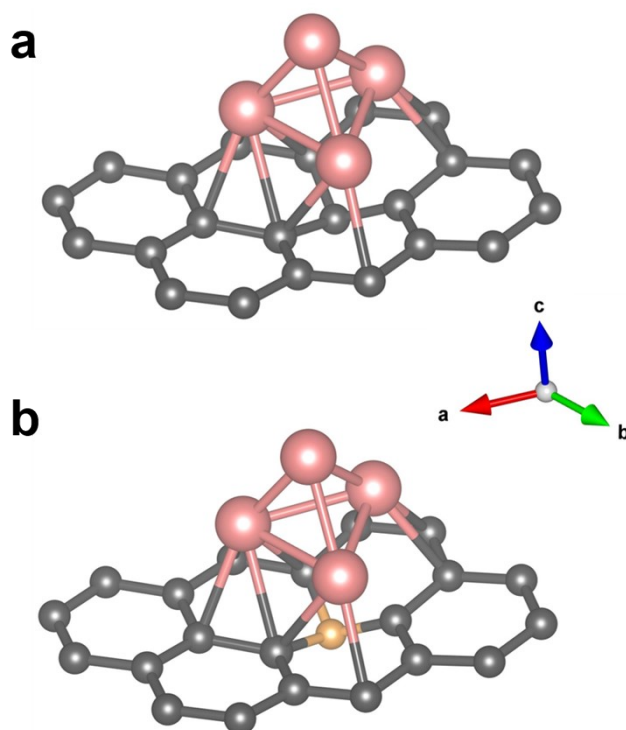


Figure S6 Optimized structures of H* adsorbed on Ru cluster anchoring on carbon nanotubes (a) and nitrogen-doped carbon nanotubes (b) model. Ruthenium, nitrogen and carbon atoms are in pink, blue, yellow and grey respectively

Table S1. Relative amounts (at.%) of the different elements on the surfaces of the materials investigated in the work. Analysis is done based in their XPS spectra.

Catalyst \ Amounts (at.%)	C	N	O	B	Ru
B,N-CNTs	36.36	2.75	37.77	23.12	-
Ru@B-CNTs	76.66	-	12.04	9.86	1.44
Ru@N-CNTs	71.74	1.87	25.63	-	0.76
Ru@B,N-CNTs	60.01	2.68	22.48	13.42	1.41

Table S2. Summary of specific surface area and pore characteristics of the materials.

Sample	BET (m²/g)	Pore volume (m³/g)	Average pore size (nm)
B,N-CNTs	45.8	0.28	3.16
Ru@B-CNTs	67.2	0.15	3.32
Ru@N-CNTs	68.5	0.27	3.41
Ru@B,N-CNTs	89.9	0.86	3.6

Table S3. Comparison of the electrocatalytic activities the materials studied for HER and OER among each other and with respect to benchmark noble metal HER and OER catalysts.

Catalysts	HER		OER	
	η_{10} (mV)	η_{100} (mV)	η_{10} (mV)	η_{100} (mV)
B,N-CNTs	290	623	467	730
Ru@B-CNTs	99	354	378	568
Ru@N-CNTs	111	430	409	666
Ru@B,N-CNTs	54	268	315	479
Ru@B,N-CNTs-500	61	328	390	580
Ru@B,N-CNTs-700	54	299	350	510
Pt/C	31	313	-	-
RuO₂	-	-	390	579

η_{10} : The overpotential required by the material to electrocatalyze the reaction at 10 mA cm⁻².

η_{100} : The overpotential required by the material to electrocatalyze the reaction at 100 mA cm⁻².

Table S4. Values of C_{dl} and R_{ct} values of the catalysts obtained from their CV curves that are obtained with different scan rates and their equivalent circuit models.

Catalyst	C_{dl} (mF cm ⁻²)	ECSA (cm ²)	R_{ct}
B,N-CNTs	2.27	37.8	57.06
Ru@B-CNTs	4.89	81.5	76.39
Ru@N-CNTs	3.39	56.5	118.5
Ru@B,N-CNTs	5.91	98.5	39.04

Table S5. Electrochemical water splitting performance comparison of Ru@B,N-CNTs with other Ru-based catalyst.

Catalyst	Cell voltage at 10 mA/cm ² current density	η_{10} (mV) for HER	η_{10} (mV) for OER	Reference
Ru@B,N-CNTs	1.57	54	315	This work
Ru-Ru ₂ PΦNPC	1.50	42	-	Adv. Funct. Mater. 2019, 29, 1901154
Ru-HPC	1.53	22.7	-	Nano Energy 2019, 58, 1–10
NiO@RuO ₂ @mC	1.52	129	270	Electrochim. Acta 2020, 334, 135653
RuCo@NC-750	1.54	25	308	Electrochim. Acta 2019, 327, 134958
RuNi-NCNFs	1.564	35	290	Adv. Sci. 2020, 7, 1901833
(Ru-Co)O _x	1.488	44.1	171.2	Angew. Chem. Int. Ed. 2020, 59, 17219–17224
Ni@Ru/CNS-10%	1.612	20.1	356	Electrochim. Acta 2019, 320, 134568
Co ₃ O ₄ -RuCo@NC	1.66	141	247	ACS Appl. Mater. Interfaces 2019, 11, 47894–47903
RuO ₂ /N-C	1.534	40	280	ACS Sustainable Chem. Eng. 2018, 6, 11529–11535

Table S6. Comparison of ruthenium mass activities (j_{Ru}) of ruthenium-based catalysts related to Figure S5.

Catalyst	Mass activity (A g ⁻¹)	Overpotential for calculating mass activity (mV)	Reference
Ru@B,N-CNTs	1740	35	This work
Cu _{0.08at%} /Ru _{0.49at%} @GN	4170	20	Appl. Catal. B: Environ. 2020, 270, 118896.
Ru/OMSNNC	3970	25	Adv. Mater. 2021, 33, 2006965.
RuNi/CQDs	1680	13	Angew. Chem. Int. Ed. 2020, 59, 1718–1726.
Ru@GnP	230	25	Adv. Mater. 2018, 30, 1803676.
Ru@CN-0.16	10	32	Energy Environ. Sci. 2018, 11, 800-806
ECM@Ru	6200	50	Adv. Energy Mater. 2020, 10, 2000882.
np-Cu ₅₃ Ru ₄₇	410	50	ACS Energy Lett. 2020, 5, 192–199.
Ru/C	200	50	Appl. Catal. B: Environ. 2019. 258, 117952.
Ru ₃₈ Pd ₃₄ Ni ₂₈ NSs	6150	70	ACS Cent. Sci. 2019, 5, 1991–1997.
Ru/C-2	1300	100	Inter. J. Hydro. 2019, 4 4, 11817-11823.
Ni@RuNi NCs	1590	70	Sci. China Mater. 2019, 62(12): 1868–1876.
Ru/Ru ₂ P	1320	130	J. Mater. Chem. A 2019, 7, 5621–5625.

Reference

1. C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters and T. F. Jaramillo. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.*, 2015, **137**, 4347–4357.
2. C. C. L. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.*, 2013, **135**, 16977-16987.