Supporting information

Tungsten Nitride on Porous Carbon Support as a Highly Durable Electrocatalyst for Hydrogen Evolution Reaction

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Synthesis of control samples

Synthesis of β-W_2N

Tungsten nitride was synthesised without carbon support as a control experiment by mixing WO_3 and urea in the ratio of 1:20, followed by the pyrolysis at 900 °C for 2 hours under N_2 atmosphere. The sample was confirmed using powder XRD as β-W_2N.

Synthesis of N-doped carbon

The N-doped carbon (carbon source is Ketjen Black) was synthesised by mixing the KB and urea in the ratio of 1:10, and pyrolysed at 900 °C for 2 hours under N_2 atmosphere. The resulting product is referred to as N-doped carbon (NC).

Electrochemical surface area calculation for WN/NC catalysts

The electrochemically active surface area (ECSA) of the catalysts was calculated from the double-layer capacitance obtained by plotting the scan rate versus charging current at a particular potential. Previously, the cyclic voltammetry experiments were performed at different scan rates at N_2-saturated electrolytes (McCrory *et al*., *J. Am. Chem. Soc.* **2015**, *137* (13), 4347-4357). Subsequently, the ECSA of the material was calculated from the equation given below.

$$ECSA = \frac{C_{dl}}{C_s}$$

Where the value of C_S is taken as 0.04 mF cm^{-2} and 0.035 mF cm^{-2} for alkaline and acidic electrolyte, respectively.

Electrochemical surface area (ECSA) calculation for Pt/C catalyst

Similarly, the ECSA of the benchmark Pt/C catalyst is calculated from the H-UPD (hydrogen under potential deposition) region, obtained from the cyclic voltammetry at different electrolytes. The H-adsorption region (0.4 – 0 V) was chosen to calculate the ECSA of Pt/C catalysts. The charge of the H-adsorption was calculated from the CVs and the scan rate, and the ECSA is calculated as shown below.

$$ECSA = \frac{Q_H}{Q_S}$$

where Q_H represents the charge corresponding to the hydrogen adsorption, and Q_S is taken as 230 μC cm^{-2} and 145 μC cm^{-2} for 0.5 M H_2SO_4 and 1 M KOH solutions, respectively. (Vidal-Iglesias *et al*., ***ACS Catal.*** *2012,* ***2***, *901−910*)

TOF calculation

The TOF of the catalyst was calculated as reported earlier (N. Logeshwaran *et. al*., *J. Energy Chem*., 86, 2023, 167-179) using the formula given below.

$$TOF = \frac{j}{F \times n \times \Gamma/N_A}$$

Where j, N_A, F, n and Γ correspond to current density, Avagadro number, Faraday constant, number of electrons and number of active sites.

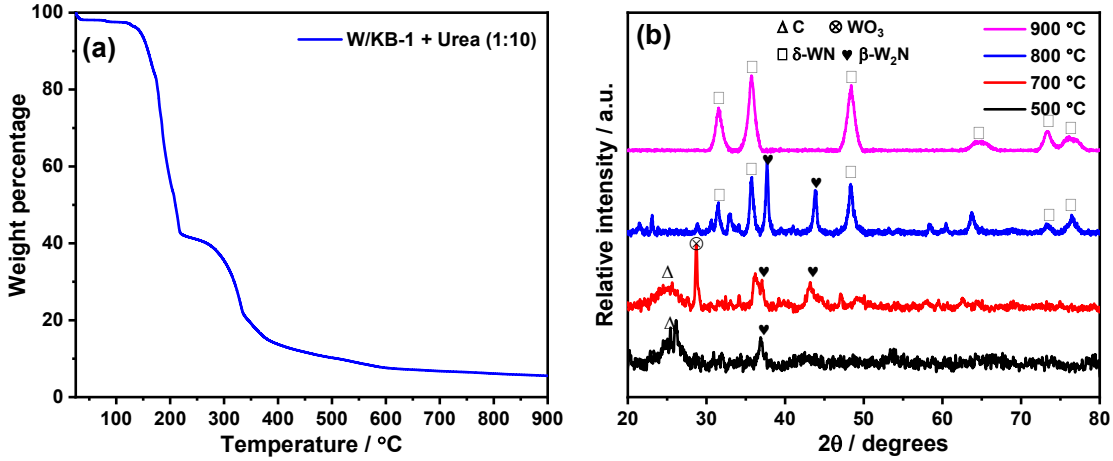

Fig. S1. (a) The thermogravimetric analysis of the precursors ($Na_2WO_4 \cdot 2H_2O$+KB+urea) in N_2-atmosphere and (b) powder XRD patterns of heated precursors at various temperatures.

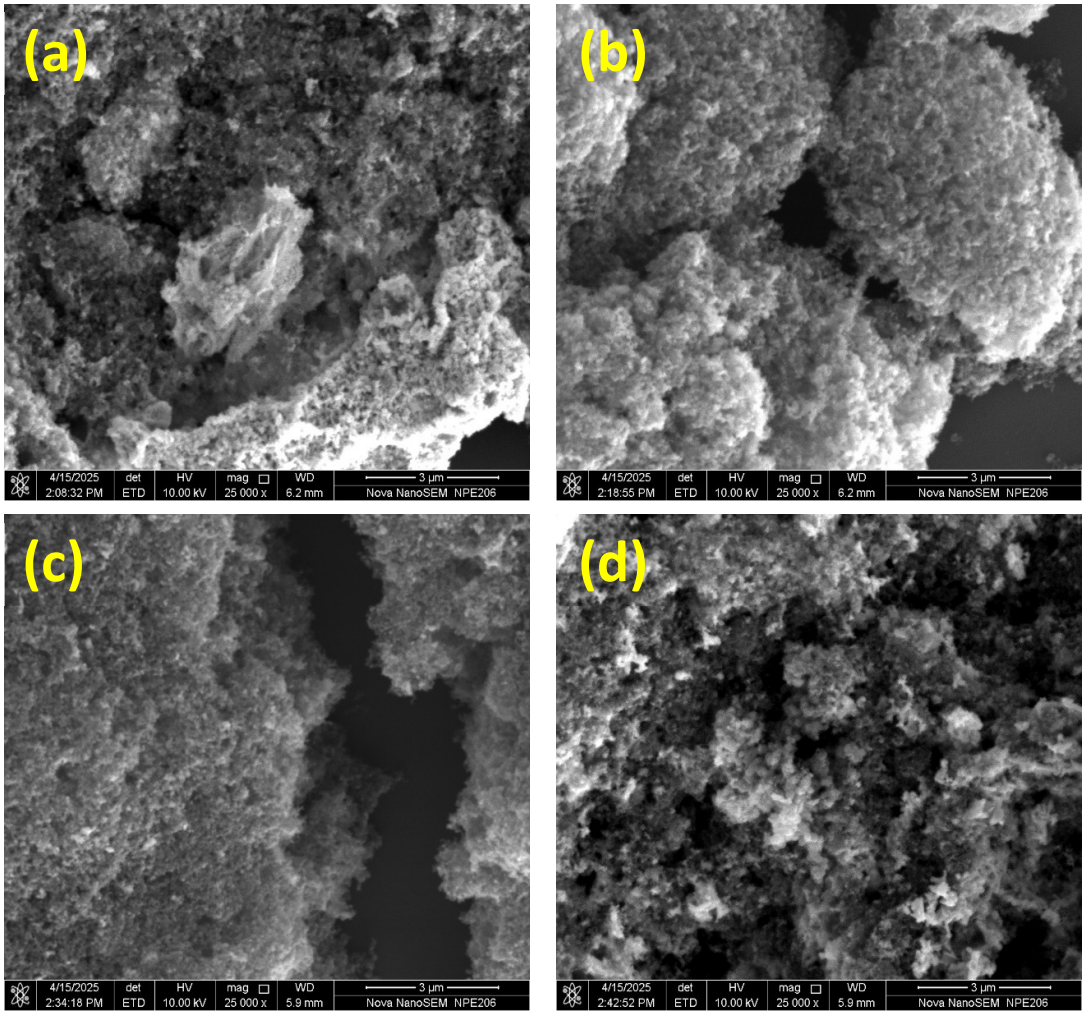

Fig. S2. Scanning electron microscopy images of (a) WN/NC-1, (b) WN/NC-2, (c) WN/NC-3 and (d) WN/NC-1A catalysts.

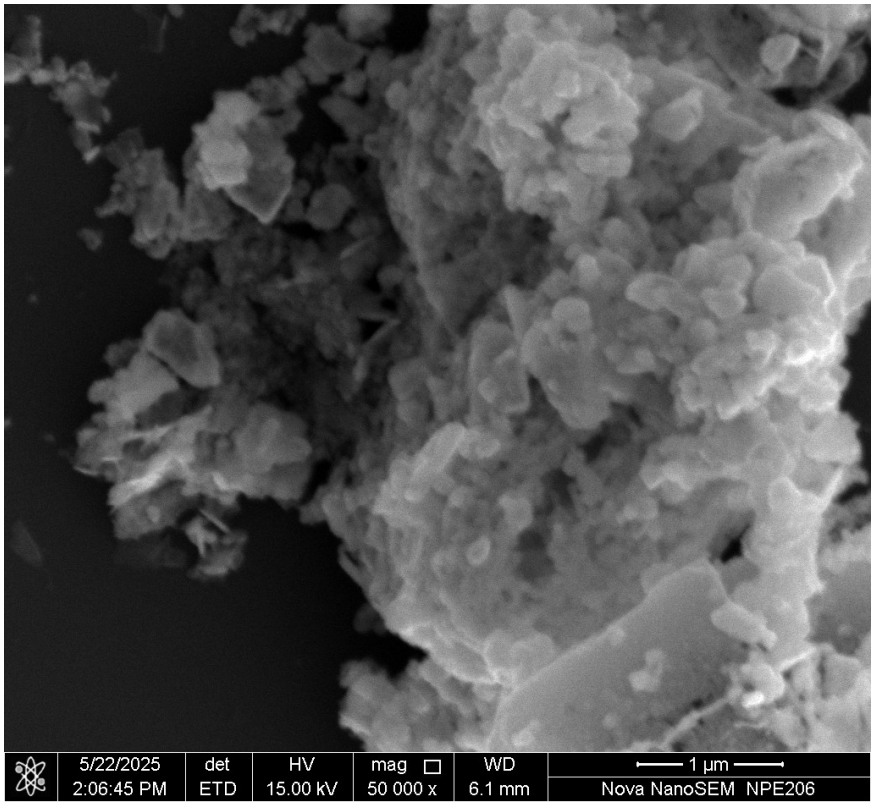

Fig. S3. Scanning electron microscopic image of β-W_2N catalyst

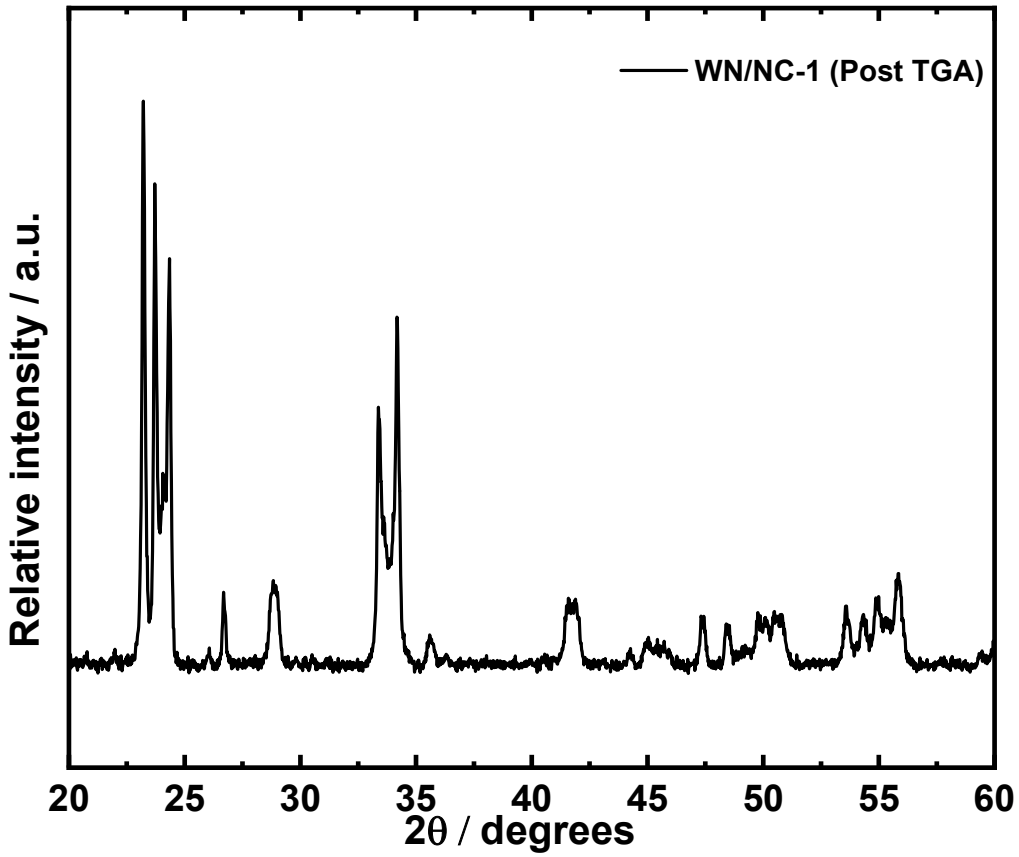

Fig. S4. Powder X-ray diffraction pattern of the residue obtained from the thermogravimetric experiment of WN/NC-1 under an air atmosphere.

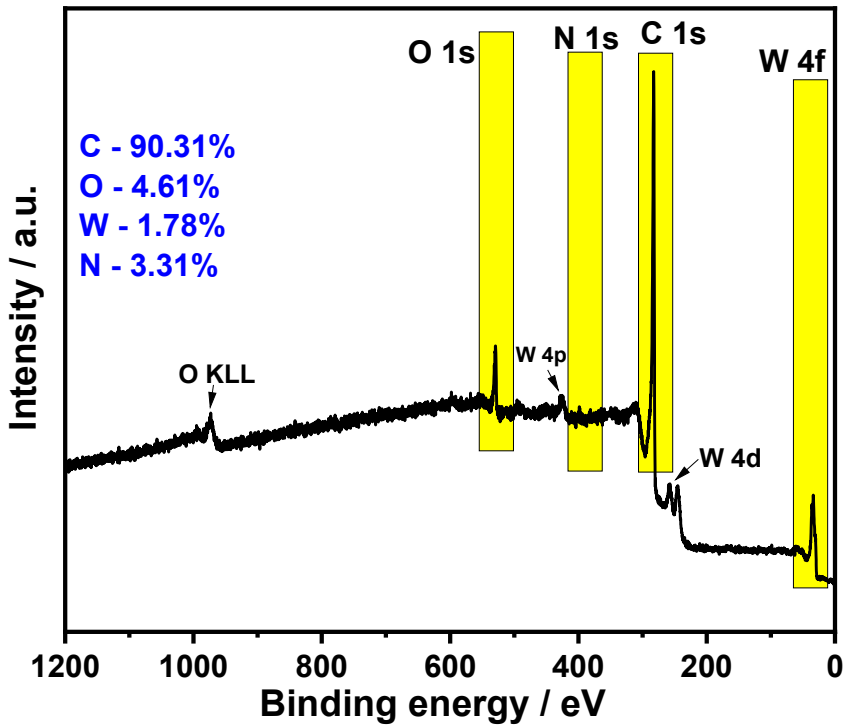

Fig. S5. Survey XPS of the WN/NC-1 catalyst.

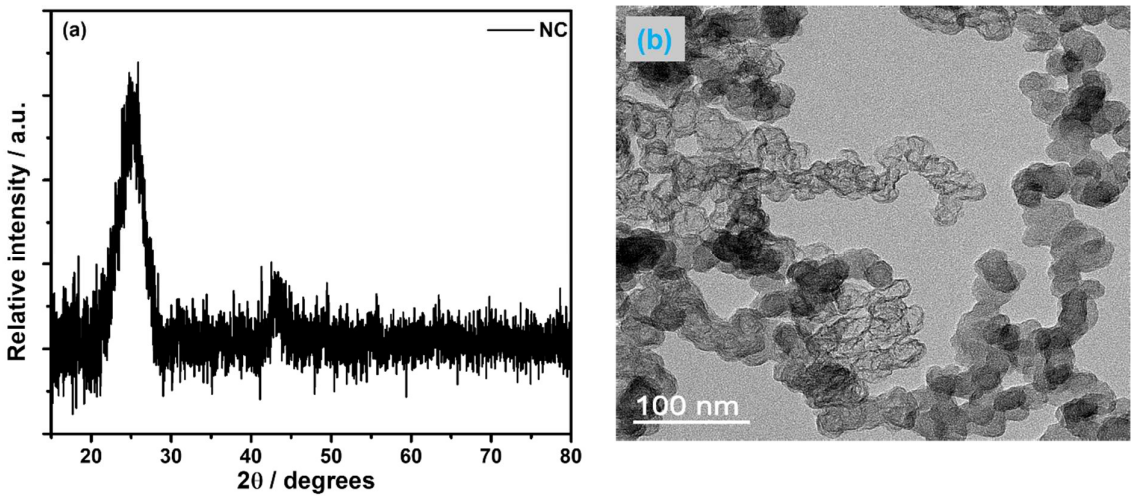

Fig. S6. Structural and morphological analysis of N-doped carbon (a) PXRD and (b) HR-TEM image

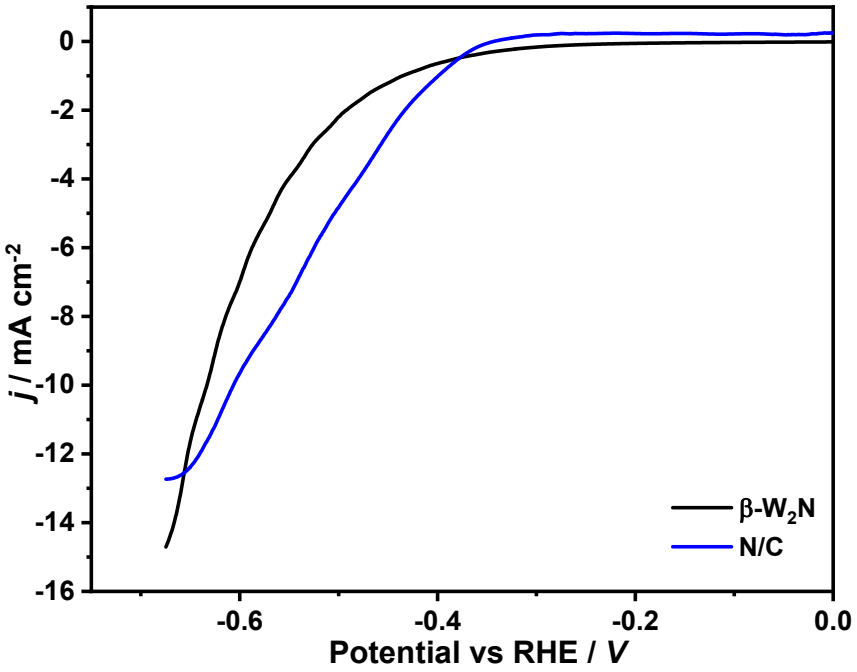

Fig. S7. Linear sweep voltammogram of β-W_2N and N/C control samples carried out in 0.5 M H_2SO_4 as electrolyte

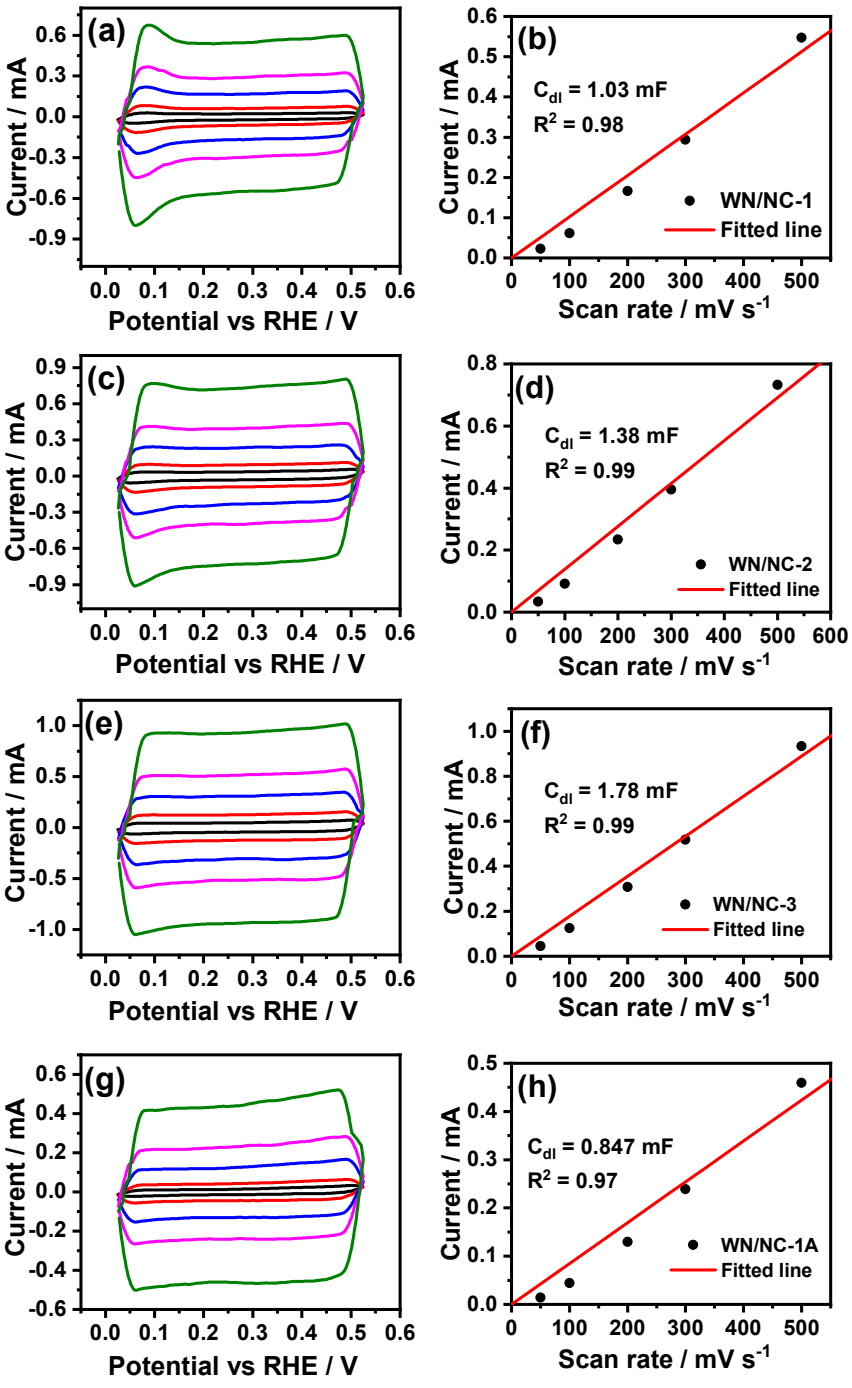

Fig. S8. Cyclic voltammetry in different scan rates (black: 50 mVs^{-1}; red: 100 mVs^{-1}; green: 200 mVs^{-1}; blue: 300 mVs^{-1}; magenta: 500 mVs^{-1};) and current vs scan rate plot of WN/NC-1 (a & b), WN/NC-2 (c & d), WN/NC-3 (e & f) and WN/NC-1A (g & h) in 0.5 M H_2SO_4 as electrolyte.

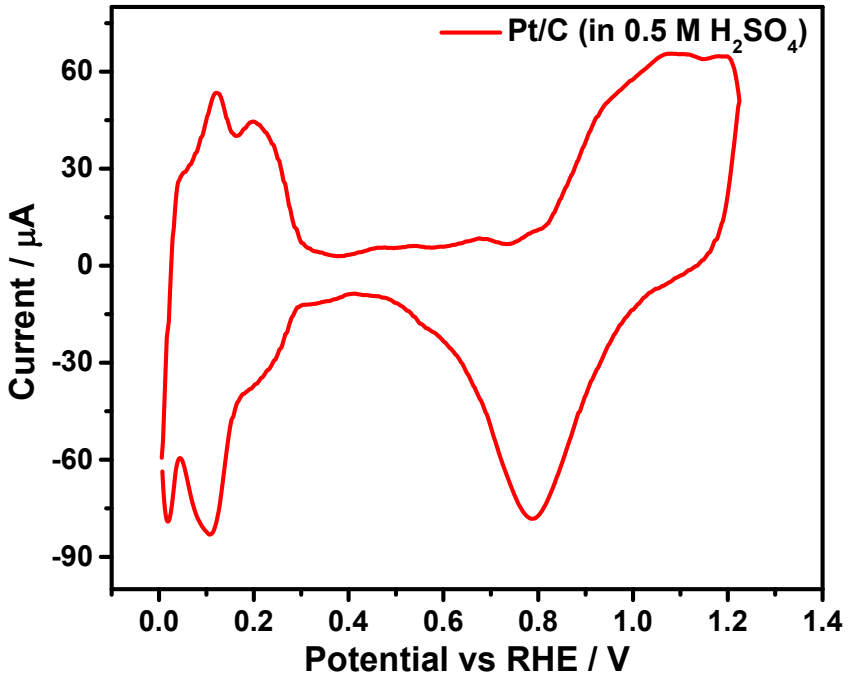

Fig. S9. Cyclic voltammogram of Pt/C catalyst at scan rate of 0.05 V s^{-1} in 0.5 M H_2SO_4 electrolyte

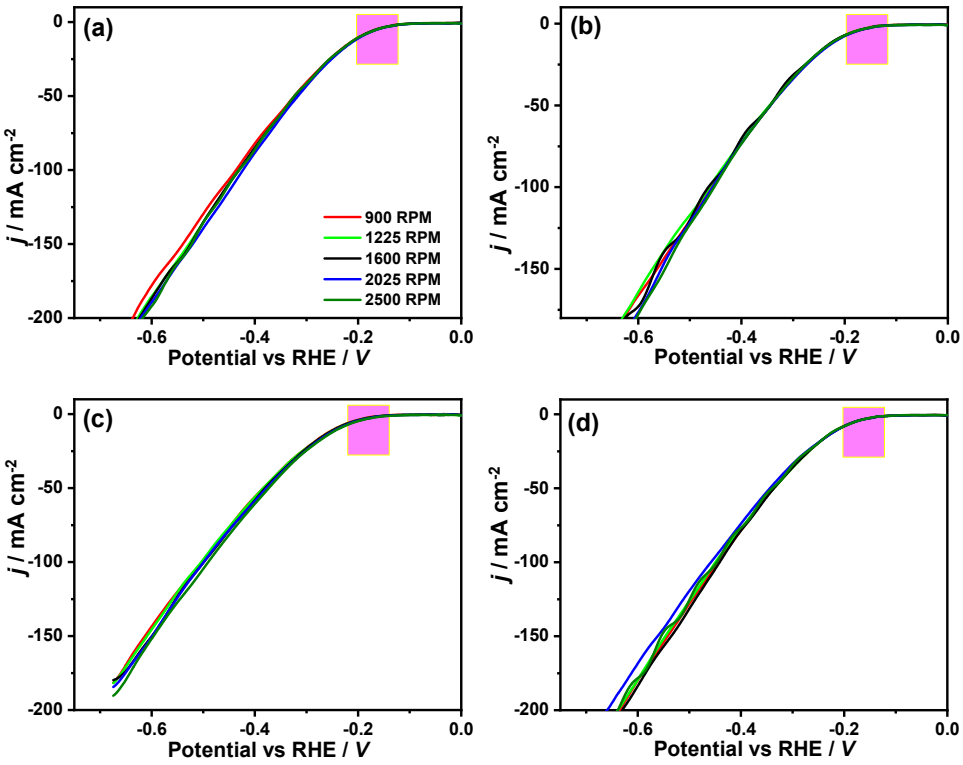

Fig. S10. Linear sweep voltammograms of (a) WN/NC-1, (b) WN/NC-2, (c) WN/NC-3 and (d) WN/NC-1A catalysts on various rotational speeds in 0.5 M H_2SO_4 as electrolyte

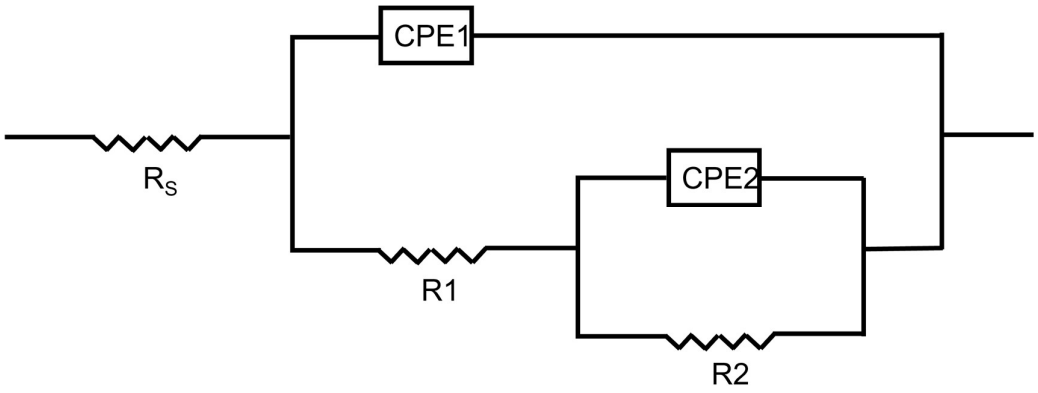

Fig. S11. Armstrong-Henderson equivalent circuit modified with constant phase element for investigation of electrochemical impedance spectroscopy

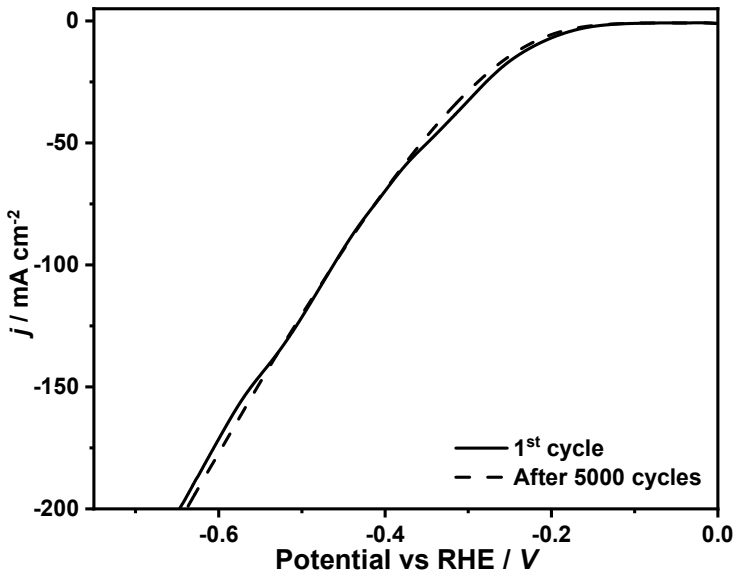

Fig. S12. Linear sweep voltammogram of WN/NC-1A catalyst before and after 5000 cyclic voltammetry cycles in HER carried out in 0.5 M H_2SO_4 as electrolyte

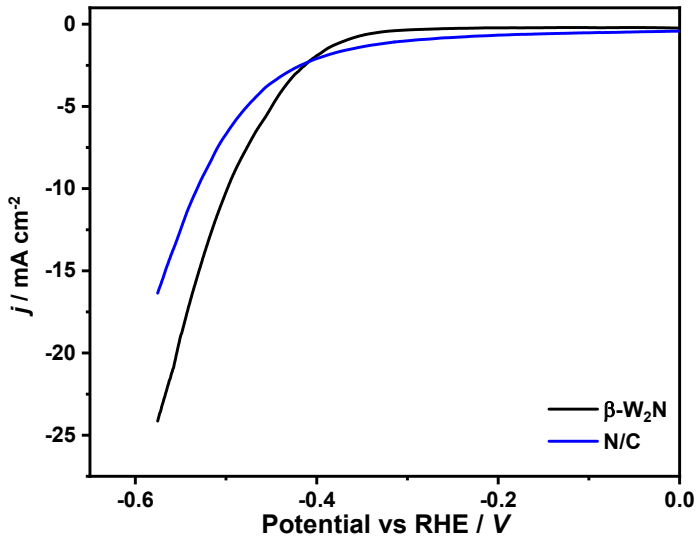

Fig. S13. Linear sweep voltammogram of β-W_2N and N/C control samples carried out in 1 M KOH as electrolyte

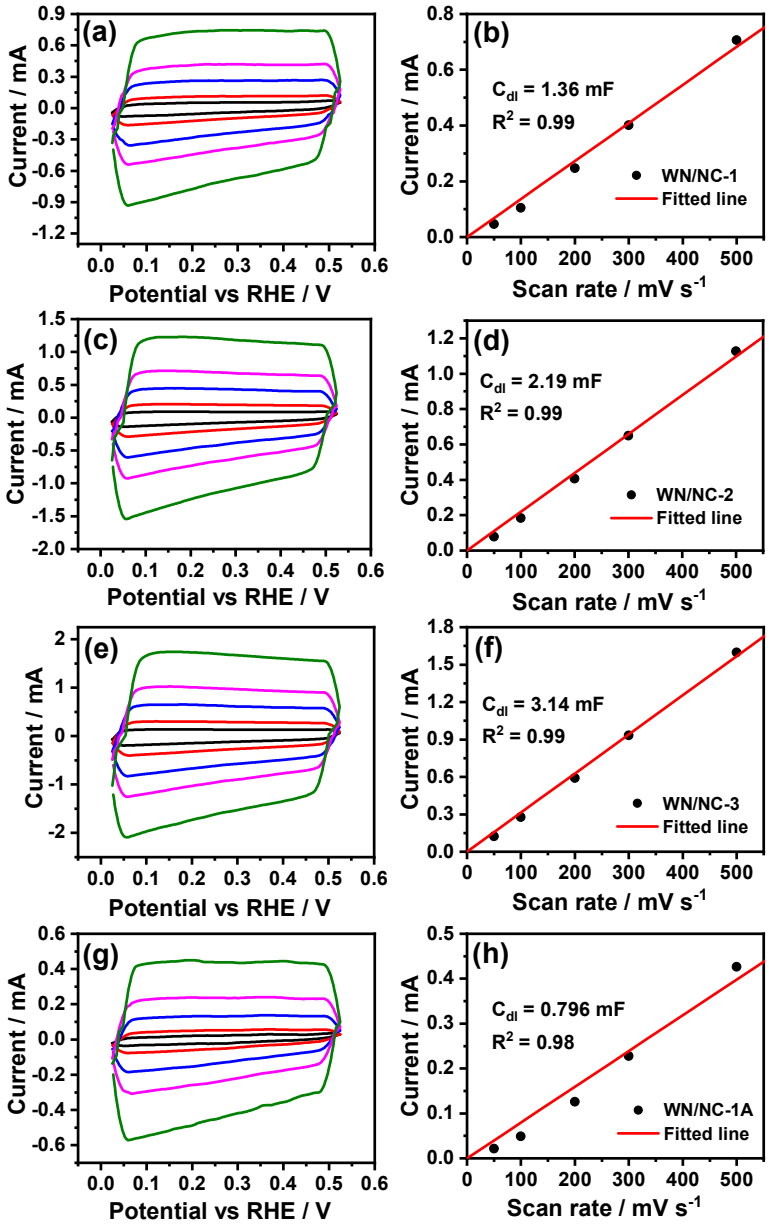

Fig. S14. Cyclic voltammetry in different scan rates (black: 50 mVs^{-1}; red: 100 mVs^{-1}; green: 200 mVs^{-1}; blue: 300 mVs^{-1}; magenta: 500 mVs^{-1};) and current vs scan rate plot of WN/NC-1 (a & b), WN/NC-2 (c & d), WN/NC-3 (e & f) and WN/NC-1A (g & h) in 1 M KOH as electrolyte.

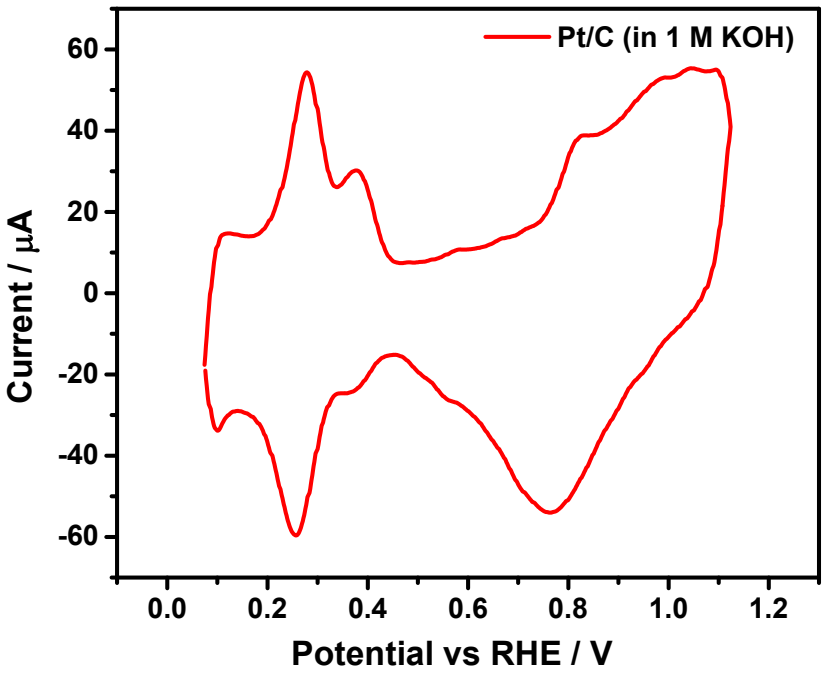

Fig. S15. Cyclic voltammogram of Pt/C catalyst at scan rate of 0.05 V s^{-1} in 1 M KOH as electrolyte

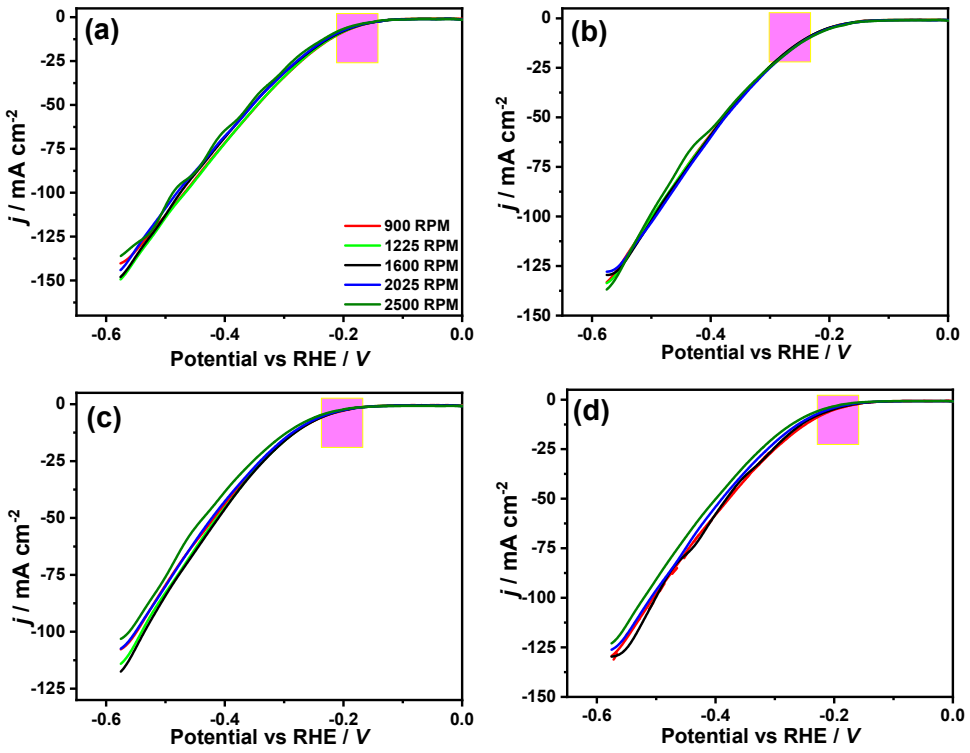

Fig. S16. Linear sweep voltammograms of (a) WN/NC-1, (b) WN/NC-2, (c) WN/NC-3 and (d) WN/NC-1A catalysts on various rotational speeds in N_2-saturated 1 M KOH electrolyte

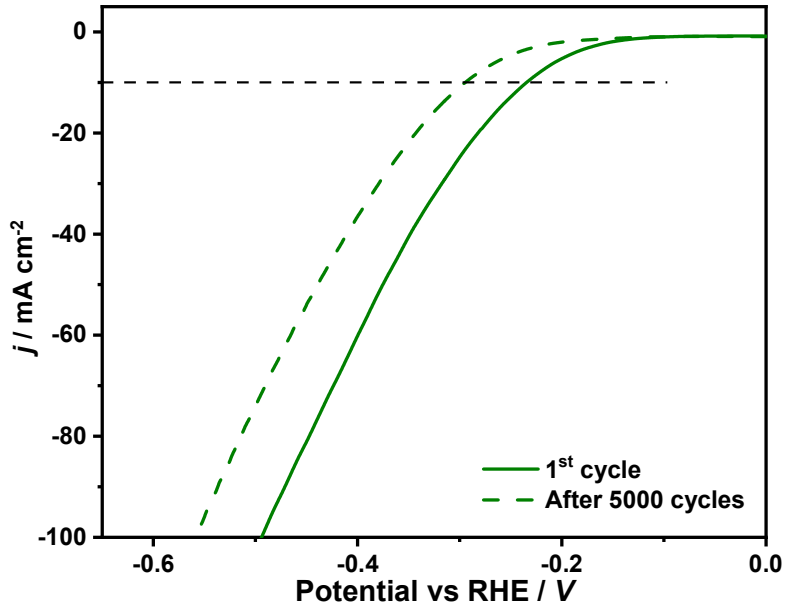

Fig. S17. Linear sweep voltammogram of WN/NC-1A catalyst before and after 5000 cyclic voltammetry cycles carried out in 1 M KOH as electrolyte

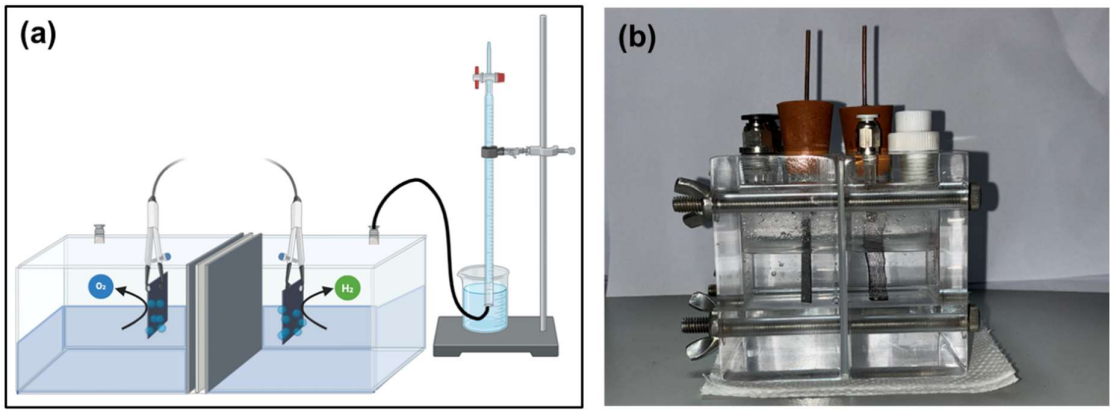

Fig. S18. (a)Typical pictorial representation of an eudiometry set-up to measure the volume of H_2 gas evolved from the water electrolyser and (b) the photographic image of the electrolyser.

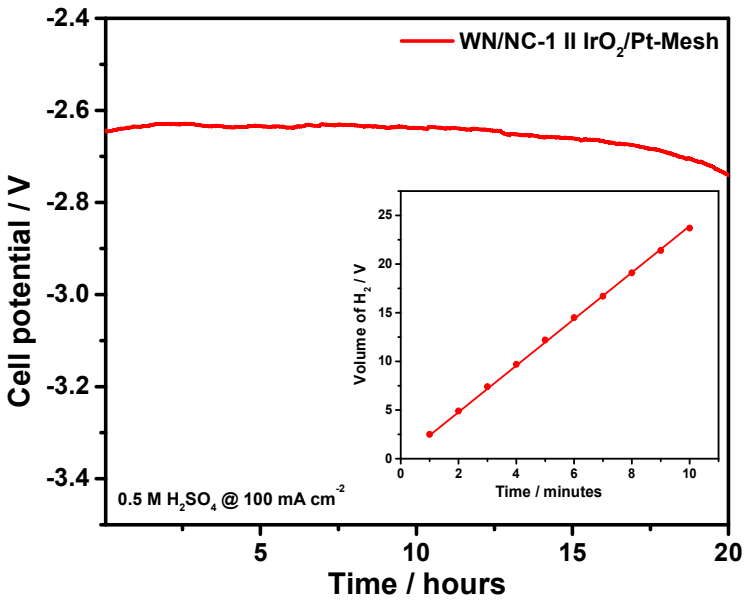

Fig. S19. Chronopotentiometry curve of WN/NC-1 catalyst employed as cathode in PEM water electrolyser at constant current density of 100 mA cm^{-2} with 0.5 M H_2SO_4 as electrolyte

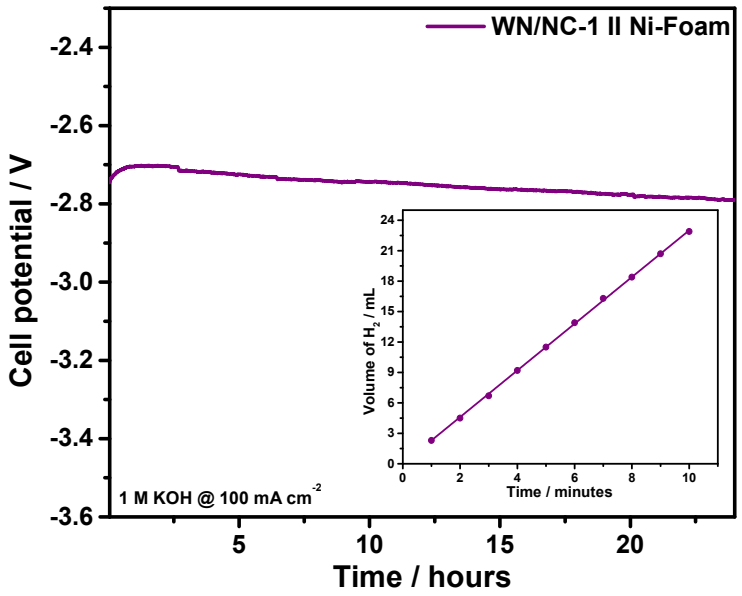

Fig. S20. Chronopotentiometry curve of WN/NC-1 catalyst employed as cathode in AEM water electrolyser at constant current density of 100 mA cm^{-2} with 1 M KOH as electrolyte

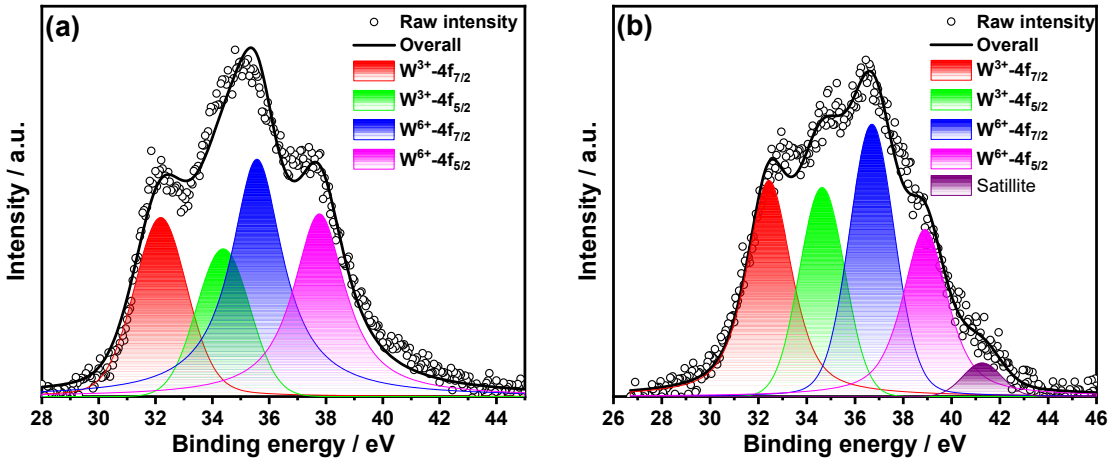

Fig. S21. The W-4f XPS of the WN/NC-1 after 100 hours of electrolysis in (a) 0.5 M H_2SO_4 and (b) 1 M KOH electrolytes.

Table S1. Parameters obtained from the analysis of the N_2-sorption isotherm of WN/NC catalysts

Compounds	S_{BET} ($m^2 g^{-1}$)	V_{BET} ($cm^3 g^{-1}$)	S_{micro} ($m^2 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)
WN/NC-1	128.43	0.263	-	-
WN/NC-2	321.16	0.426	47.87	0.024
WN/NC-3	480.22	0.546	99.36	0.048
WN/NC-1A	108.12	0.203	-	-

Table S2. The solution resistance (R_s), charge transfer resistance (R_{ct}) and pseudocapacitive resistance (R_{ps}) parameters obtained from Electrochemical impedance spectroscopy (EIS) technique for WN/NC catalysts in 0.5 M H_2SO_4 as electrolyte

Compounds	R_s (Ω)	R_{ct} (Ω)	R_{ps} (Ω)
WN/NC-1	5.4	18.02	0.351
WN/NC-2	5.4	25.54	0.124
WN/NC-3	5.5	26.48	0.977
WN/NC-1A	6.2	25.16	0.895

Table S3. The solution resistance (R_S), charge transfer resistance (R_{ct}) and pseudocapacitive resistance (R_{ps}) parameters obtained from Electrochemical impedance spectroscopy (EIS) technique for WN/NC catalysts in 1 M KOH as electrolyte

Compounds	R_S (Ω)	R_{ct} (Ω)	R_{ps} (Ω)
WN/NC-1	6.2	20.56	0.624
WN/NC-2	5.8	32.16	0.465
WN/NC-3	6.4	32.75	0.346
WN/NC-1A	6.2	34.19	0.122