Al, P-Co-doping and interface engineering synergistically boost the electrocatalytic performance of $WS_2/Ni_3S_2/NiS$ nanosheets heterostructure for an efficient hydrogen evolution reaction

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Supporting Information

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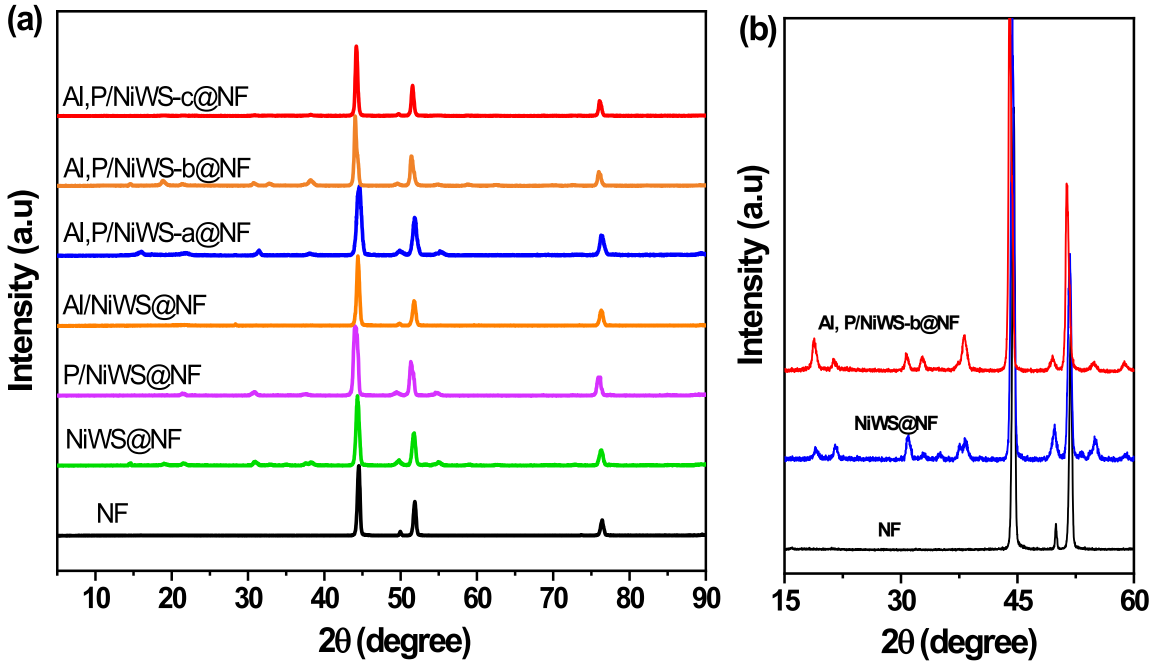

Fig. S1 **(a)** XRD patterns of the NF, NiWS@NF, Al/NiWS@NF, P/NiWS@NF, and Al, P/NiWS-x@NF samples. (b) XRD patterns of the NF, NiWS@NF, and Al, P/NiWS-b@NF.

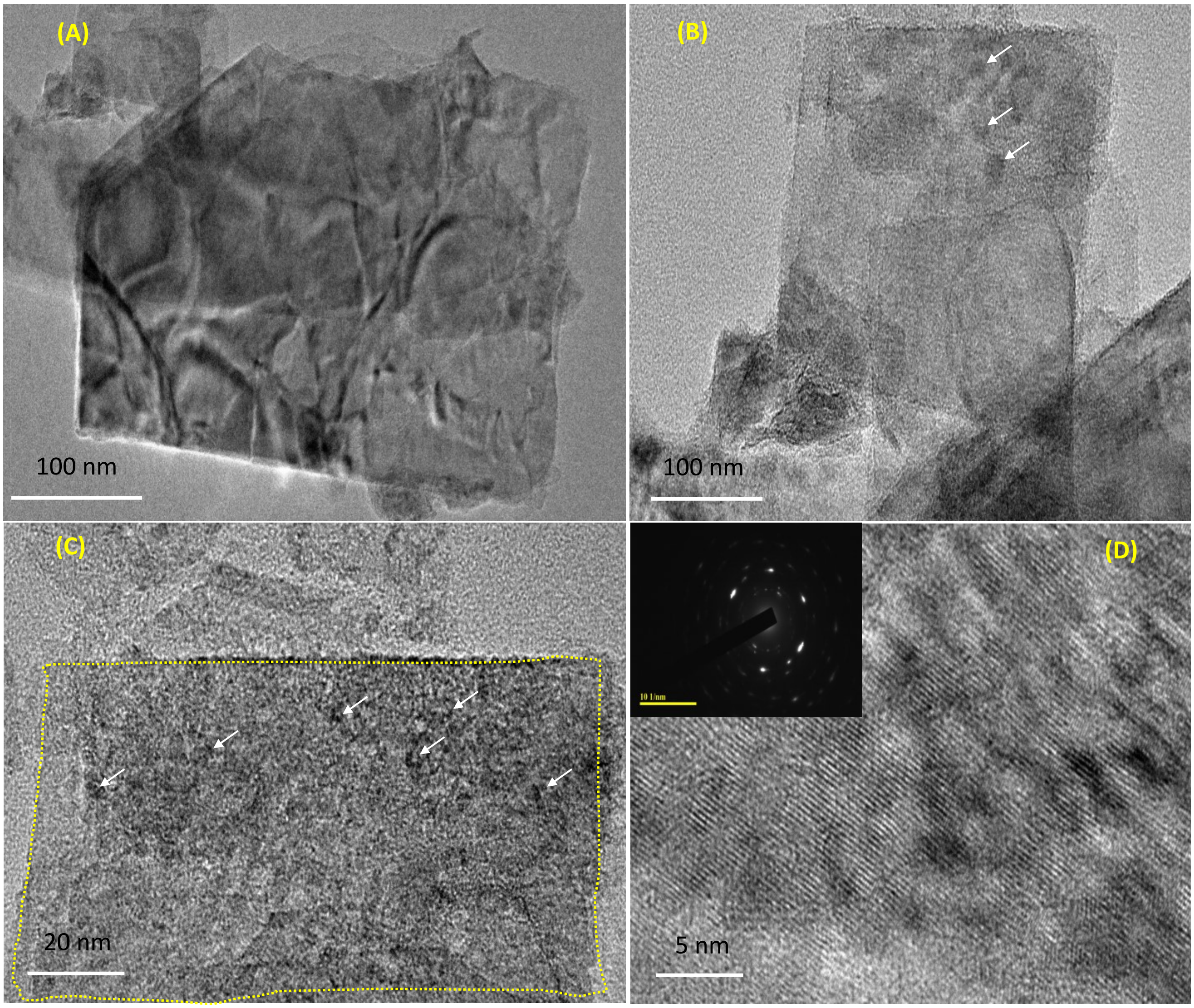

Fig. S2 HR-TEM images of Al, P/NiWS-b@NF sample (a-d), obtained by hydrothermal method, in site (d) selected area electron diffraction (SAED) pattern of Al, P/NiWS-b@NF.

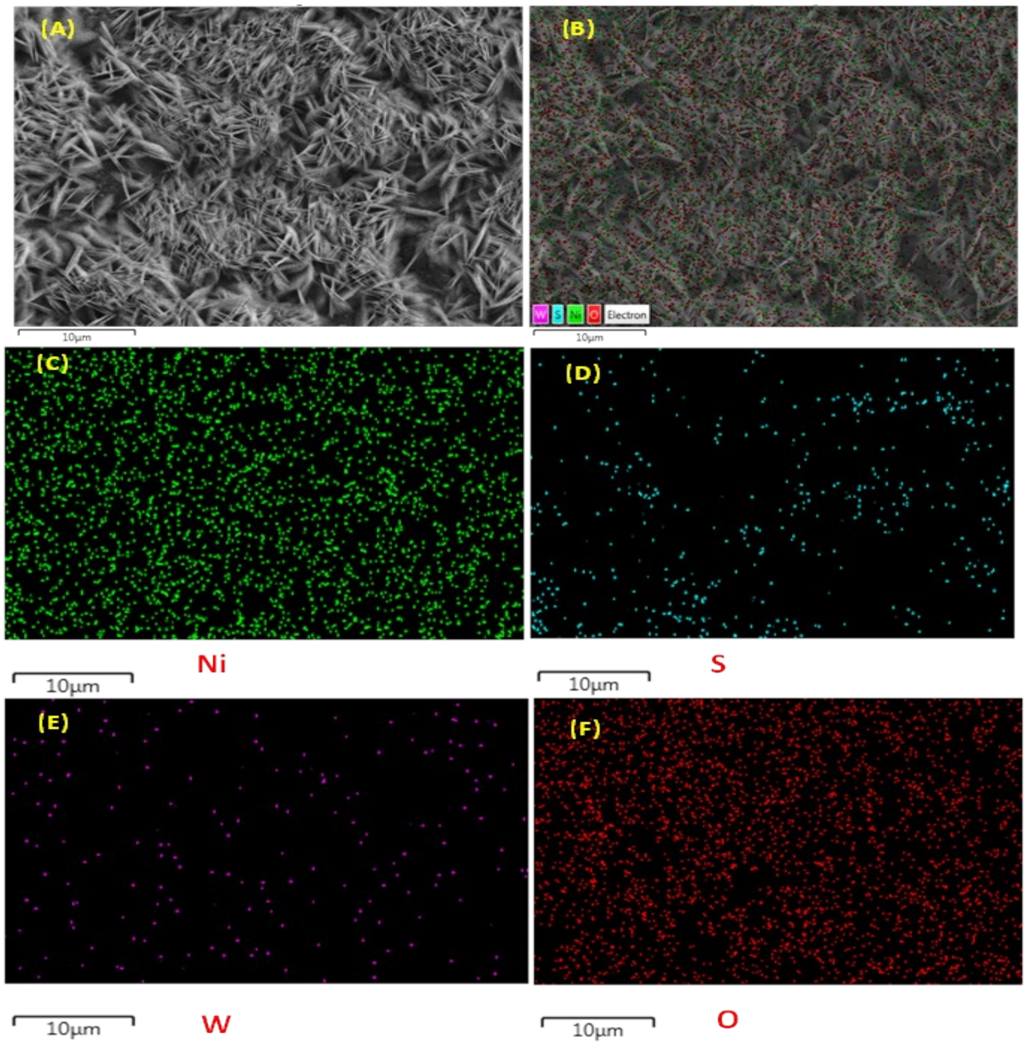

Fig. S3 (a and b) FE-SEM image and corresponding elemental mapping of NiWS@NF showing the presence of individual constituent elements: (c) Nickel (Ni), (d) Sulphur (S), (e) Tungsten (W), and (f) oxygen (O).

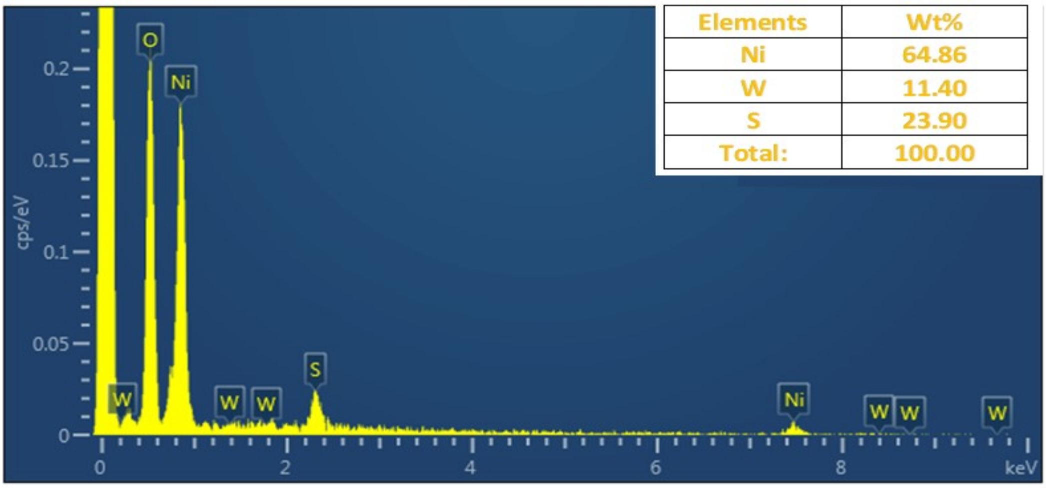

Fig. S4 EDS elemental analysis of NiWS@NF.

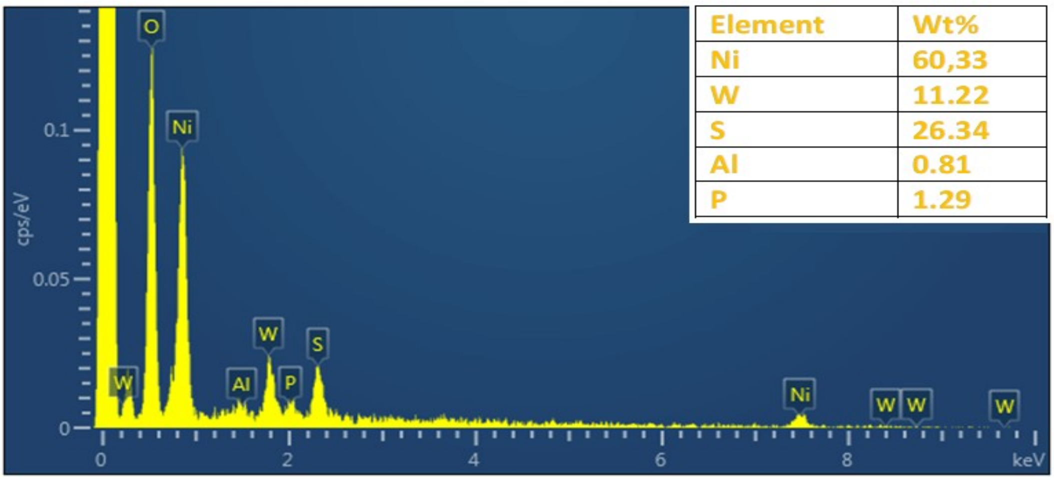

Fig. S5 EDS elemental analysis of Al, P/NiWS-b@NF.

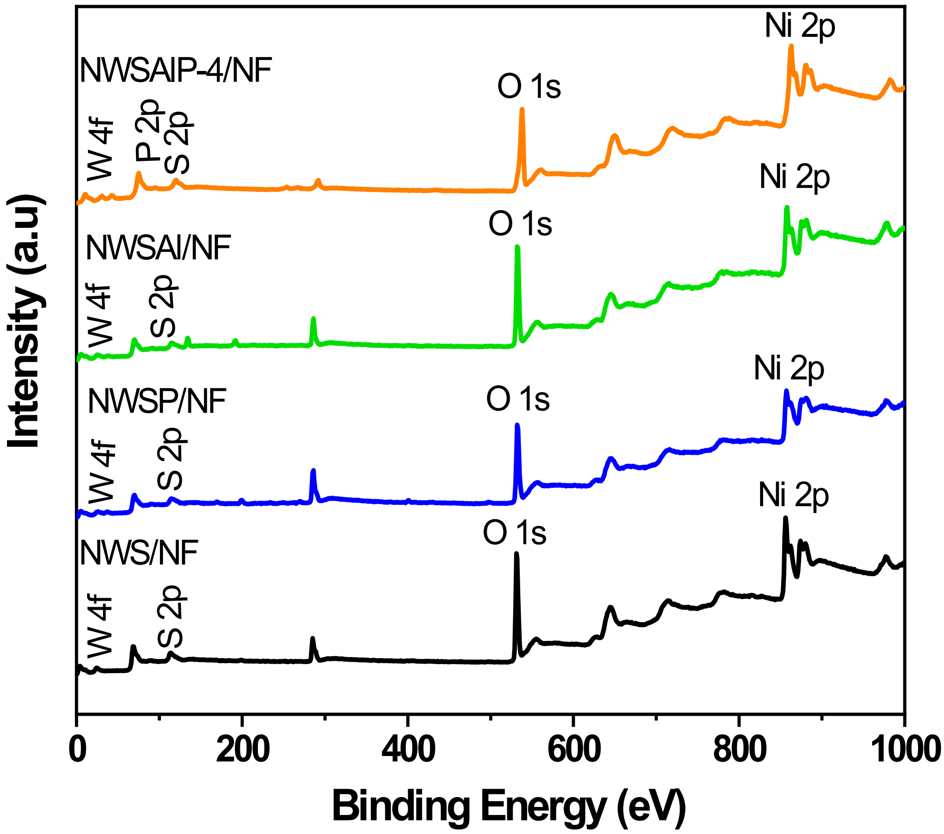

Fig. S6 X-ray photoelectron spectroscopy (XPS) spectrum analysis (a) Full XPS spectrum of NiWS@NF, Al/NiWS@NF, P/NiWS@NF, and Al, P/NiWS@NF.

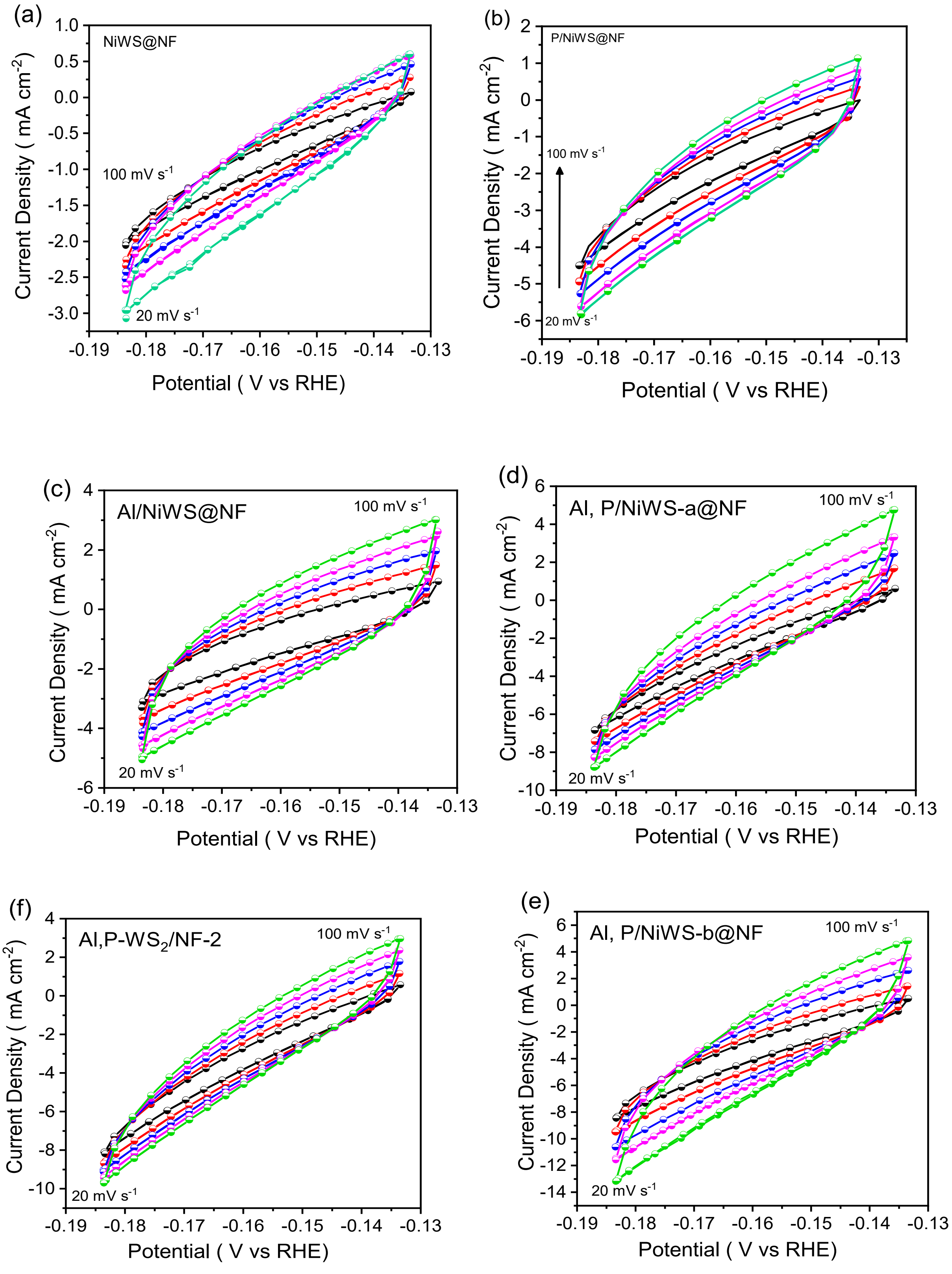

Fig. S7 (a-f) CV curves of as prepared samples at different scan rates.

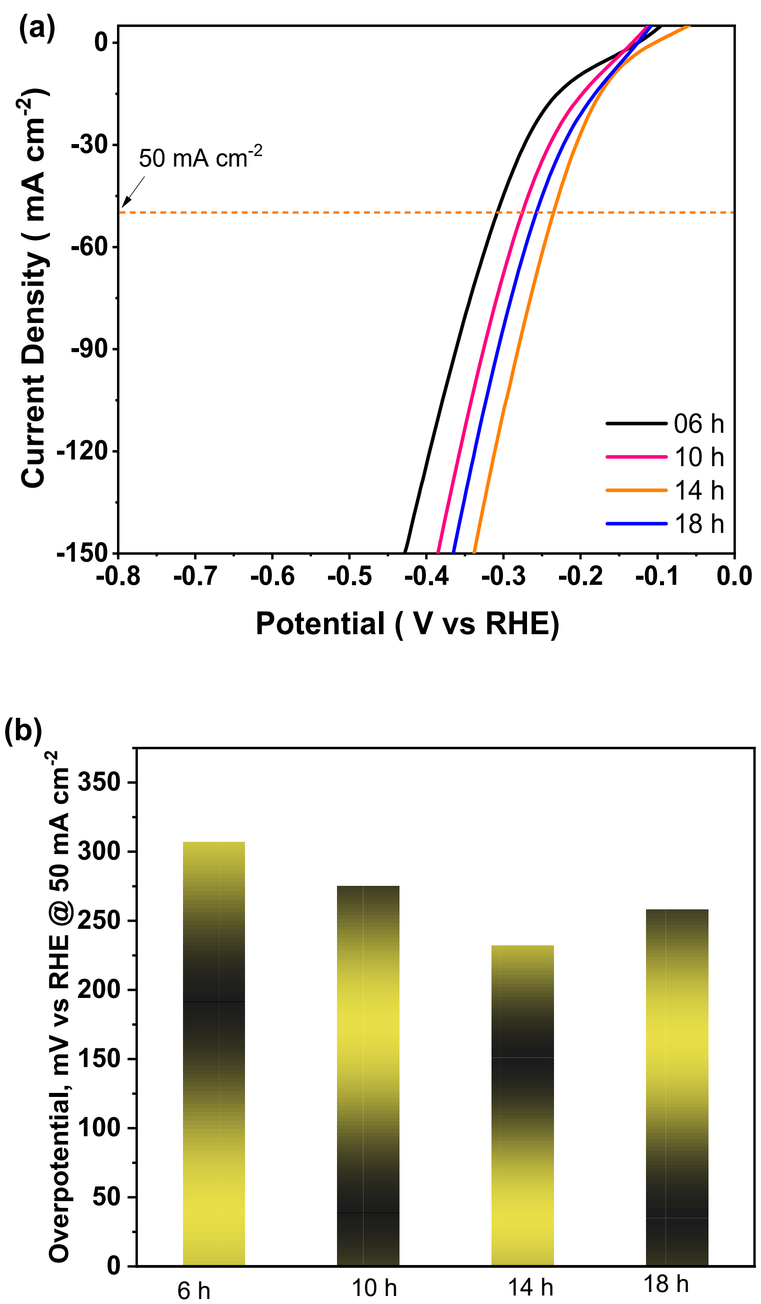

Fig. S8 (a) LSV of Al, P/NiWS-b@NF at different time in 0.5 M H_2SO_4 (b) Comparison of the overpotential (η_{50}) of Al, P/NiWS-b@NF sample at different times.

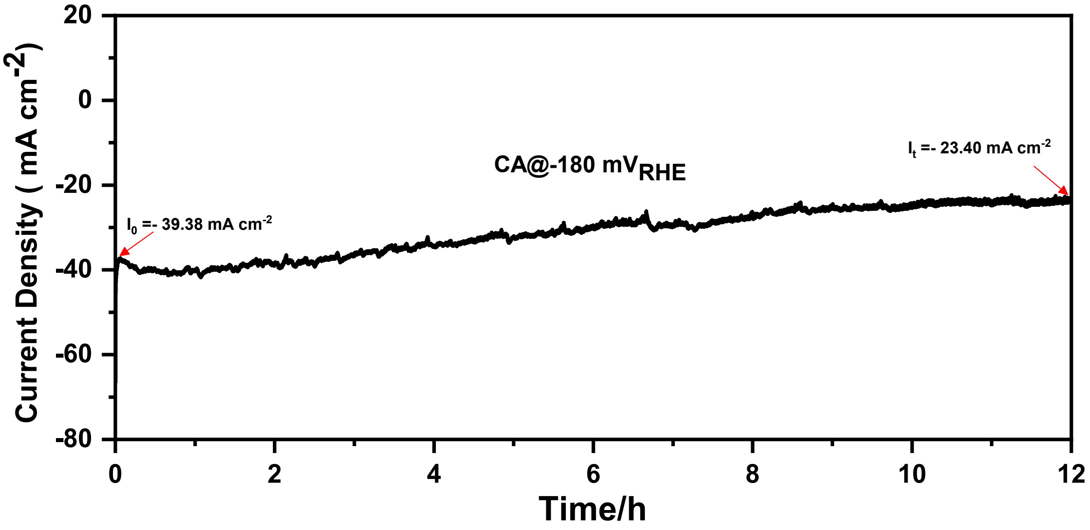

Fig. S9 The chronoamperometry of 20 % Pt/C@NF electrode measured for 12 hours at -180 mV_{RHE} in 0.5 M H_2SO_4. According to Fig. S9, commercial 20 % Pt/C showed a 59.40 % drop in current density after continuous electrocatalysis for 12 h in 0.5 M H_2SO_4 electrolyte.

Note S1.

The calculation of mass activity, and turnover frequency (TOF) in this work is based on literature published by Anantharaj S, *et al.* [1], and the details are shown below.

The values of mass activity (A g^{-1}) were calculated from the catalyst loading m (0.2 mg cm_{geo}^{-2}) and the measured current density j (mA cm_{geo}^{-2}) at η = -0.300 V:

$$mass\ activity = \frac{j}{m}$$

The values of turnover frequency (TOF) were calculated by assuming that every metal atom is involved in the catalysis (lower TOF limits were calculated):

$$TOF = \frac{jS_{geo}}{2F.n}$$

Here, j (mA cm_{geo}^{-2}) is the measured current density at η = 0.300 V, S_{geo} (1 cm^2) is the surface area of Nickle Foam (NF) electrode, the number 2 means 2 electrons per mole of H_2, F is Faraday's constant (96485.3 C mol^{-1}), and n is the moles of the metal atom on the electrode calculated from m and the molecular weight of the coated catalysts.

Table S1. Summary of the HER catalytic activities for the studied catalysts

Catalysts	Mass activity (A g^{-1})	Turnover frequency (s^{-1})
NF	35	0.045
NiWS@NF	112	0.146
P/NiWS@NF	227	0.315
Al/NiWS@NF	367	0.513
Al,P-b/NiWS@NF	575	0.804
Pt/C	760	0.772

[1] Anantharaj, Sengeni, Pitchiah Esakki Karthik, and Suguru Noda. "The significance of properly reporting turnover frequency in electrocatalysis research." *Angewandte Chemie International Edition* 60, no. 43 (2021): 23051-23067.