

## Supporting information

### **Boosting alkaline hydrogen evolution performance with alkaline electro-activated ultrafine candied haws-shaped PtW<sub>Ni</sub> nanoalloys**

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†. Yanfei Zhong, Liping Huang and Qianqian Wu completed the same workload.

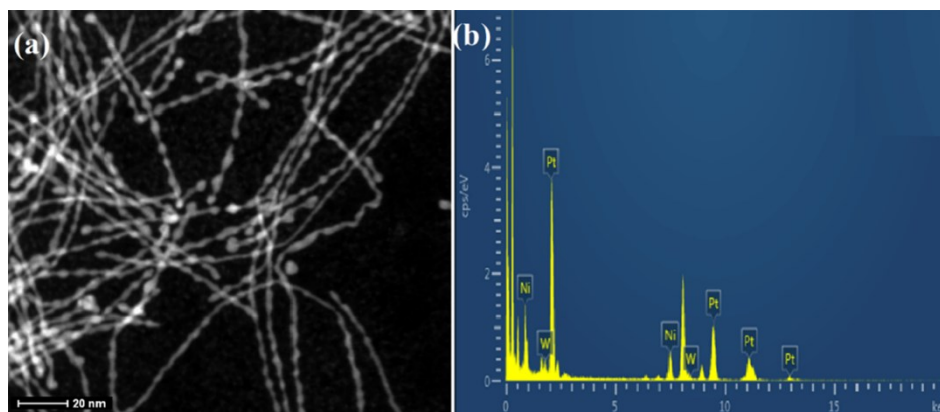


Fig. S1 (a) TEM image and (b) EDS spectrum of the PtWNI NAs

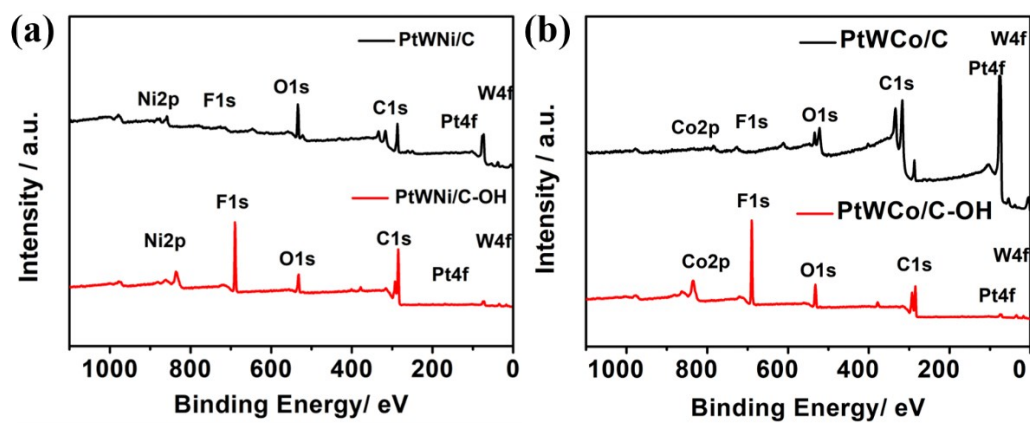


Fig. S2 Comparison of XPS survey spectra of the (a) PtWNI/C NAs (b) PtWCo/C NAs before and after the electrochemical test.

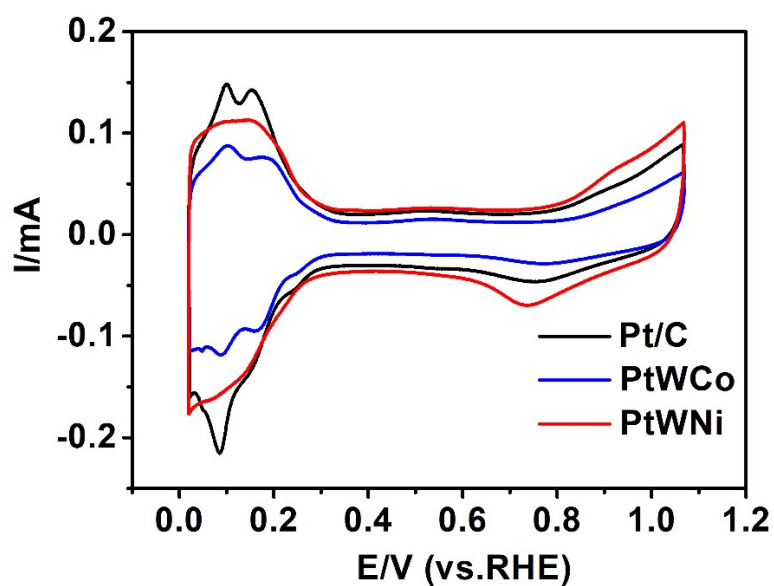


Fig. S3 CV curves of PtWNI NAs, PtWCo NAs and commercial Pt/C conducted in 0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution at the scanning rate of  $100 \text{ mV s}^{-1}$ .

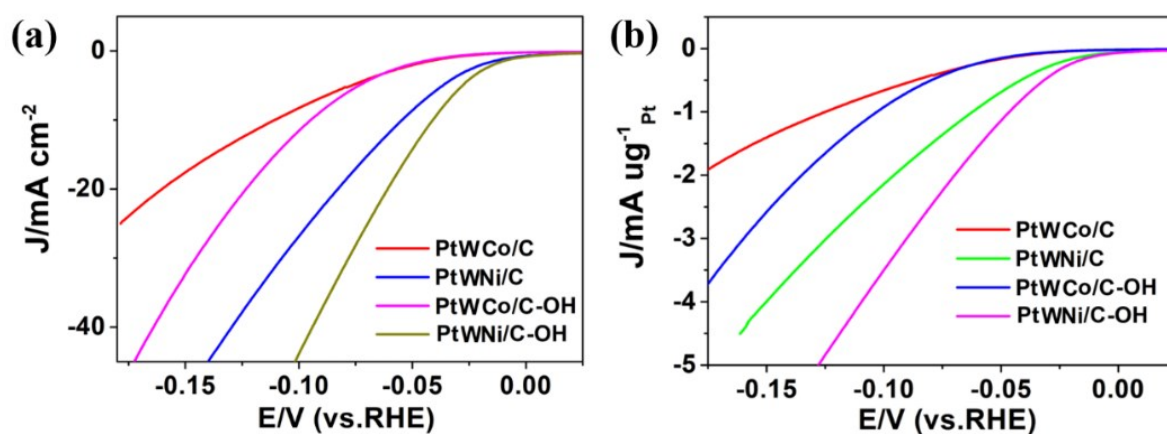


Fig. S4 HER polarization curves of the PtWNI/C and PtWCo/C catalysts before and after electrochemical activation in 1 M KOH electrolyte. ECSA normalized (a) and Pt mass loading normalized (b) HER LSV results at a scan rate of  $5 \text{ mV s}^{-1}$ .

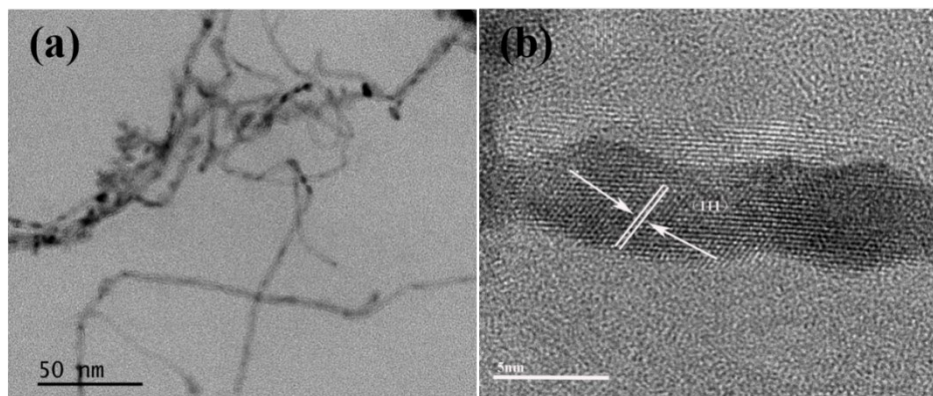


Fig. S5 (a) TEM image and (b) HRTEM image of PtWNI NAs loaded on Vulcan carbon after electrochemical activation in 1 M KOH.

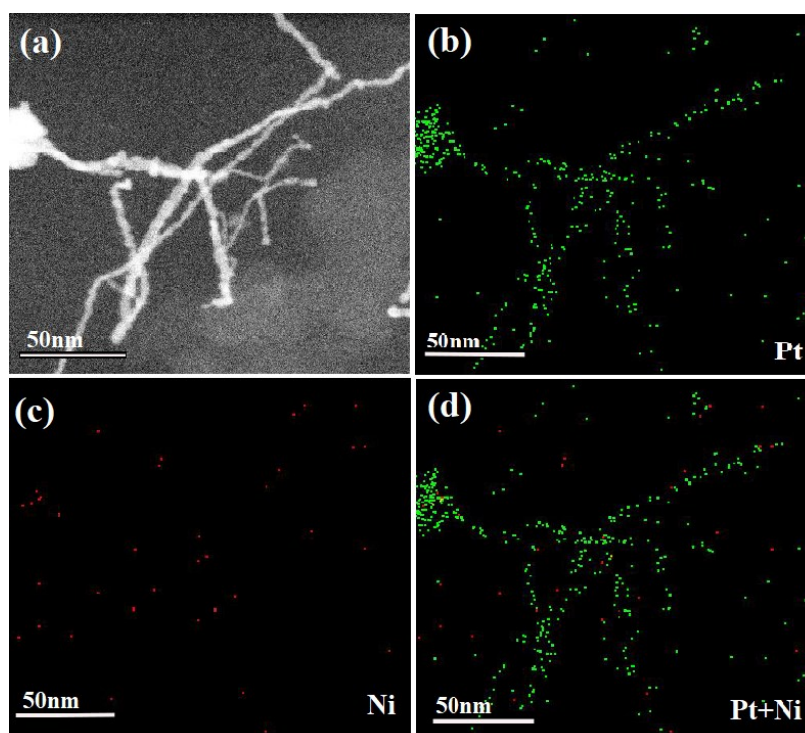


Fig. S6 EDS mapping of PtWNI NAs loaded on Vulcan carbon after electrochemical activation in 1 M KOH.

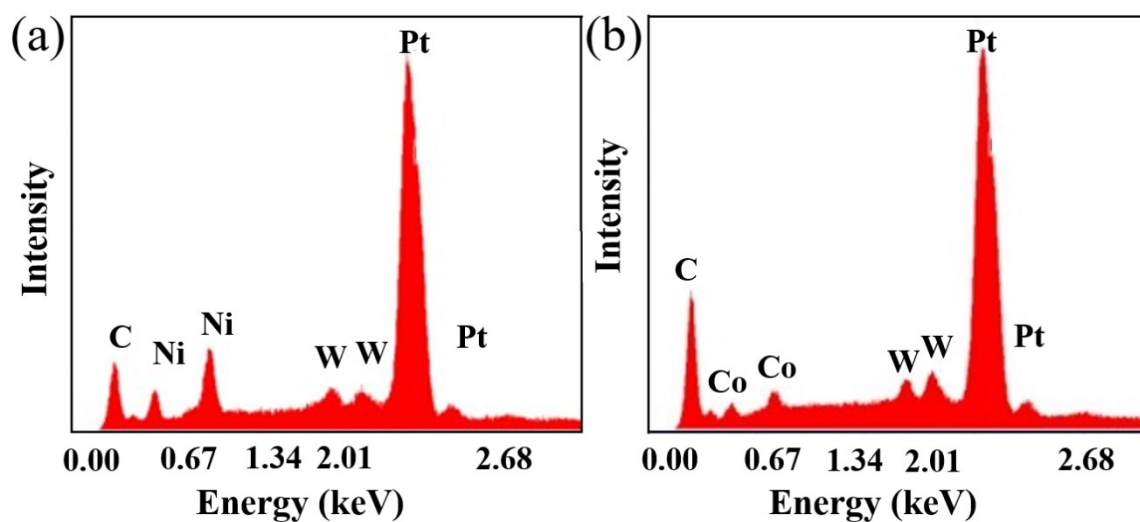


Fig. S7 EDS spectra of the PtWNI NAs (a) and PtWCo NAs (b) after the CV cycles.

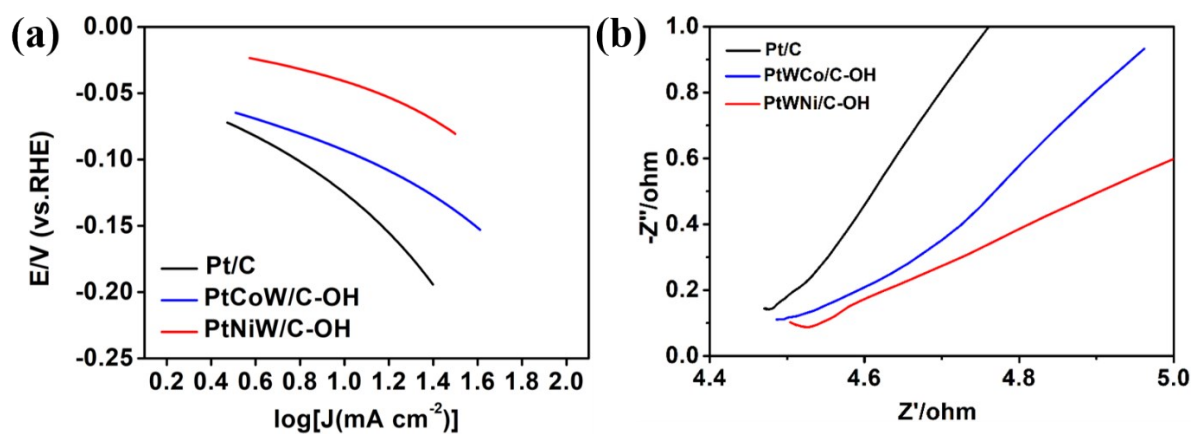


Fig. S8 The corresponding Tafel plots (a) and (b) Nyquist plots of PtWCo/C-OH, PtWNI/C-OH and Pt/C in  $\text{N}_2$ -saturated 1 M KOH solution at 1600 rpm.

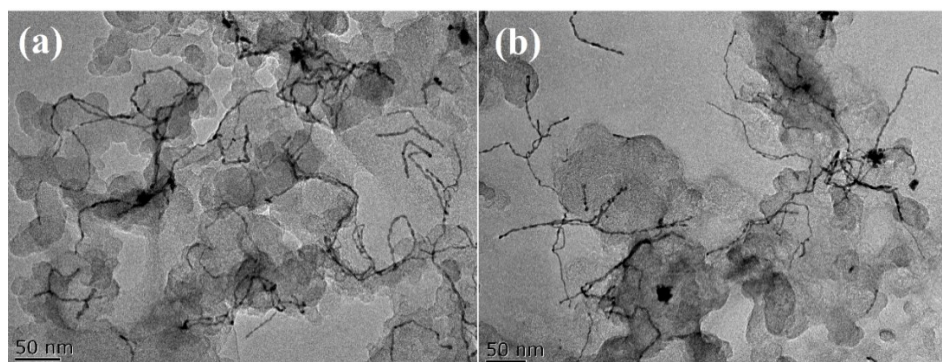


Fig. S9 TEM images of the PtWNI NAs loaded on Vulcan carbon (a) before and (b) after electrochemical test.

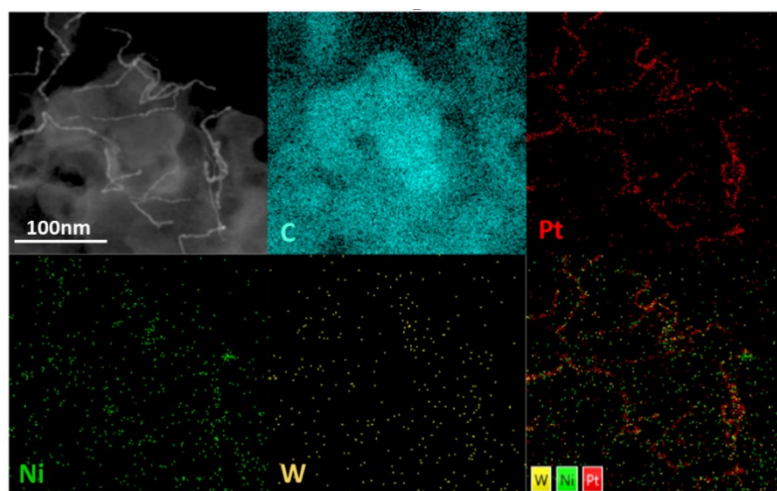


Fig. S10 TEM image and EDS elemental mapping images (Pt: red, Ni: green, W: yellow, C: blue) of the PtWNi NAs after electrochemical test.

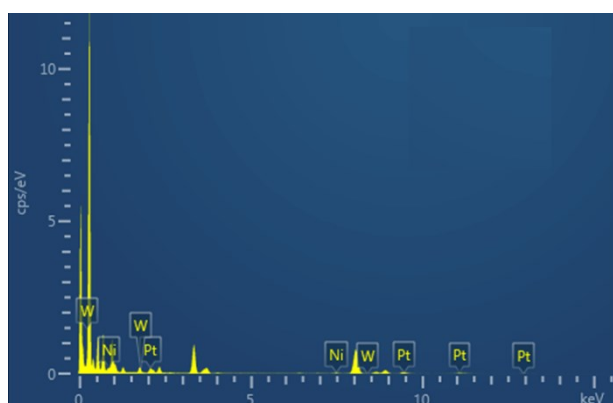


Fig. S11 EDS spectrum of the PtWNi NAs after electrochemical test.