## **Supporting Information**

## Ternary platinum-copper-nickel nanoparticles anchored to hierarchical carbon supports as free-standing hydrogen evolution electrodes

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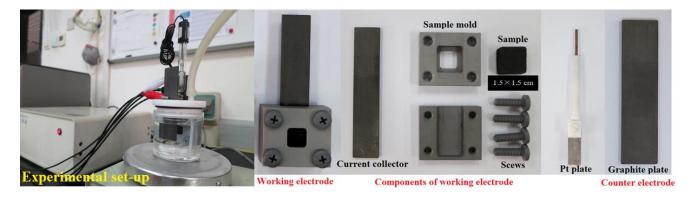
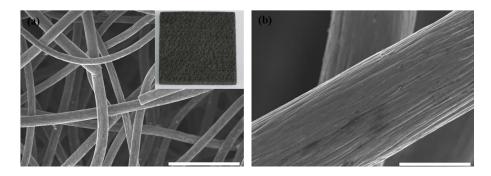
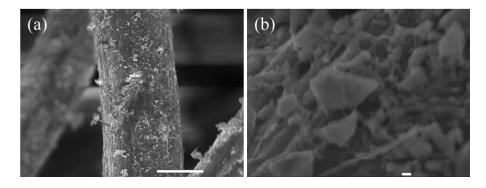


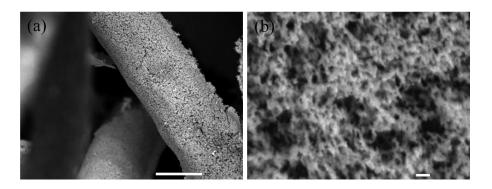
Figure S1 Experimental set-up of electrochemical measurements.



**Figure S2** FESEM micrographs of pristine carbon felt (Inset in (a) is an optical image of a piece of  $5 \times 5 \times 0.5$  cm carbon felt sheet.) Scale bars,  $100 \, \mu m$  (a),  $10 \, \mu m$  (b)



**Figure S3** FESEM micrographs of nickel-copper oxalates decorated carbon felt. Scale bars,  $10 \mu m$  (a), 100 nm (b).



**Figure S4** FESEM micrographs of metallic nickel-copper decorated carbon felt. Scale bars, 10  $\mu$ m (a), 100 nm (b).

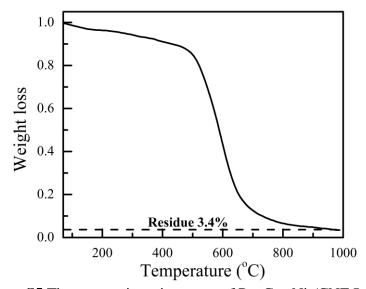
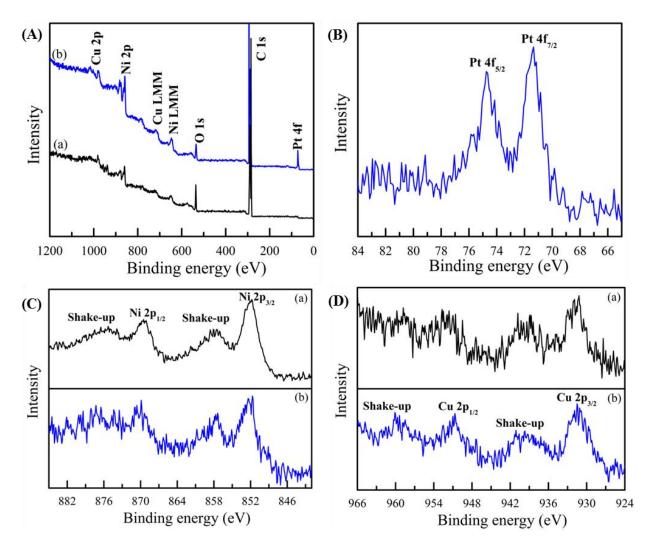
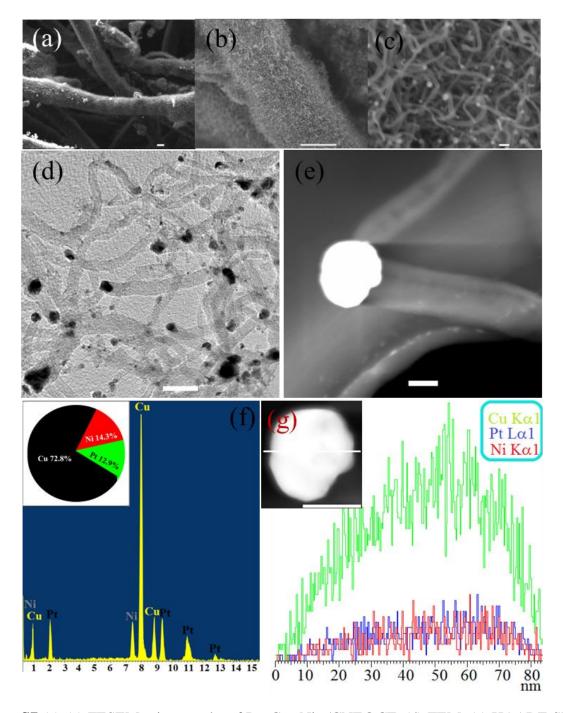


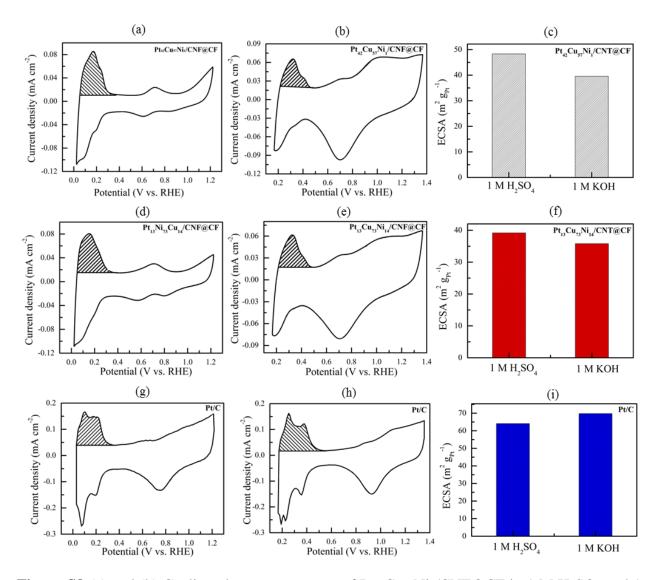
Figure S5 Thermogravimetric curves of  $Pt_{42}Cu_{57}Ni_1/CNF@CF$ .



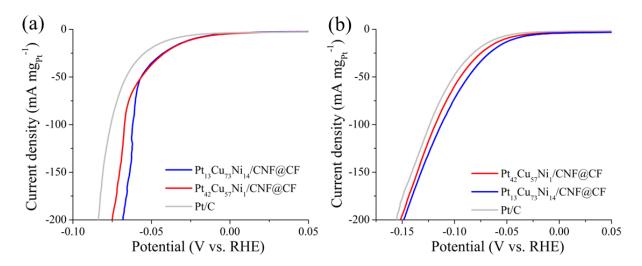
**Figure S6** (A) Survey spectra, XPS profiles of (B) Pt 4f, (C) Ni 2p and (D) Cu 2p in (a)  $Ni_{65}Cu_{35}/CNF@CF$  and (b)  $Pt_{13}Cu_{73}Ni_{14}/CNF@CF$ 



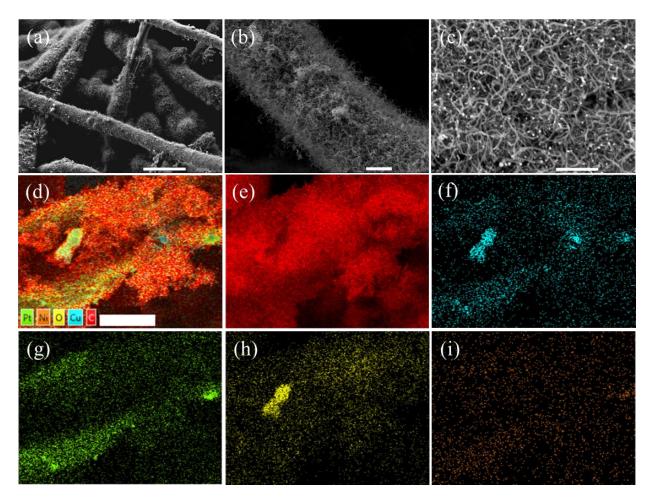
**Figure S7** (a)-(c) FESEM micrographs of  $Pt_{13}Cu_{73}Ni_{14}/CNF@CF$ , (d) TEM, (e) HAADF-STEM micrographs of isolated  $Pt_{13}Cu_{73}Ni_{14}/CNF@CF$ , (f) EDS profile of  $Pt_{13}Cu_{73}Ni_{14}$  NPs (inset in (f), atomic composition of  $Pt_{13}Cu_{73}Ni_{14}$  NPs), (g) line scan and elemental distribution of a  $Pt_{13}Cu_{73}Ni_{14}$  NP. Scale bars, 10  $\mu$ m (a, b), 100 nm (c), 200 nm (d), 50 nm (e) and (g)



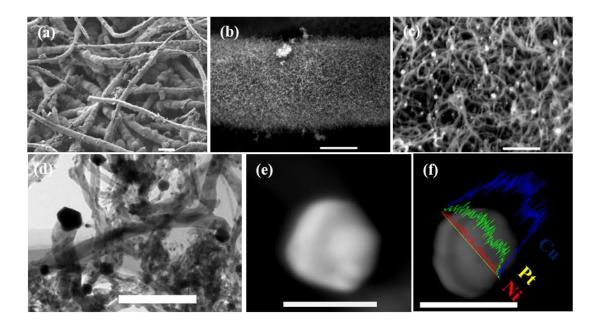
**Figure S8** (a) and (b) Cyclic voltammetry curves of  $Pt_{42}Cu_{57}Ni_1/CNF@CF$  in 1 M  $H_2SO_4$  and 1 M KOH with a can rate of 50 mV  $s^{-1}$ , respectively, and (c) ECSA values of  $Pt_{42}Cu_{57}Ni_1/CNF@CF$  in 1 M  $H_2SO_4$  and 1 M KOH; (d) and (e) cyclic voltammetry curves of  $Pt_{13}Cu_{73}Ni_{14}/CNF@CF$  in 1 M  $H_2SO_4$  and 1 M KOH with a can rate of 50 mV  $s^{-1}$ , respectively, and (f) ECSA values of  $Pt_{13}Cu_{73}Ni_{14}/CNF@CF$  in 1 M  $H_2SO_4$  and 1 M KOH; (g) and (h) cyclic voltammetry curves of Pt/C in 1 M  $Pt_2SO_4$  and 1 M KOH with a can rate of 50 mV  $pt_3$ 0 mV  $pt_4$ 1, respectively, and (i) ECSA values of Pt/C in 1 M  $Pt_4SO_4$  and 1 M KOH.



**Figure S9** (a) and (b) Pt-mass normalized polarization curves of catalysts in 1 M  $H_2SO_4$  and 1 M KOH, respectively.



**Figure S10** (a)-(c) FESEM micrographs of spent  $Pt_{13}Cu_{73}Ni_{14}/CNF@CF$  in 1 M  $H_2SO_4$ , (d) overall EDS micrograph, (e)-(i) elemental mapping micrographs of carbon, copper, platinum, oxygen, and nickel, respectively. Scale bar, 10  $\mu$ m.



**Figure S11** (a)-(c) FESEM micrographs of spent  $Pt_{42}Cu_{57}Ni_1/CNF@CF$  in 1 M  $H_2SO_4$ , (d) TEM micrograph of isolated  $Pt_{42}Cu_{57}Ni_1/CNF@CF$ , (e) high-resolution HAADF-STEM micrograph of a typical  $Pt_{42}Cu_{57}Ni_1$  NP, (f) line scan and elemental distribution of a  $Pt_{42}Cu_{57}Ni_1$  NP. Scale bars, 100  $\mu$ m (a), 10  $\mu$ m (b), 1  $\mu$ m (c) and (d), 100 nm (e) and (f)