Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Galvanic-replacement Mediated Synthesis of Copper-Nickel Nitrides as Electrocatalyst for Hydrogen Evolution Reaction

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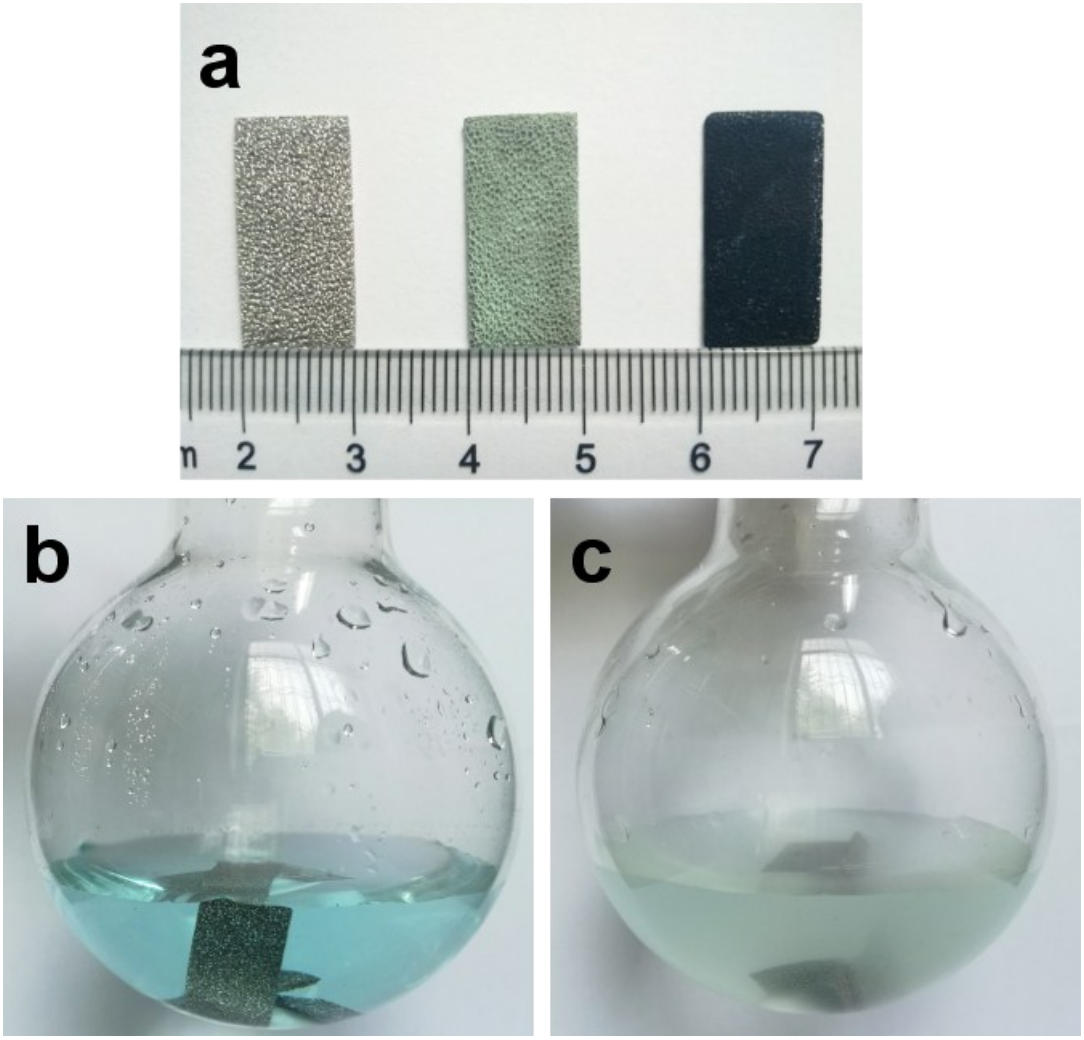


Fig S1. (a) Optical images of pristine Ni foam, Cu_2O@$Ni(OH)_2$/NF and $Cu_xNi_{4-x}N$/NF. Images of reactor (b) before and (c) after the wet synthesis process.

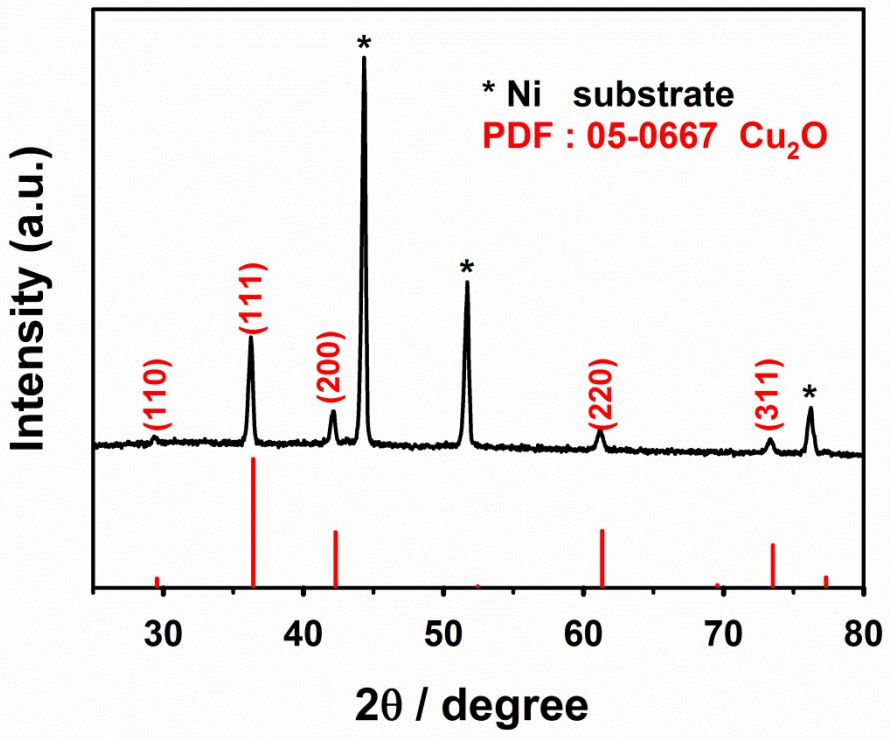


Fig S2. XRD pattern of Cu_2O@$Ni(OH)_2$/NF.

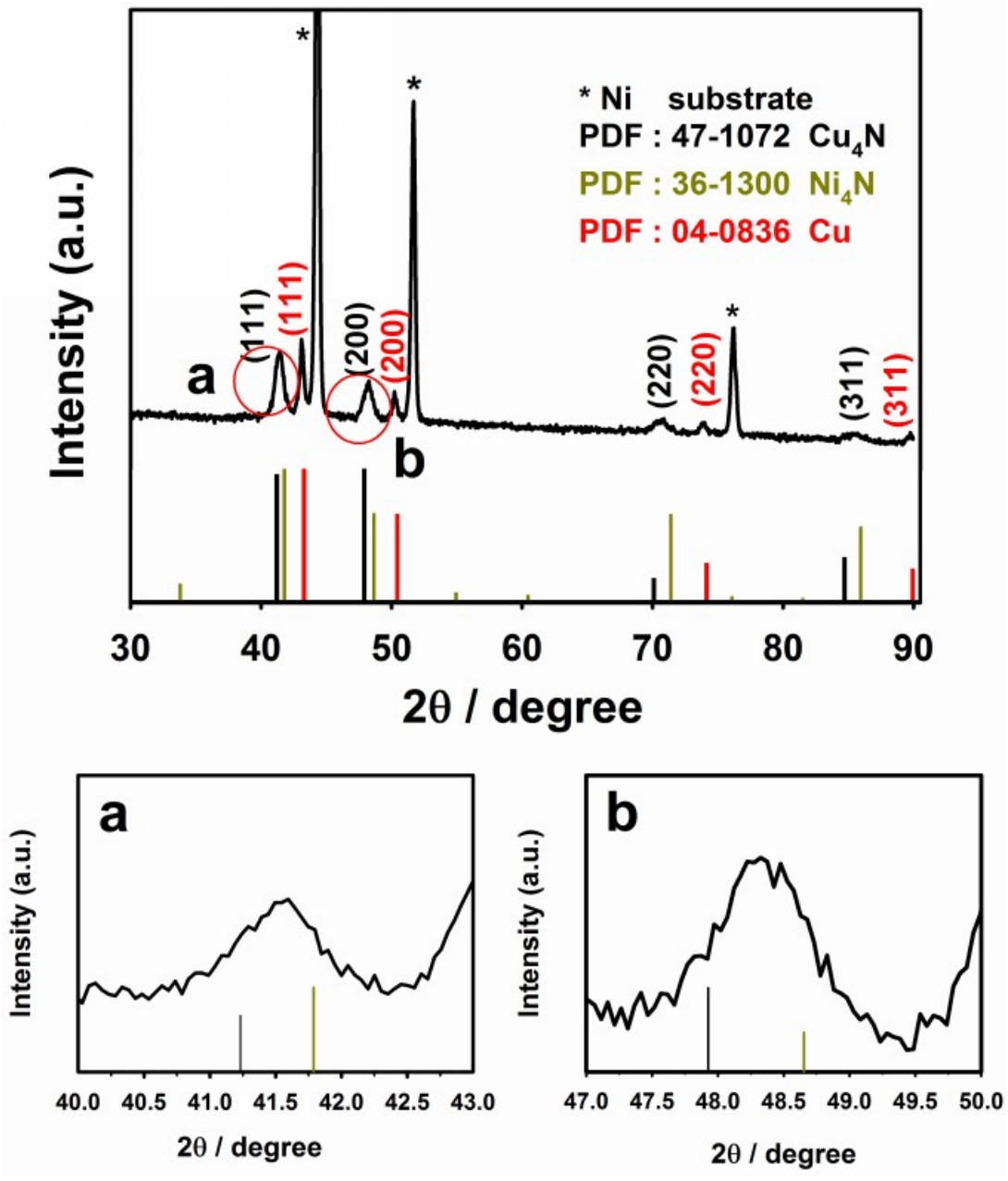


Fig S3. Slow scan micro-zone XRD patterns of $Cu_xNi_{4-x}N$/NF.

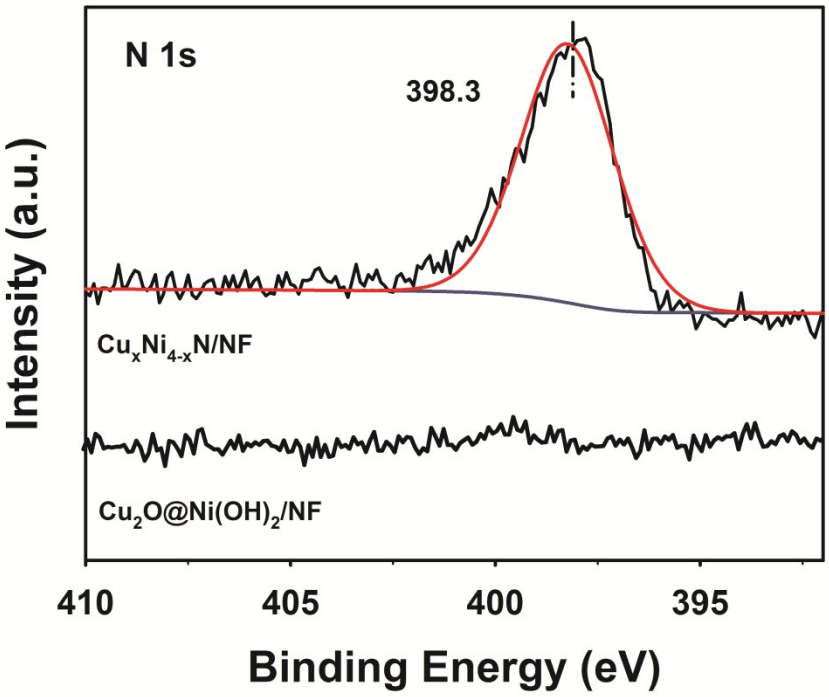
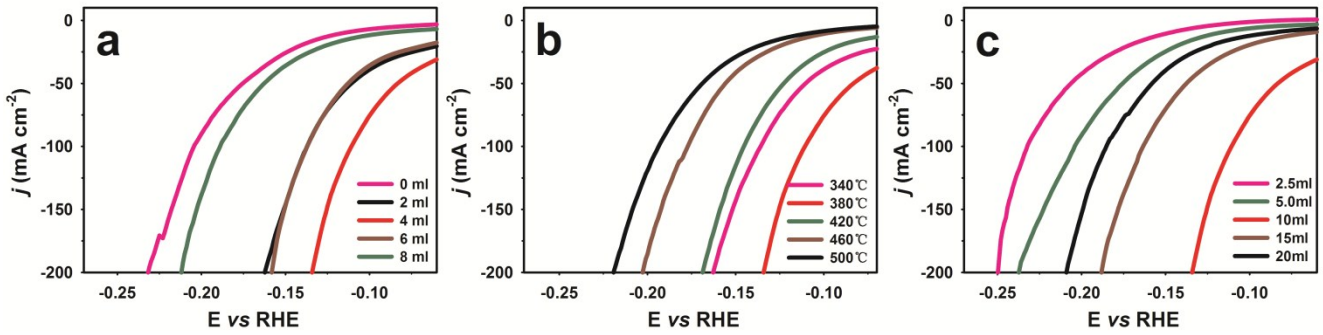


Fig S4. XPS spectra of $Cu_xNi_{4-x}N$/NF and $Cu_2O@Ni(OH)_2$/NF .



Figu S5. *iR*-corrected LSV curves of catalysts derived from varying additions of SCT (a), CuCl (b) and nitridation temperatures (c) in 1 M KOH. Scan rate: 5 mV s^{-1}.

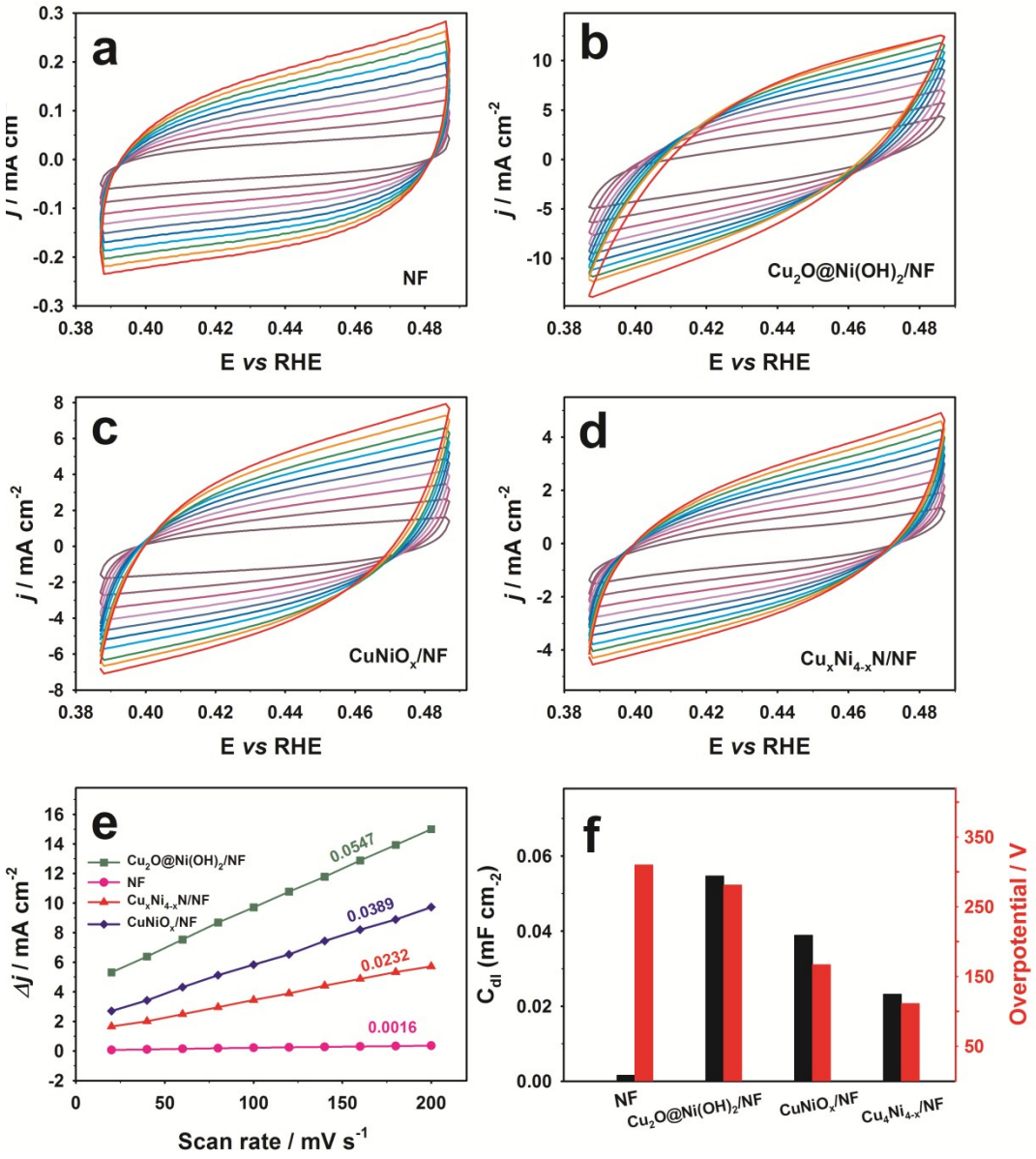


Fig S6. (a-d) CVs of NF, $Cu_2O@Ni(OH)_2$/NF, $CuNiO_x$/NF, and Cu_xNi_{4-x}NF at various scan rates. (e) The currents as a function of scan rate ($\Delta j = ja - jb$). (f) The relationship between the C_{dl} and overpotential (at the current density of 100 mA cm^{-2}).

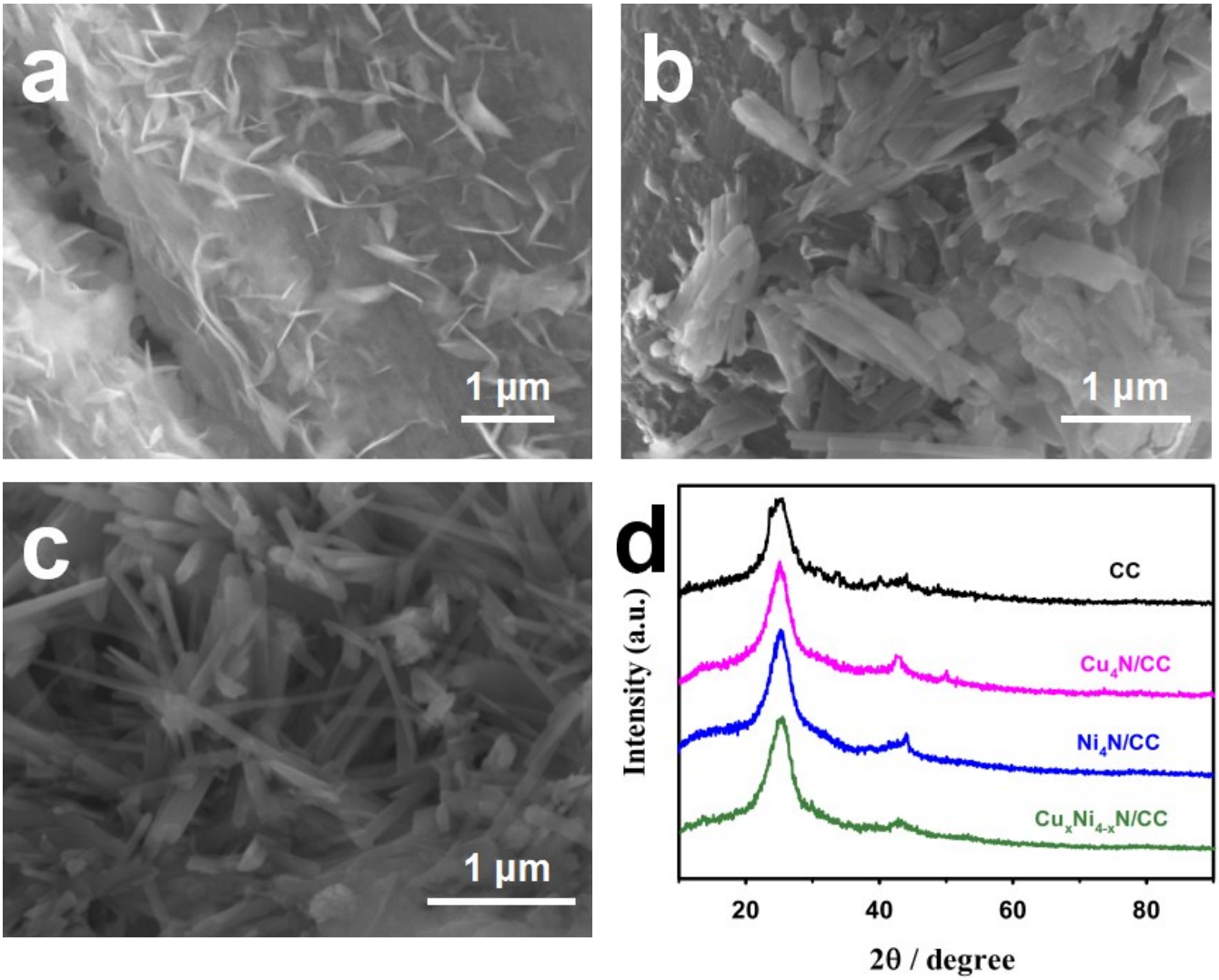


Fig S7. (a-c) SEM images of Ni_4N/CC, Cu_4N/CC and $Cu_xNi_{4-x}N$/CC. (d) XRD patterns of Cu_4N/CC, Ni_4N/CC, $Cu_xNi_{4-x}N$/CC and CC.

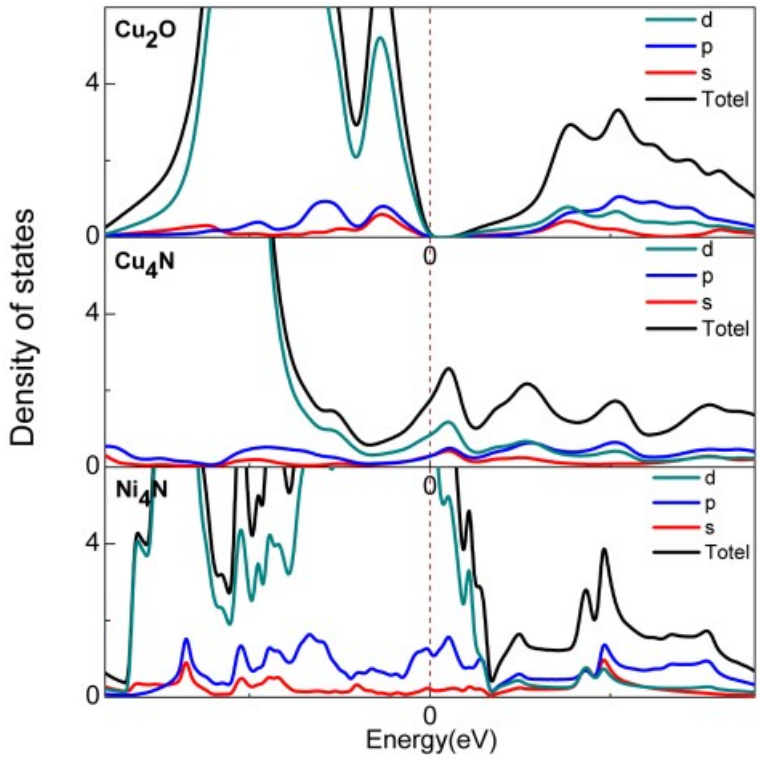


Fig S8. Total and partial electronic density of states (TDOS and PDOS) calculated for Cu_2O Cu_4N and Ni_4N and. The Fermi level is set at 0 eV.

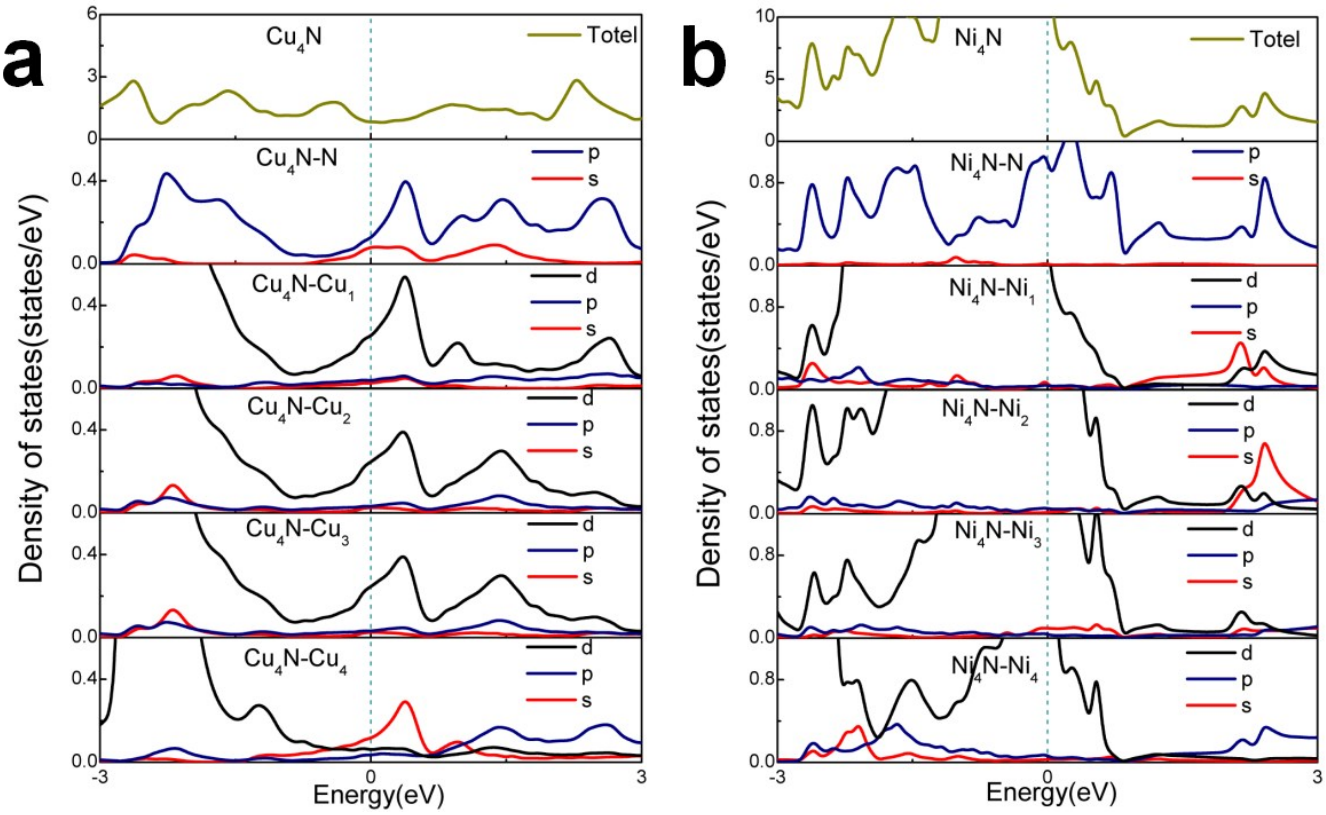


Fig S9. (a, b) Calculated DOS for each element in Cu_4N and Ni_4N. The Fermin level was set at 0 eV.

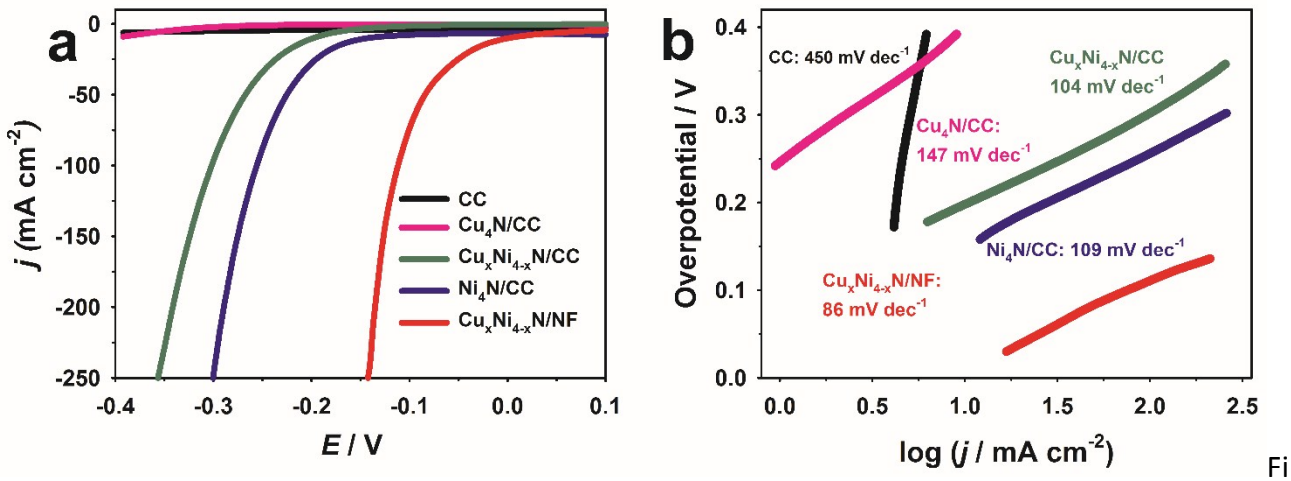


Fig S10. (a) *iR*-corrected polarization curves of Cu_4N/CC, Ni_4N/CC, $Cu_xNi_{4-x}N$/CC and CC in 1 M KOH medium. (b) Corresponding Tafel plots of electrodes.

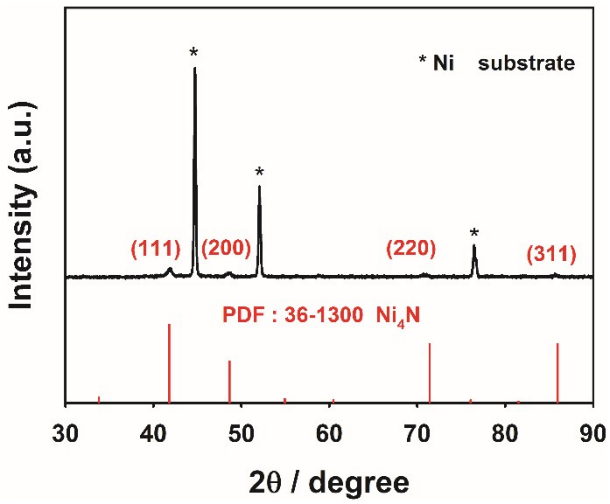


Fig S11. XRD pattern of Ni_4N/NF.

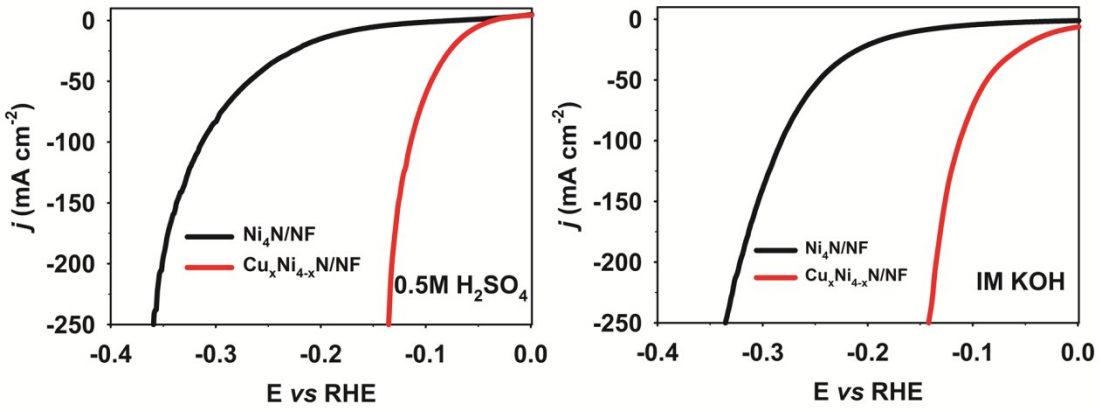


Fig. S12. Linear sweep voltammetry (LSV) curves with iR-corrected for HER in acidic and alkaline.

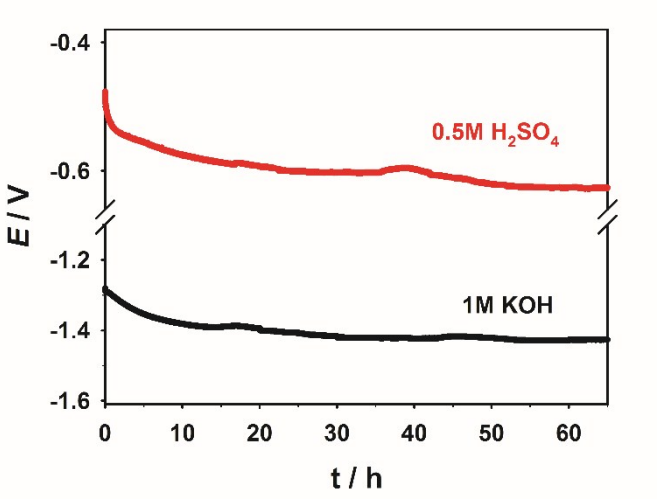


Fig S13. Chronopotentiometric curve of HER of N_4N/NF in 0.5 M H_2SO_4 and 1 M KOH with a constant current density of 20 mA cm^{-2}.

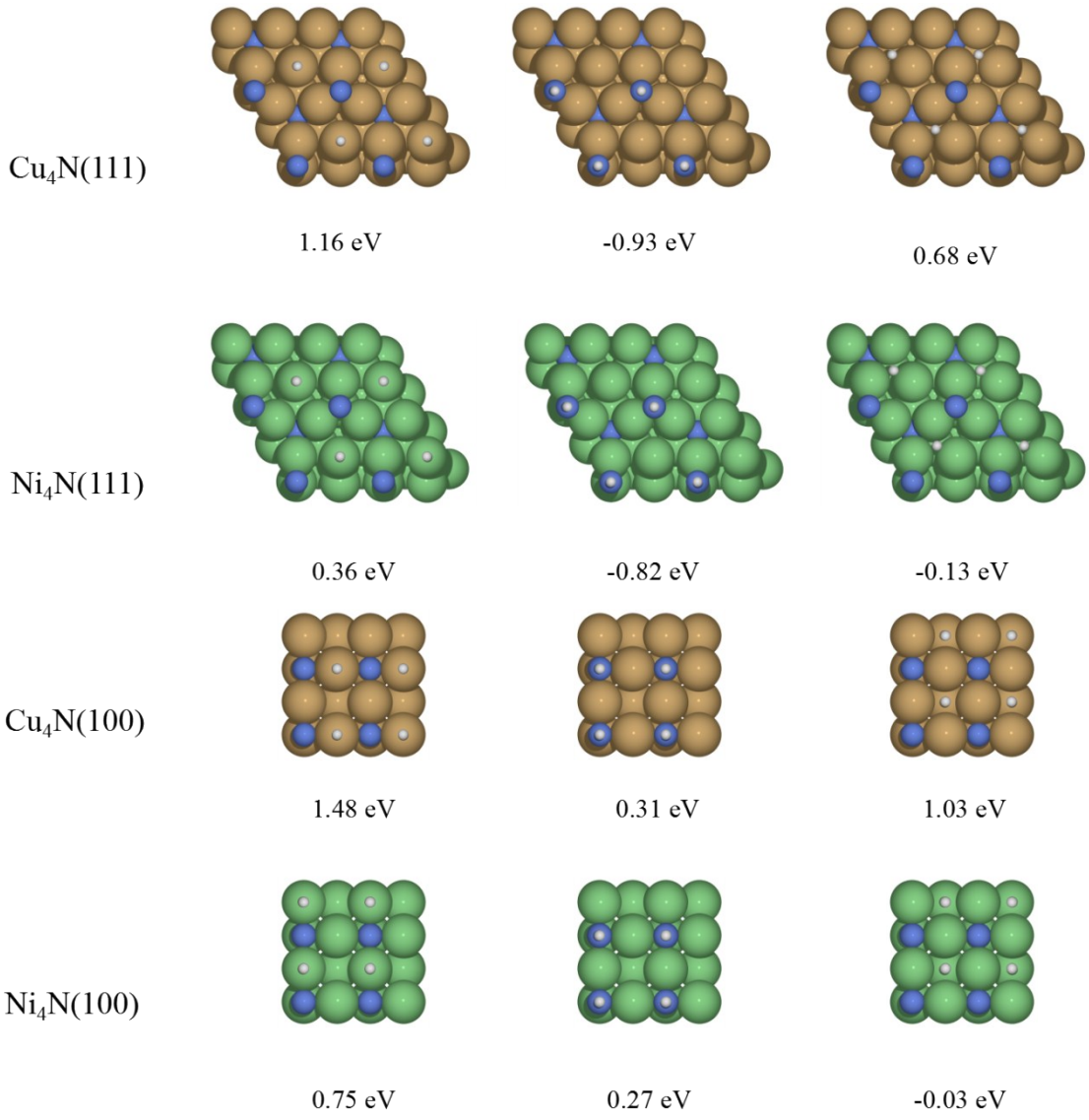


Fig S14. Schematic structural representations for hydrogen adsorption at different site of Cu_4N (111,100) and Ni_4N (111,100). (The brown ball represents Cu atom, the light green ball represents Ni atom, the light grey ball represents H atom and light blue ball represents N atom)

Table S1. A brief comparison of HER in 0.5 M H_2SO_4 reported recently.

Catalyst	Overpotential (mV)		Tafel slope (mV dec^{-1})	Reference
	η_{10}[a]	η_{100}[b]		
$Cu_xNi_{4-x}N$/NF	52	112	59	This work
CNF@CoS_2	110	~225	66.8	*Inorg. Chem. Front*. **2016**,*3,1280-1288*
MoP/SNG-650	99	~175	54	*ACS Catal.* **2017**, *7, 3030-3038*
MoP-C	136	>200	82	*Nano Energy. 32.* **2017** *511–519*
$NiCo_2P_x$	104	~140	59.6	*Adv. Mater.* **2017**, *29, 1605502*
N-$MoSe_2$/VG	89	>150	49	*Adv. Mater.* **2017**, *29, 1700748*
$Fe_{0.5}Co_{0.5}P$/CC	37	>150	30	*Nano lett.* **2016**. *6617-6621*
Co_9S_8-30@MoS_x/CC	98	~160	64.8	*Nano Energy. 32.* **2017** *470–478*
$Ni_{0.89}Co_{0.11}Se_2$ MNSN/NF	52	~150	39	*Adv. Mater.* **2017**, *1606521*
Ni–Mo–N	~50	>150	40	*Nano Energy.* **2016**. *22, 111–119*

[a] overpotential of the electrocatalyst at a current density of 10 mA cm^{-2}. [b] overpotential of the electrocatalyst at a current density of 100 mA cm^{-2}.

Table S2. A brief comparison of HER in 1 M KOH reported recently.

Catalyst	Overpotential (mV)		Tafel slope (mV dec^{-1})	Reference
	η_{10}[a]	η_{100}[b]		
$Cu_xNi_{4-x}N$/NF	12	111	86	This work
CNF@CoS_2	207	~375	113	*Inorg. Chem. Front*. **2016**,*3,128-1288*
MoP/SNG-20%	49	~151	31	*ACS Catal.* **2017**, *7, 3030-3038*
Mo_2C-C	149	>250	66	*Nano Energy. 32* **2017**, *511–519*
$Ni_{0.89}Co_{0.11}Se_2$ MNSN/NF	85	~158	52	*Adv. Mater.* **2017**, *1606521*
Ni–Mo–N	~50	>150	39	*Nano Energy.* **2016**,*22, 111–119*
$NiCo_2Px$	58	127	34.3	*Adv. Mater.* **2017**, *29, 1605502*
$MoNi_4/MoO_2$@Ni	15	~50	30	*Nat Commun.* **2017**; *8: 15437.*
$NiCo_2O_4$	~100	>150	53	*Angew. Chem. Int. Ed.* **2016,** *55,* 1

[a] overpotential of the electrocatalyst at a current density of 10 mA cm^{-2}. [b] overpotential of the electrocatalyst at a current density of 100 mA cm^{-2}.