Electronic Supplementary Information

Bimetallic **MOF-based catalysts with enhanced activity for** electrochemical hydrogen evolution **in acid and alkaline electrolytes**

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Table S1. MOF-based HER electrocatalysts applied in acidic electrolyte.

Catalysts	Categories	η_{10} (mV)	Electrolyte	Stability	Reference
Ni-NKU-100	3D MOF	224	0.5 M H_2SO_4	24 h	This work
$Cu_{0.22}Ni_{0.78}$-NKU-100					
Co-MOF	3D MOF	357	0.5 M H_2SO_4	96 h	[1]
Co-MOF	3D MOF	223	0.5 M H_2SO_4	72 h	[2]
THAT-Co-single layer	2D MOF	283	0.5 M H_2SO_4	4 h	[3]
THTA-Co-powder		332			
THTA-Co-graphene		230			
CTGU-9	3D MOF	424	0.5 M H_2SO_4	21 h	[4]
AB: CTGU-9=3: 4		128			
UU-100(Co)	3D MOF	450	$NaClO_4$ (0.1 M)/ acetate (0.2 M) buffer at pH 4	~5 h	[5]
THT-Ni	2D MOF	333	0.5 M H_2SO_4		[6]
Cu-MOF	3D MOF	440	1 M H_2SO_4		[7]
NENU-5	3D MOF	585	0.5 M H_2SO_4		[8]
HKUST-1		691			
NENU-500		237			
NENU-501		392			
NENU-499		570			
ε(trim)4/3		515			
NU-1000	3D MOF	640	0.1 M HCl	2 h	[9]
NU-1000_Ni-S	3D MOF + sulfide	238			
bulk NiFe-MOF	3D MOF	196	0.5 M H_2SO_4	2 h	[10]
HKUST-1 ED		590			
HKUST-1 HT		660			
Ni-NKU-100	3D MOF	324	0.5 M H_2SO_4	24 h	[11]
$Cu_{0.19}Ni_{0.81}$-NKU-101					

Table S2. MOF-based HER electrocatalysts applied in alkaline electrolyte.

Catalysts	Categories	η_{10} (mV)	Electrolyte	Stability	Reference
Ni-NKU-100	3D MOF	249	1 M KOH	24 h	This work
$Fe_{0.24}Ni_{0.76}$-NKU-100					
Co-BDC	2D MOF	529	1 M KOH	15 h	[12]
Co-BDC-MoS_2	2D MOF + sulfide	248			
NiFe-MOF		134		5.5 h	
Ni-MOF	3D MOF	177	0.1 M KOH		[13]
bulk NiFe-MOF		196			
Co–BTC/CC	3D MOF	437	1 M KOH		[14]
CuCo-CAT	3D MOF	52	1 M KOH	10 h	[15]
$Fe(OH)_x$@Cu-MOF	3D MOF	112	1 M KOH	30 h	[16]
Fe_2Zn-MOF	3D MOF	221	0.1 M KOH	24 h	[17]
$Ni_3(Ni_3{\cdot}HAHATN)_2$	3D MOF	115	0.1 M KOH	10 h	[18]

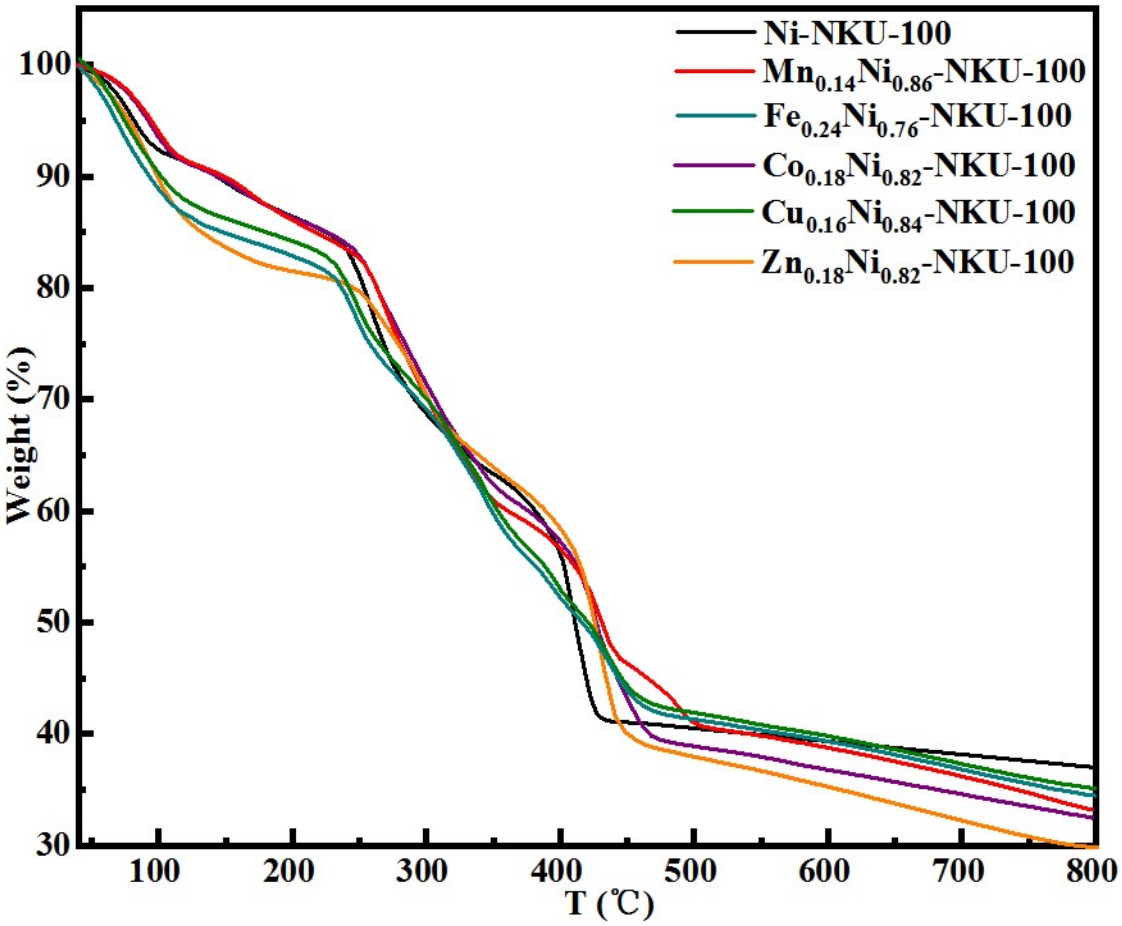

Fig. S1 Thermogravimetric analysis of Ni-NKU-100 and M_xNi_{1-x}-NKU-100 (M = Mn, Fe, Co, Cu, Zn).

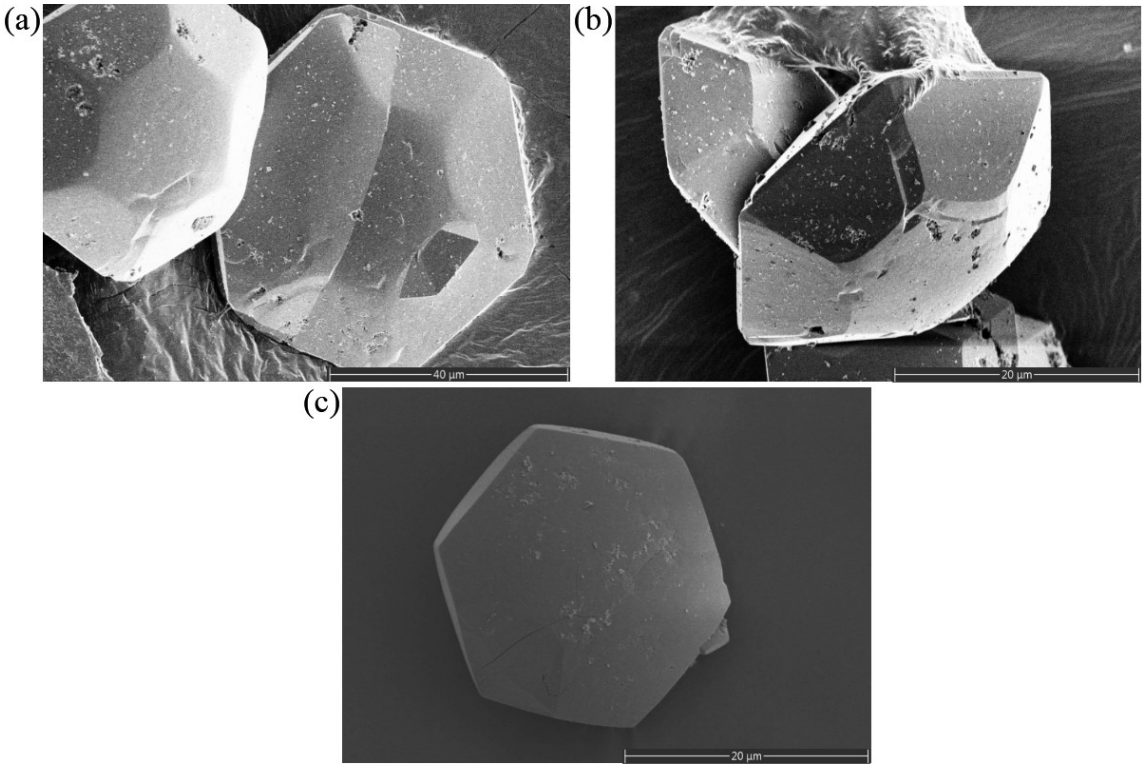

Fig. S2 FESEM images of Ni-NKU-100 (a), $Cu_{0.16}Ni_{0.84}$-NKU-100 (b) and $Fe_{0.24}Ni_{0.76}$-NKU-100 (c).

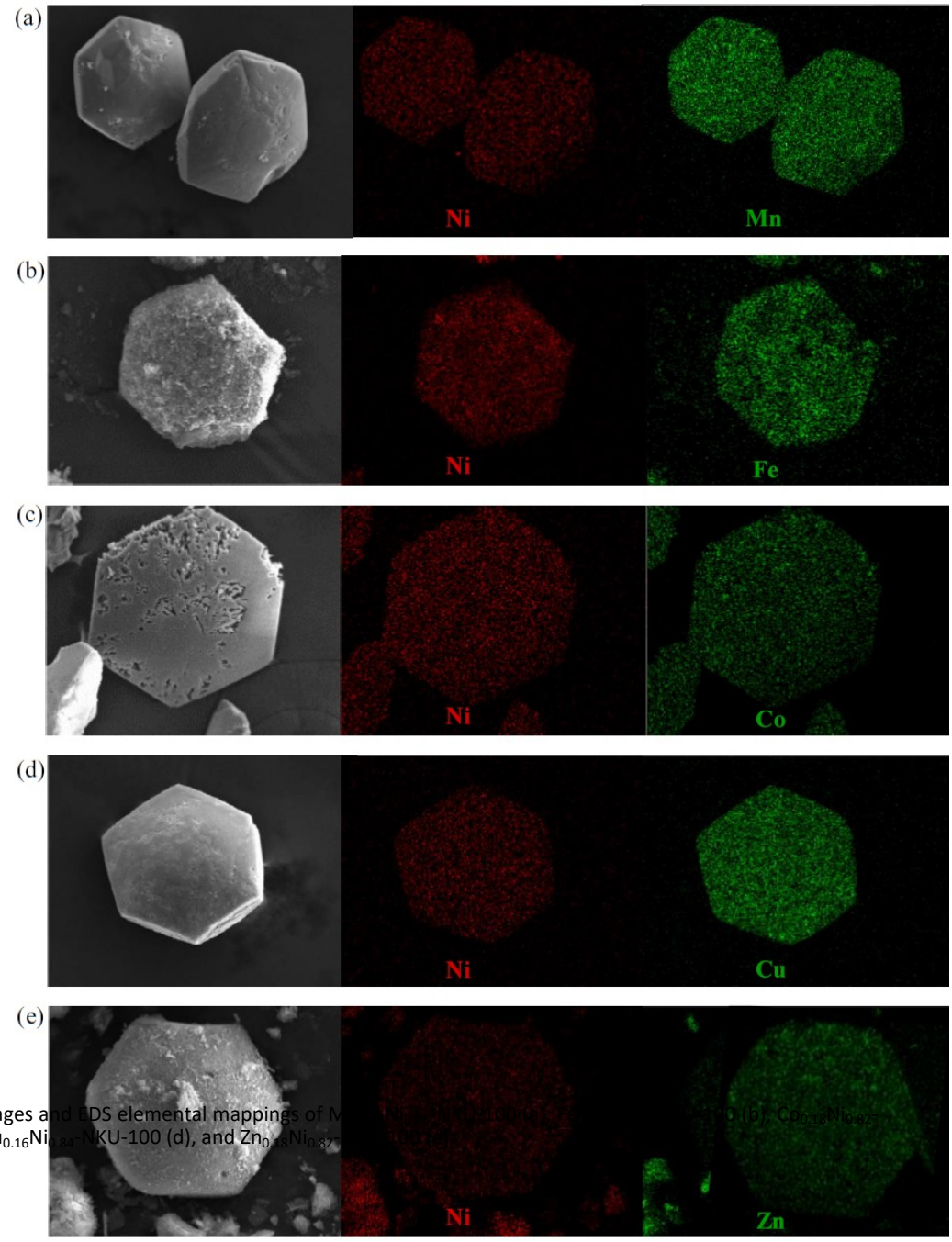

Fig. S3 SEM images and EDS elemental mappings of M[illegible]-100 (a), [illegible]-100 (b), $Co_{0.18}Ni_{0.82}$-NKU-100 (c), $Cu_{0.16}Ni_{0.84}$-NKU-100 (d), and $Zn_{0.18}Ni_{0.82}$-[illegible]-100 (e).

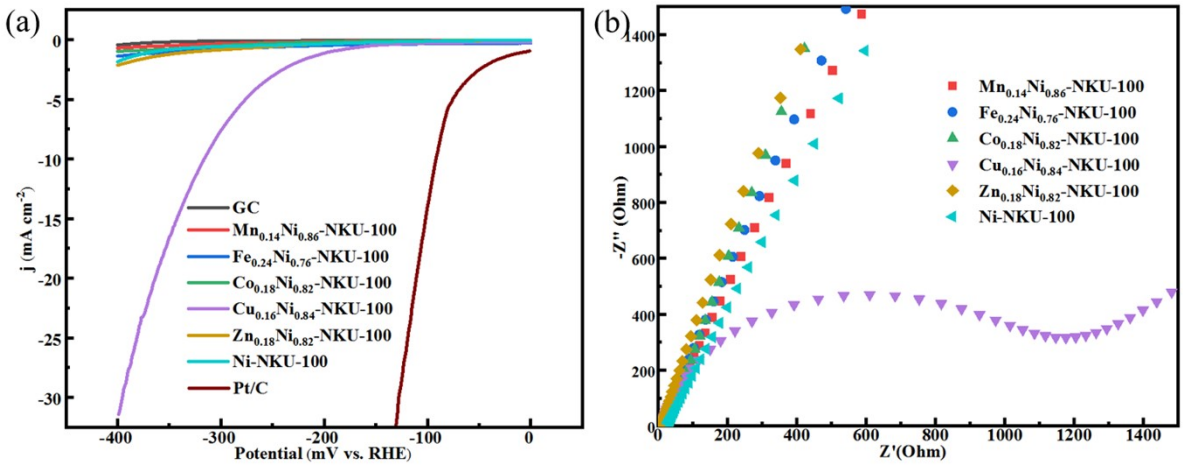

Fig. S4 (a) LSV curves at a scan rate of 5 mV·s^{-1} and (b) EIS Nyquist plots of M_xNi_{1-x}-NKU-100 (M = Mn, Fe, Co, Cu, Zn) in 0.5 M H_2SO_4 electrolyte.

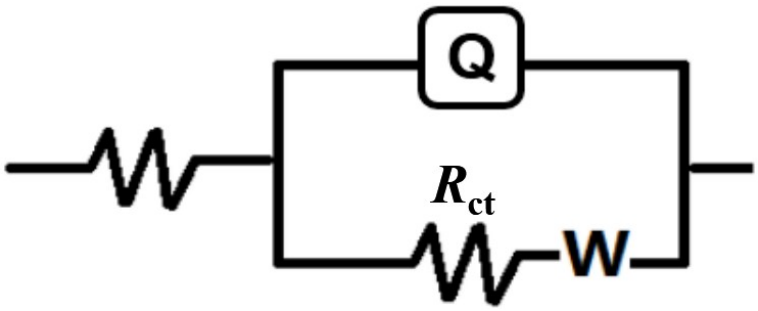

Fig. S5 The equivalent circuit for fitting electrochemical impedance.

Table S3 R_{ct} of Cu_xNi_{1-x}-NKU-100 in 0.5 M H_2SO_4 electrolyte.

Electrode material	R_{ct} (Ω)
Ni-NKU-100	86500
$Cu_{0.09}Ni_{0.91}$-NKU-100	53400
$Cu_{0.11}Ni_{0.89}$-NKU-100	3729
$Cu_{0.16}Ni_{0.84}$-NKU-100	2768
$Cu_{0.22}Ni_{0.78}$-NKU-100	702
$Cu_{0.25}Ni_{0.75}$-NKU-100	1066

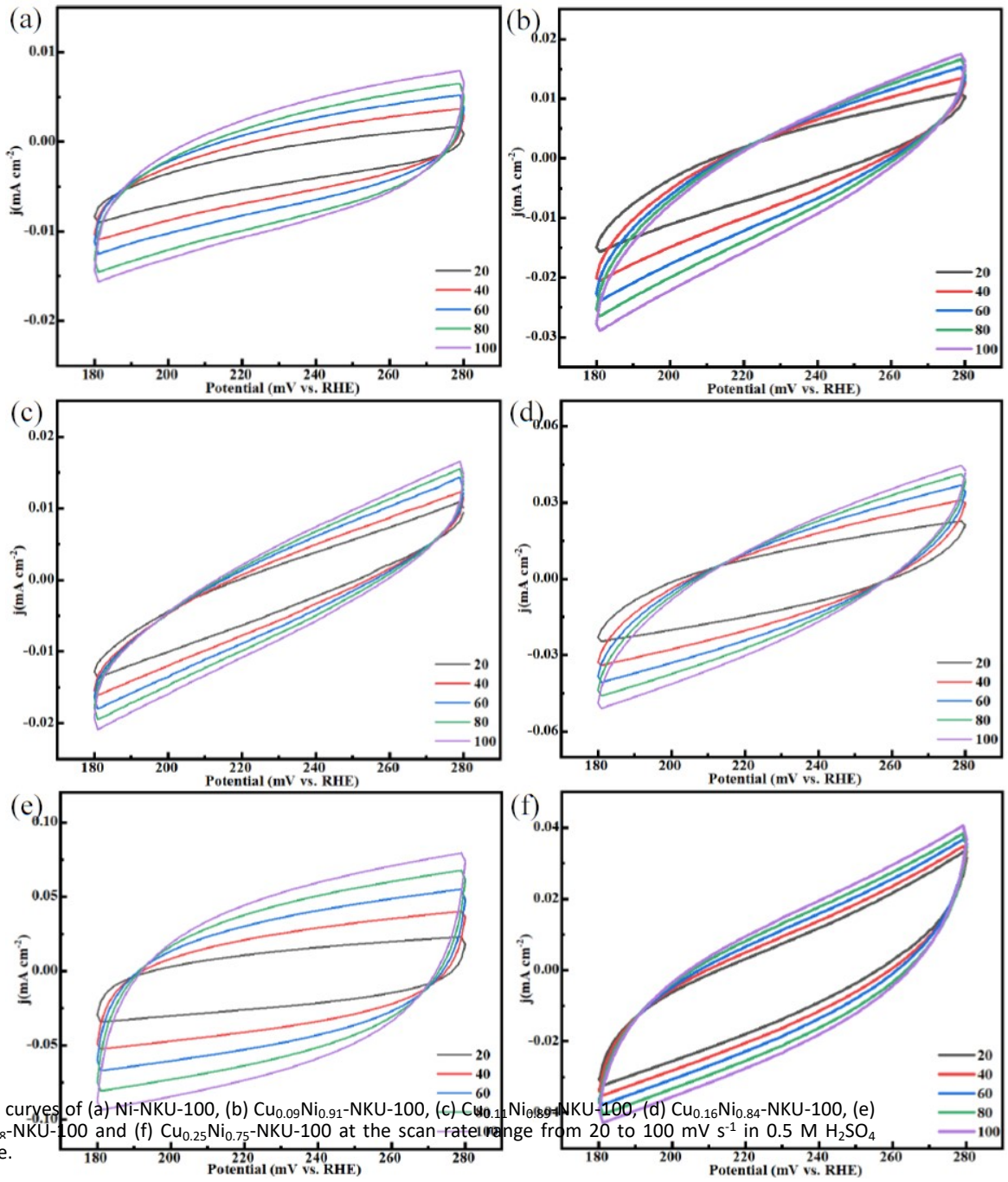

Fig. S6 CV curves of (a) Ni-NKU-100, (b) $Cu_{0.09}Ni_{0.91}$-NKU-100, (c) $Cu_{0.11}Ni_{0.89}$-NKU-100, (d) $Cu_{0.16}Ni_{0.84}$-NKU-100, (e) $Cu_{0.22}Ni_{0.78}$-NKU-100 and (f) $Cu_{0.25}Ni_{0.75}$-NKU-100 at the scan rate range from 20 to 100 mV s^{-1} in 0.5 M H_2SO_4 electrolyte.

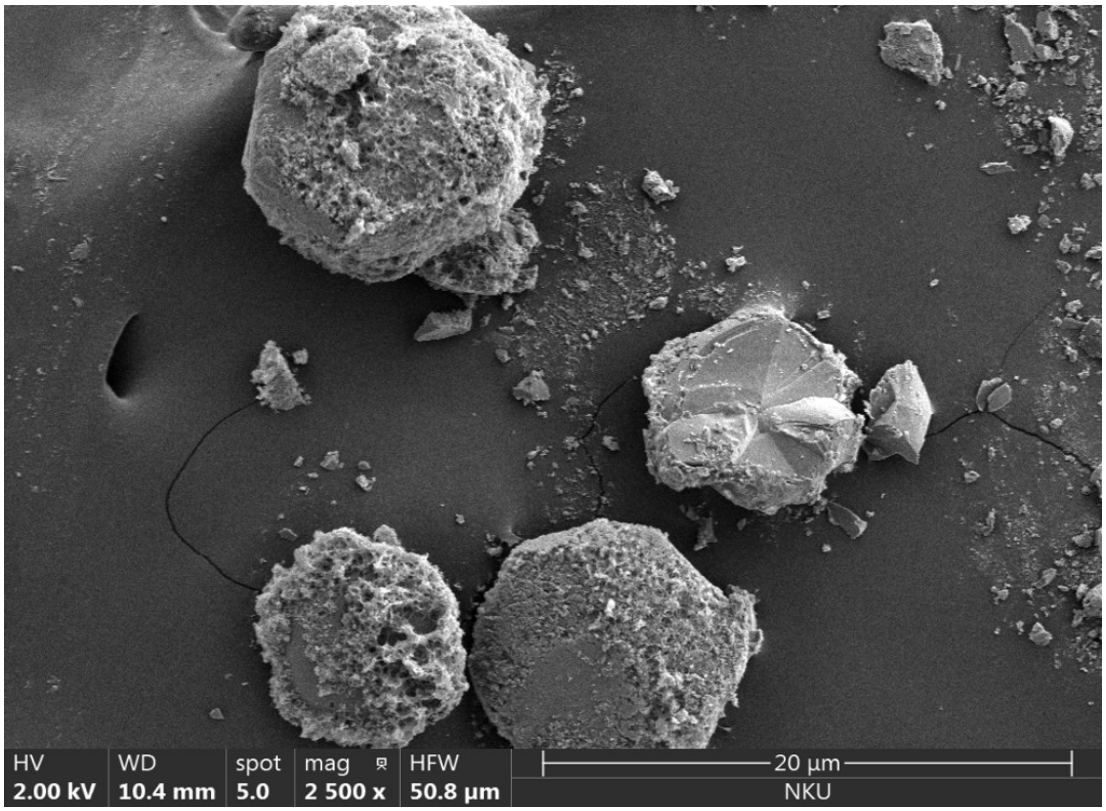

Fig. S7 SEM images of $Cu_{0.22}Ni_{0.78}$-NKU-100 after long-time electrocatalytic test in 0.5 M H_2SO_4 electrolyte.

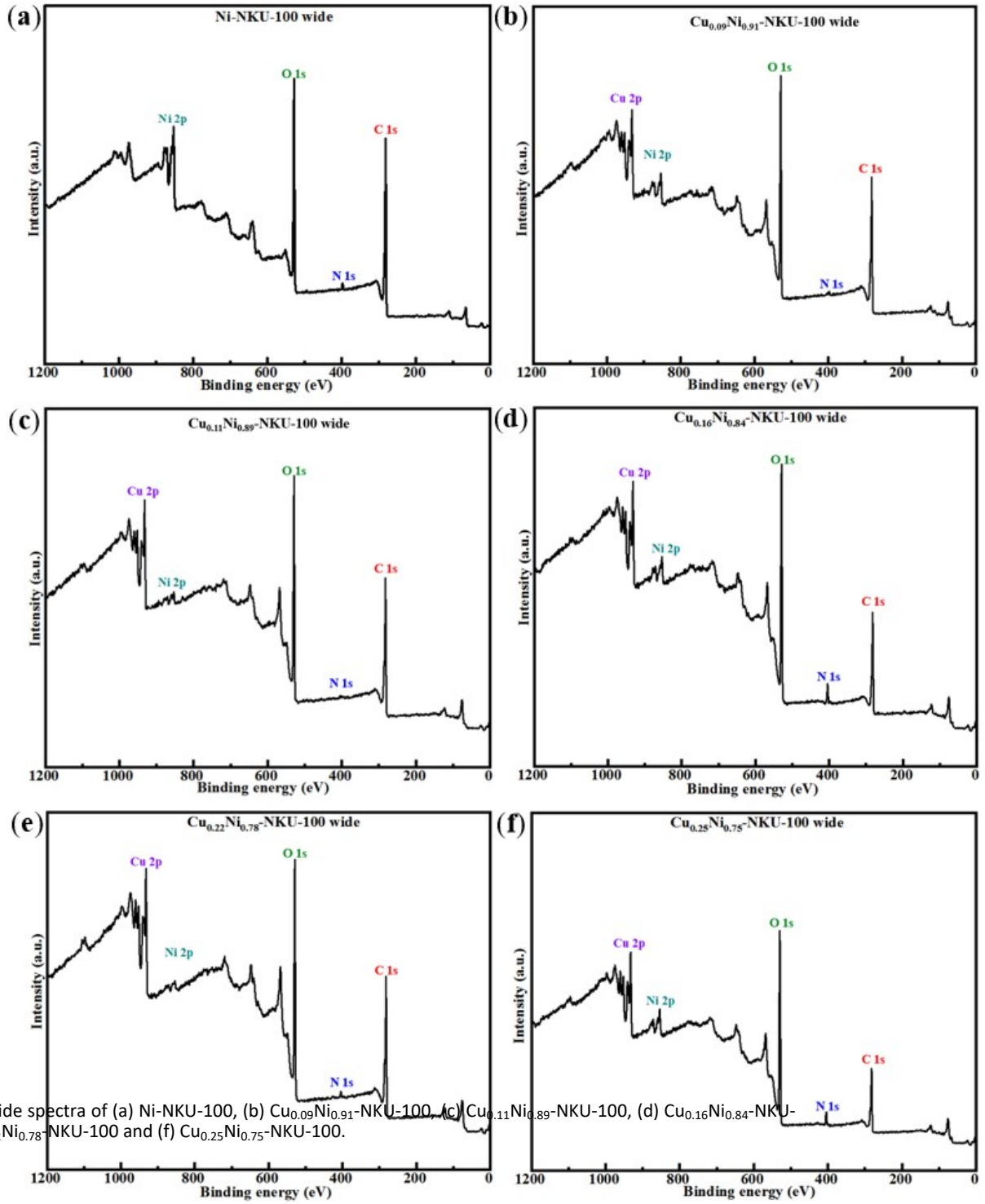

Fig. S8 XPS wide spectra of (a) Ni-NKU-100, (b) $Cu_{0.09}Ni_{0.91}$-NKU-100, (c) $Cu_{0.11}Ni_{0.89}$-NKU-100, (d) $Cu_{0.16}Ni_{0.84}$-NKU-100, (e) $Cu_{0.22}Ni_{0.78}$-NKU-100 and (f) $Cu_{0.25}Ni_{0.75}$-NKU-100.

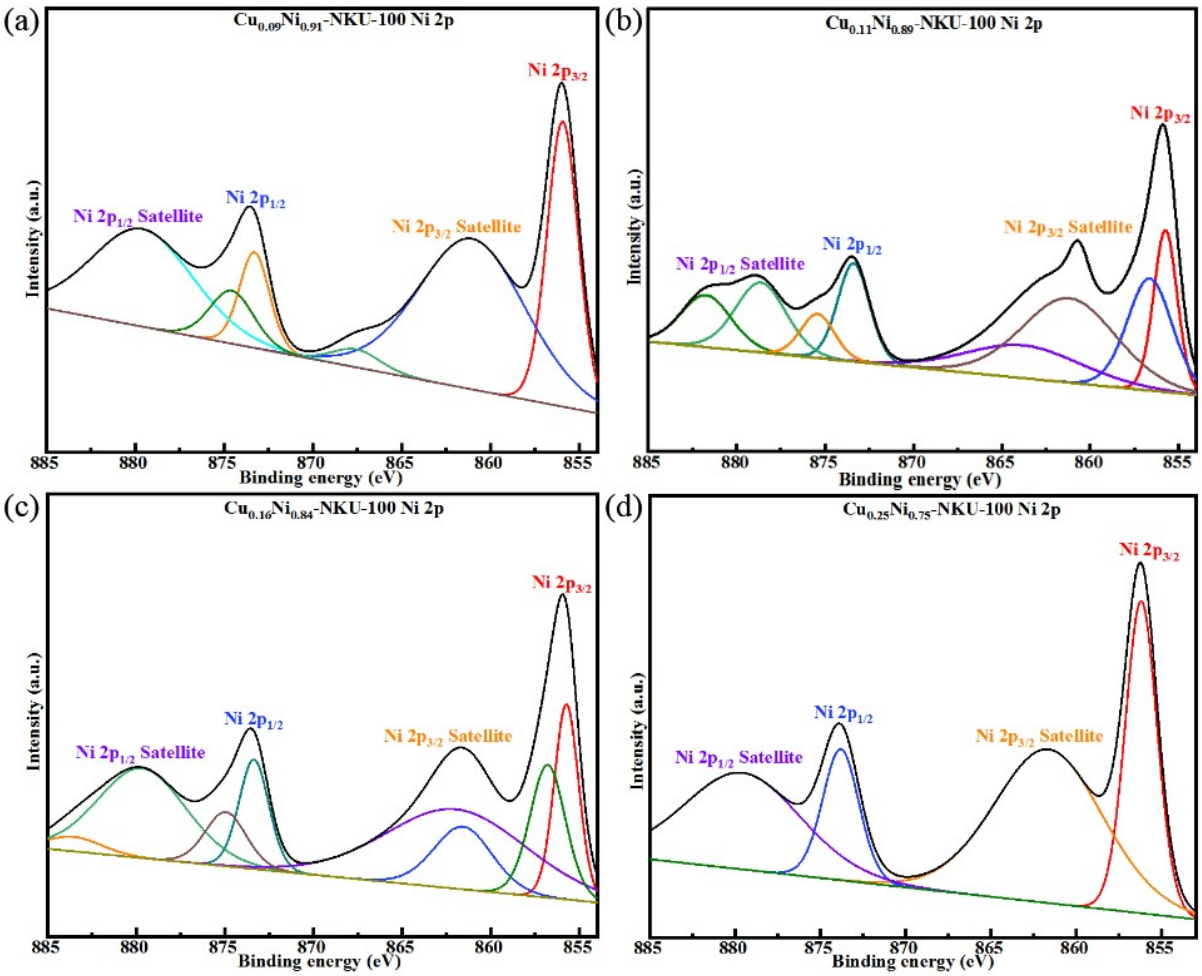

Fig. S9 High-resolution XPS of Ni 2p for (a) $Cu_{0.09}Ni_{0.91}$-NKU-100, (b) $Cu_{0.11}Ni_{0.89}$-NKU-100, (c) $Cu_{0.16}Ni_{0.84}$-NKU-100 and (d) $Cu_{0.25}Ni_{0.75}$-NKU-100.

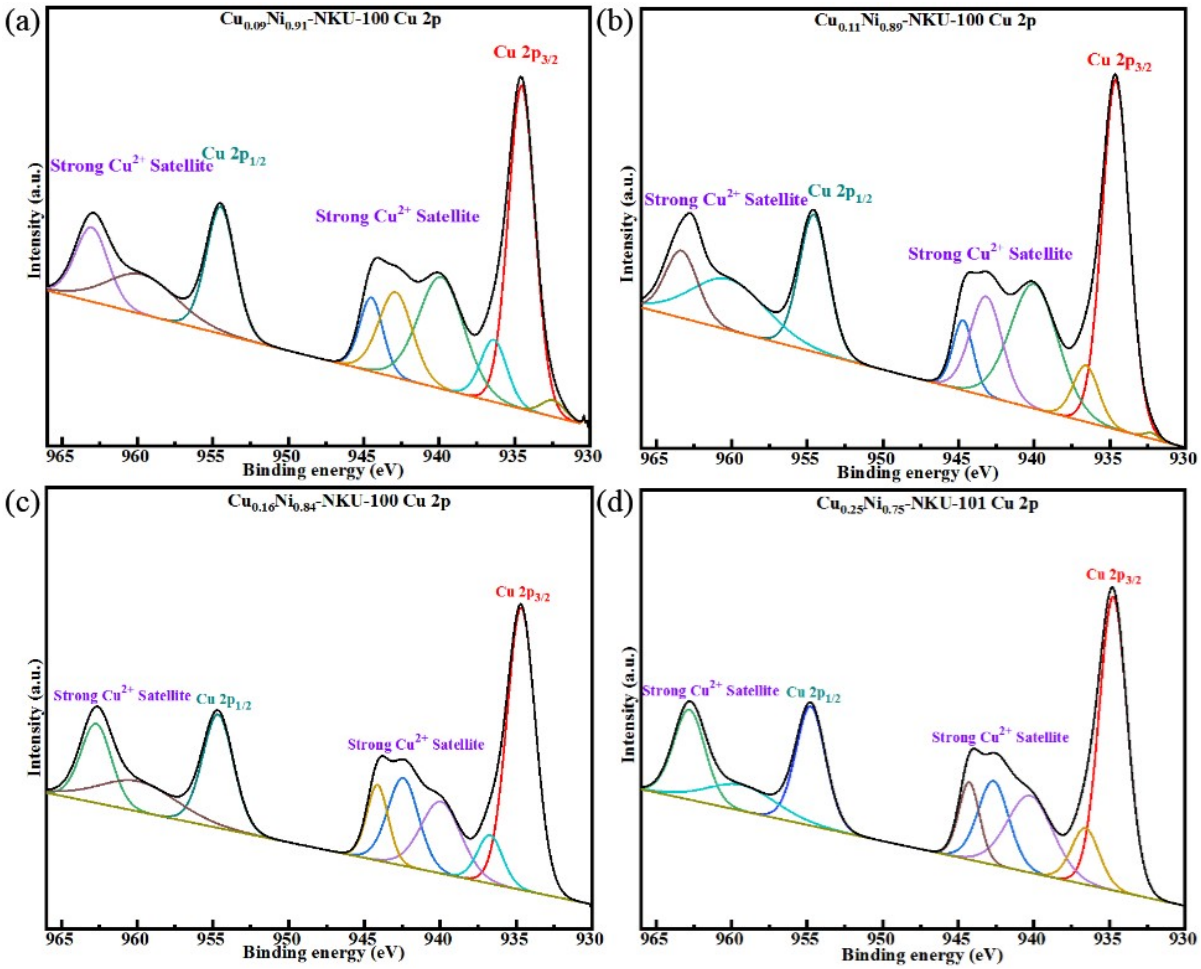

Fig. S10 High-resolution XPS of Cu 2p for (a) $Cu_{0.09}Ni_{0.91}$-NKU-100, (b) $Cu_{0.11}Ni_{0.89}$-NKU-100, (c) $Cu_{0.16}Ni_{0.84}$-NKU-100 and (d) $Cu_{0.25}Ni_{0.75}$-NKU-100.

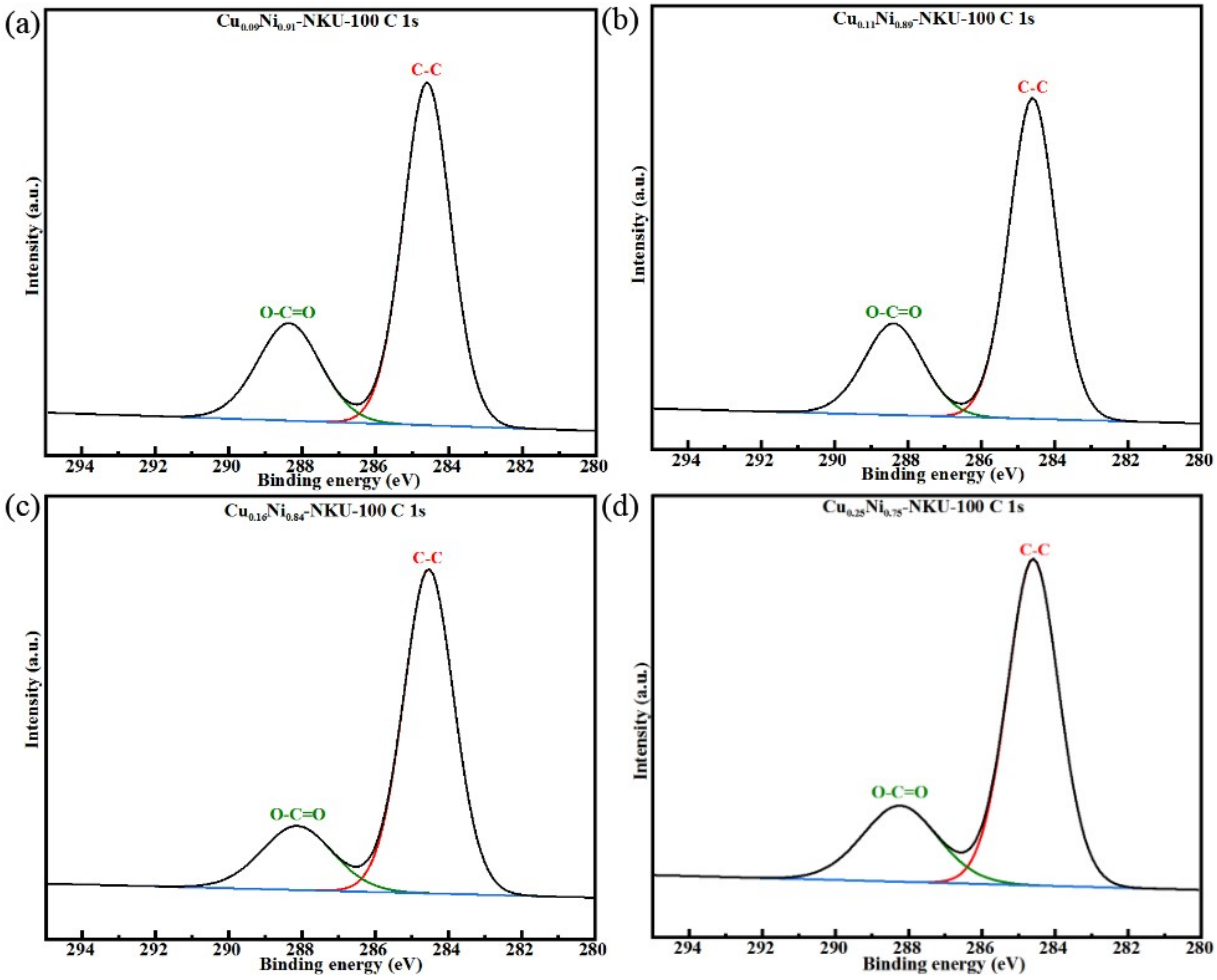

Fig. S11 High-resolution XPS of C 1s for (a) $Cu_{0.09}Ni_{0.91}$-NKU-100, (b) $Cu_{0.11}Ni_{0.89}$-NKU-100, (c) $Cu_{0.16}Ni_{0.84}$-NKU-100 and (d) $Cu_{0.25}Ni_{0.75}$-NKU-100.

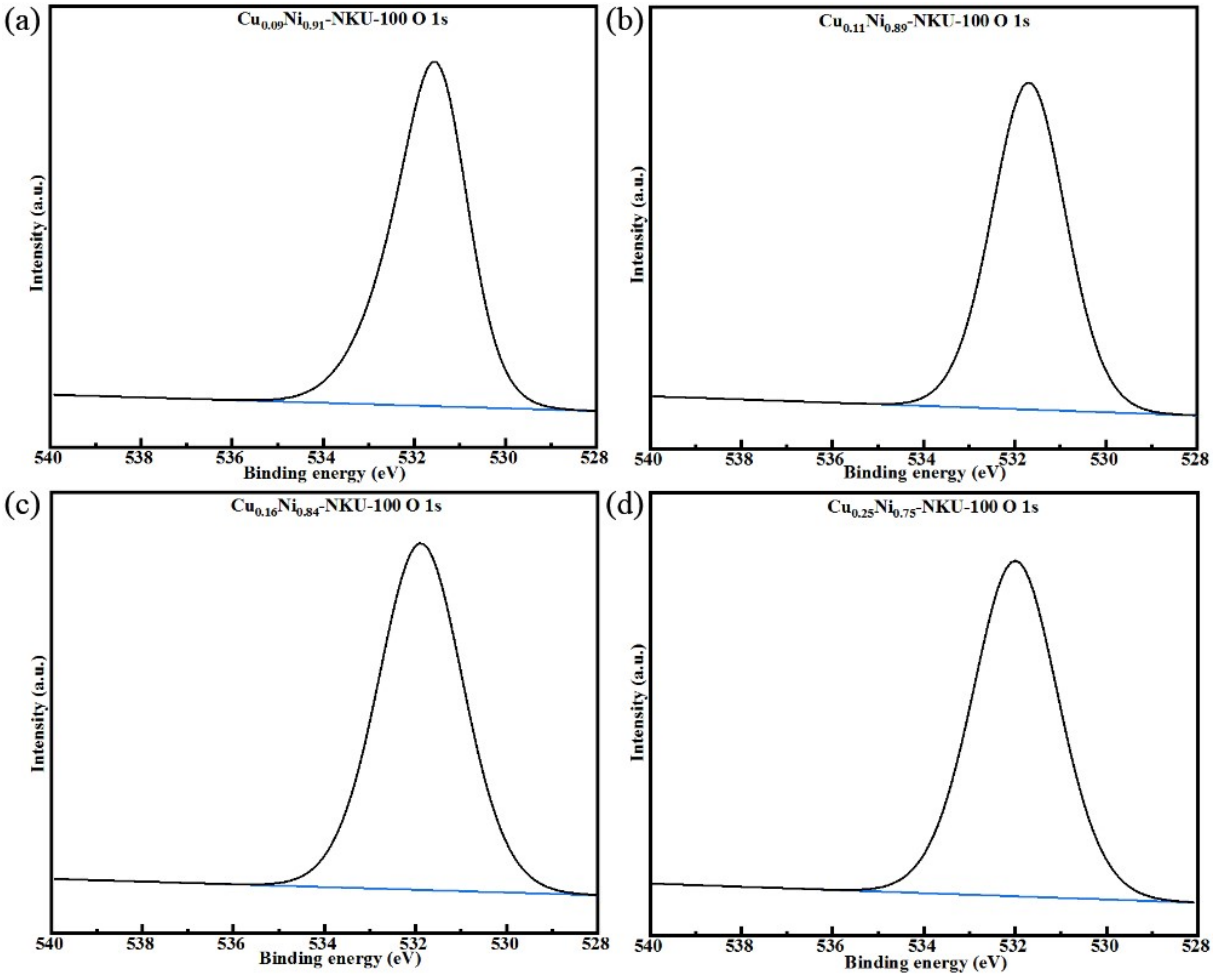

Fig. S12 High-resolution XPS of O 1s for (a) $Cu_{0.09}Ni_{0.91}$-NKU-100, (b) $Cu_{0.11}Ni_{0.89}$-NKU-100, (c) $Cu_{0.16}Ni_{0.84}$-NKU-100 and (d) $Cu_{0.25}Ni_{0.75}$-NKU-100.

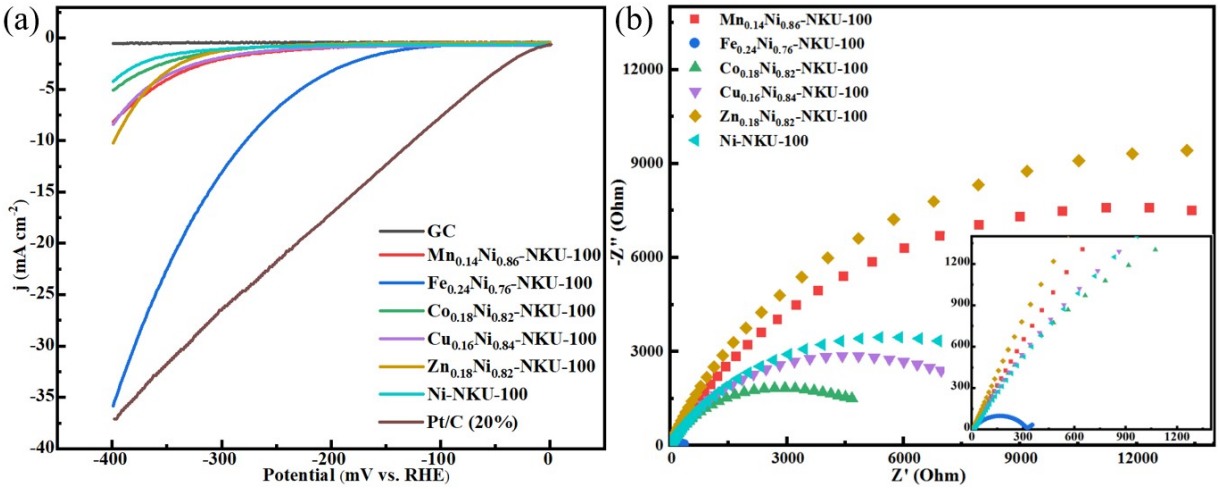

Fig. S13 (a) LSV curves at a scan rate of 5 mV·s^{-1} and (b) EIS Nyquist plots of M_xNi_{1-x}-NKU-100 (M = Mn, Fe, Co, Cu, Zn) in 1 M NaOH electrolyte.

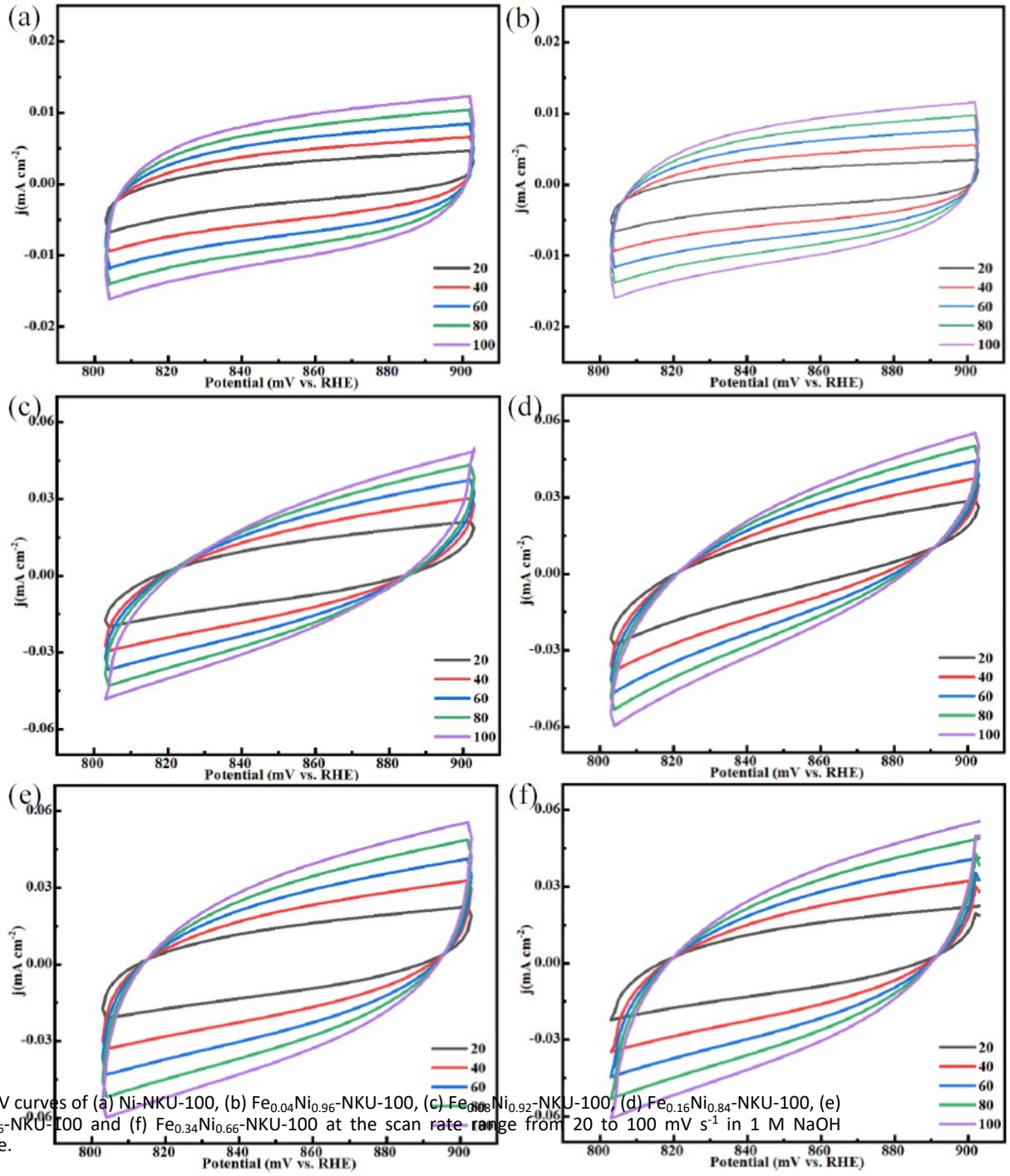

Fig. S14 CV curves of (a) Ni-NKU-100, (b) $Fe_{0.04}Ni_{0.96}$-NKU-100, (c) $Fe_{0.08}Ni_{0.92}$-NKU-100, (d) $Fe_{0.16}Ni_{0.84}$-NKU-100, (e) $Fe_{0.24}Ni_{0.76}$-NKU-100 and (f) $Fe_{0.34}Ni_{0.66}$-NKU-100 at the scan rate range from 20 to 100 mV s^{-1} in 1 M NaOH electrolyte.

Tab. S4 R_{ct} of Fe_xNi_{1-x}-NKU-100 in 1 M NaOH electrolyte.

Electrode material	R_{ct} (Ω)
Ni-NKU-100	35070
$Fe_{0.04}Ni_{0.96}$-NKU-100	2115
$Fe_{0.08}Ni_{0.92}$-NKU-100	577
$Fe_{0.16}Ni_{0.84}$-NKU-100	410
$Fe_{0.24}Ni_{0.76}$-NKU-100	204
$Fe_{0.34}Ni_{0.66}$-NKU-100	809

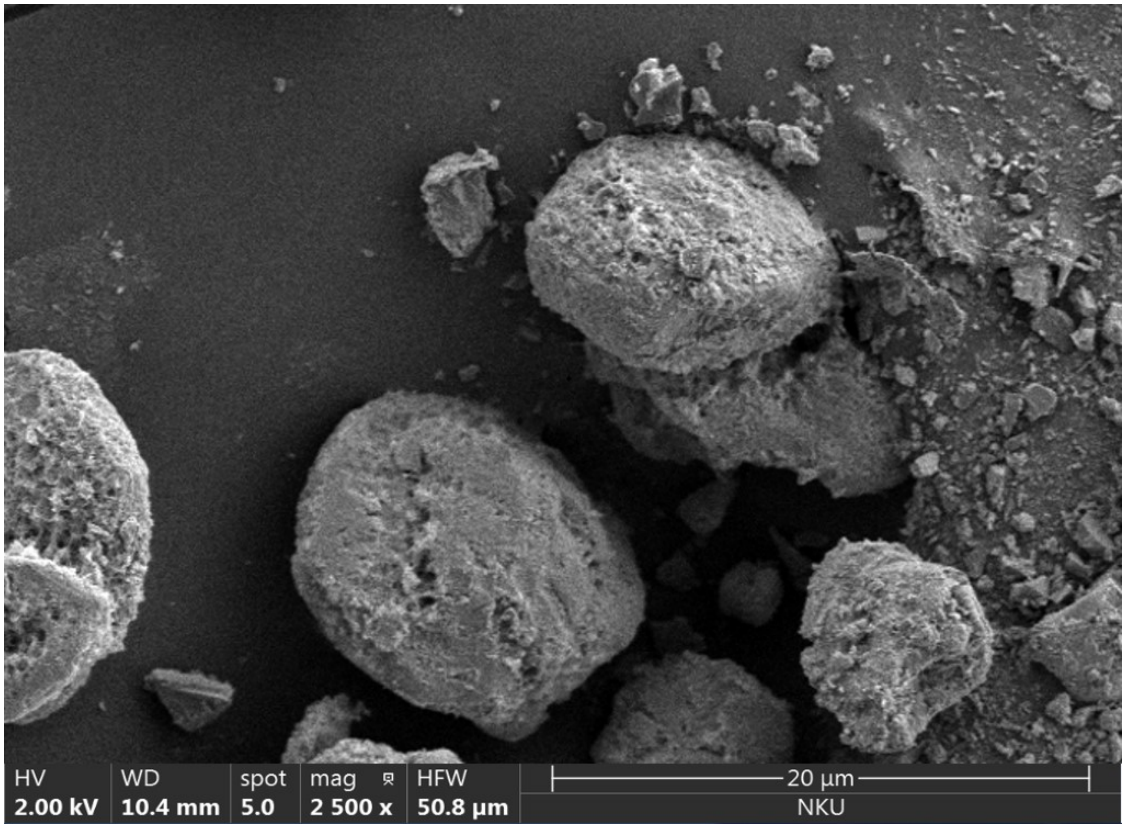

Fig. S15 SEM images of $Fe_{0.24}Ni_{0.76}$-NKU-100 after long-time electrocatalytic test in 1 M NaOH electrolyte.

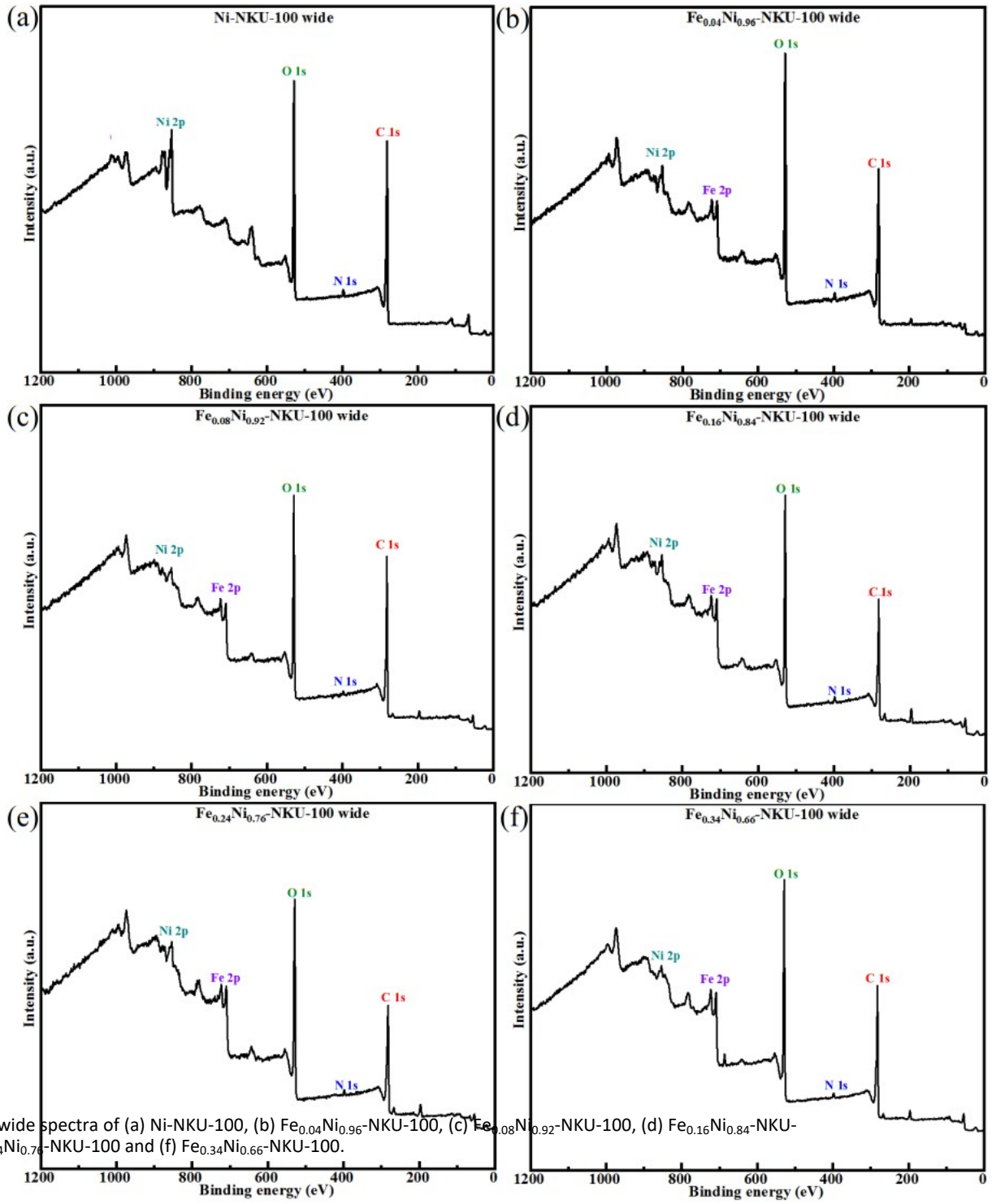

Fig. S16 XPS wide spectra of (a) Ni-NKU-100, (b) $Fe_{0.04}Ni_{0.96}$-NKU-100, (c) $Fe_{0.08}Ni_{0.92}$-NKU-100, (d) $Fe_{0.16}Ni_{0.84}$-NKU-100, (e) $Fe_{0.24}Ni_{0.76}$-NKU-100 and (f) $Fe_{0.34}Ni_{0.66}$-NKU-100.

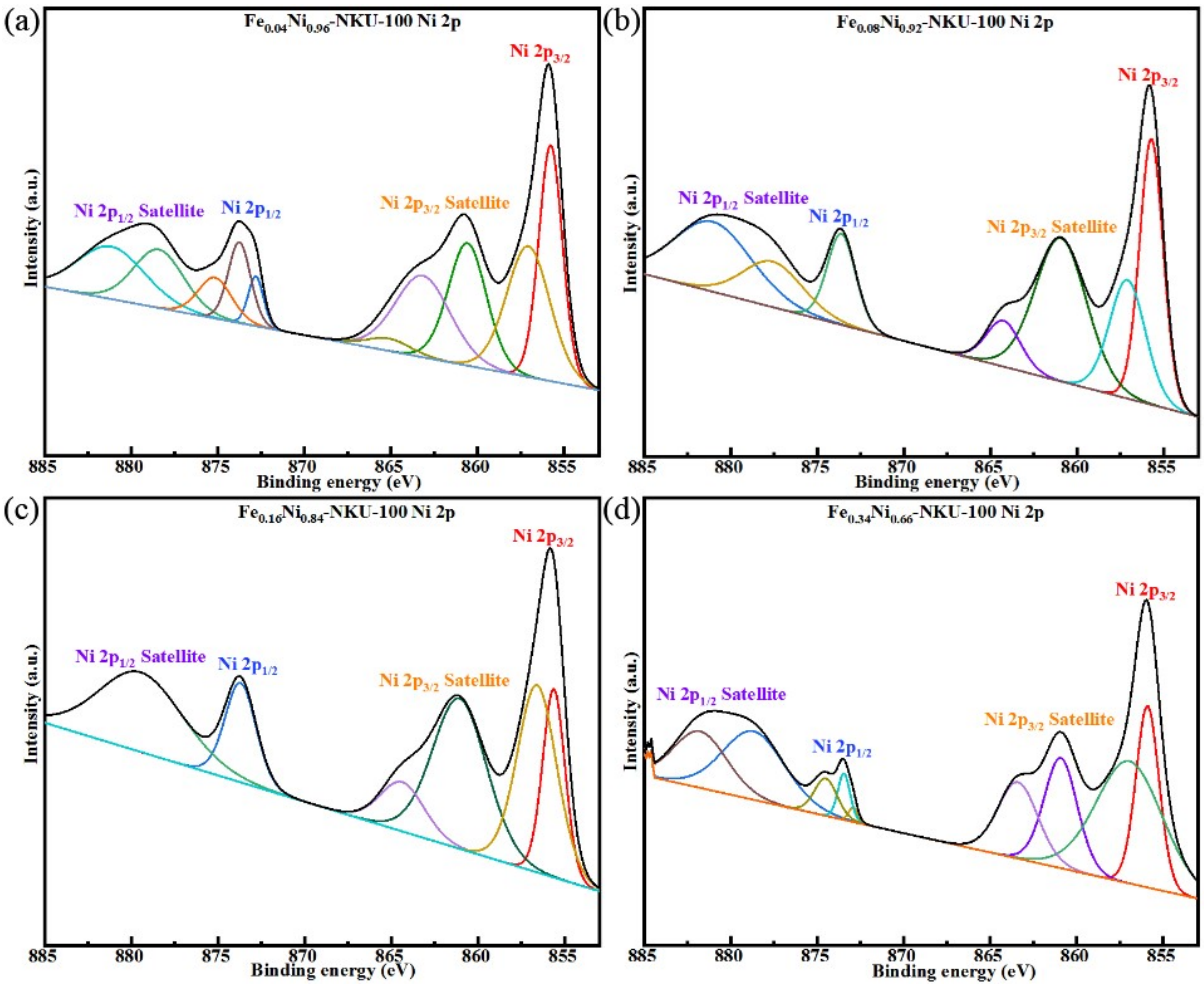

Fig. S17 High-resolution XPS of Ni 2p for (a) $Fe_{0.04}Ni_{0.96}$-NKU-100, (b) $Fe_{0.08}Ni_{0.92}$-NKU-100, (c) $Fe_{0.16}Ni_{0.84}$-NKU-100 and (d) $Fe_{0.34}Ni_{0.66}$-NKU-100.

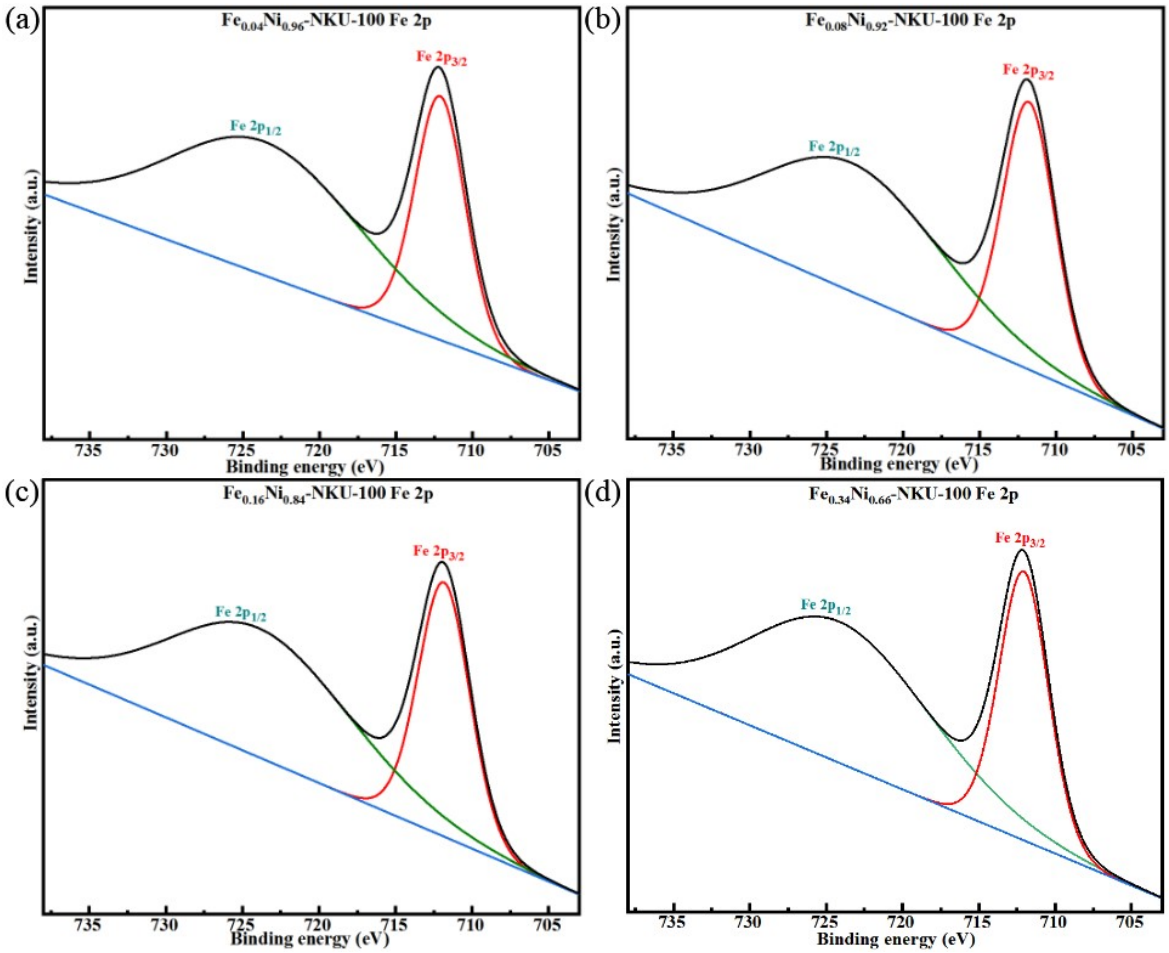

Fig. S18 High-resolution XPS of Fe 2p for (a) $Fe_{0.04}Ni_{0.96}$-NKU-100, (b) $Fe_{0.08}Ni_{0.92}$-NKU-100, (c) $Fe_{0.16}Ni_{0.84}$-NKU-100 and (d) $Fe_{0.34}Ni_{0.66}$-NKU-100.

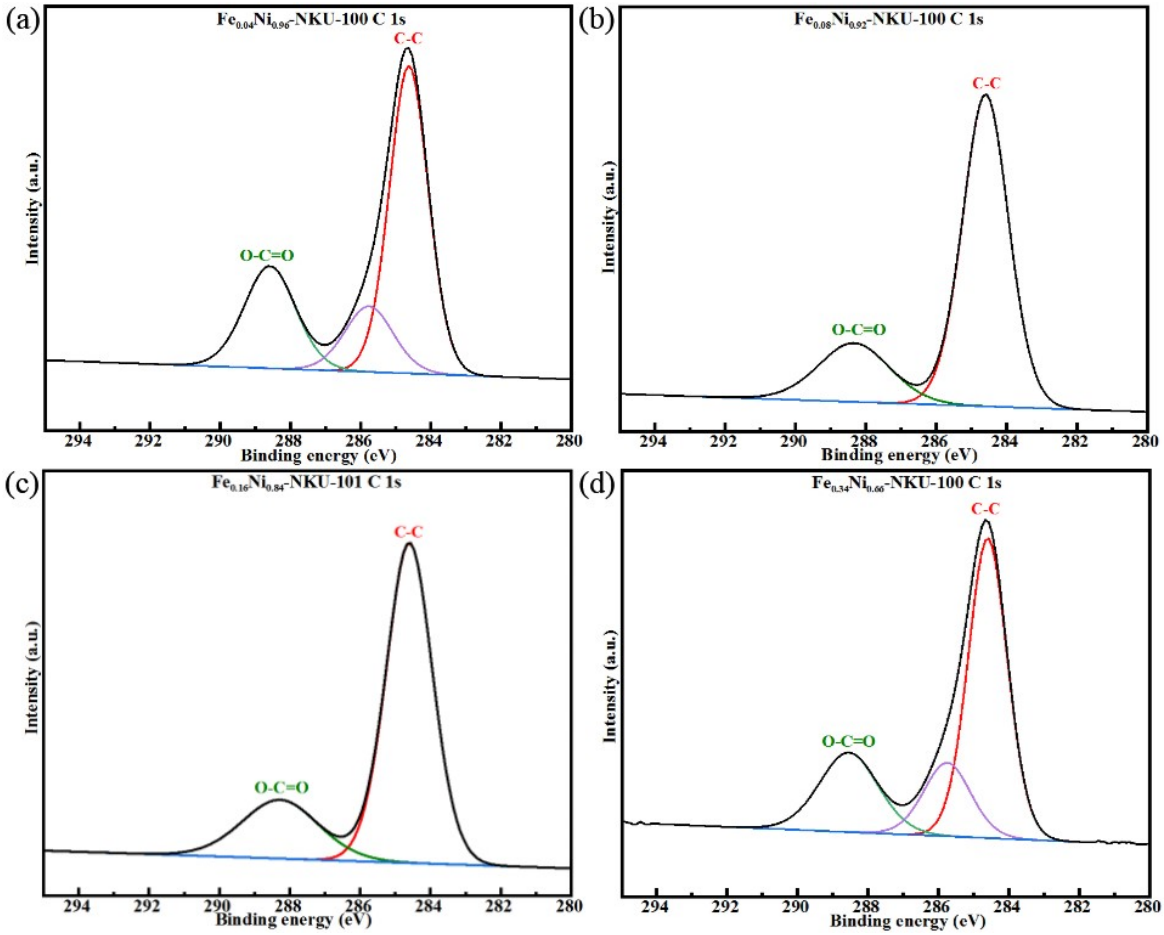

Fig. S19 High-resolution XPS of C 1s for (a) $Fe_{0.04}Ni_{0.96}$-NKU-100, (b) $Fe_{0.08}Ni_{0.92}$-NKU-100, (c) $Fe_{0.16}Ni_{0.84}$-NKU-100 and (d) $Fe_{0.34}Ni_{0.66}$-NKU-100.

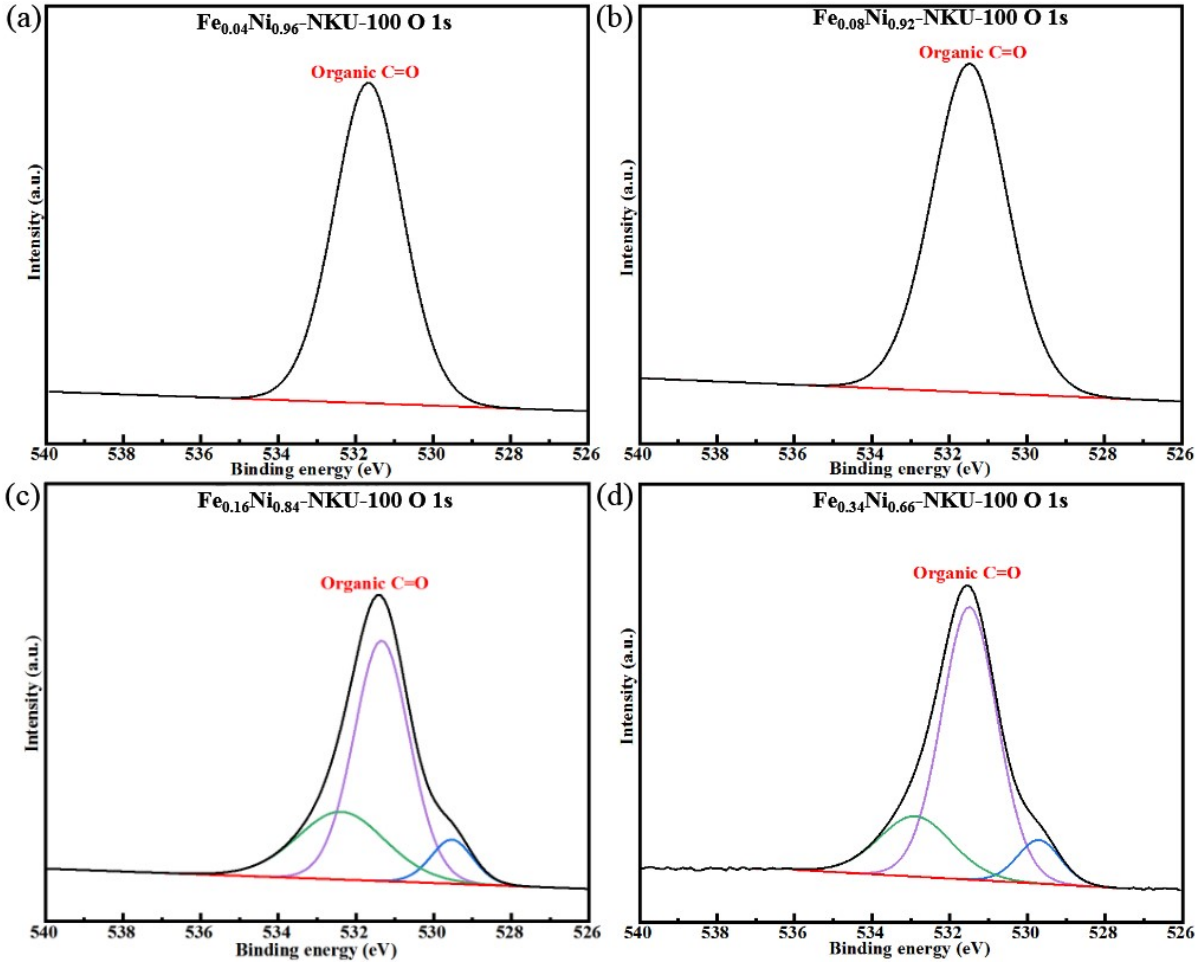

Fig. S20 High-resolution XPS of O 1s for (a) $Fe_{0.04}Ni_{0.96}$-NKU-100, (b) $Fe_{0.08}Ni_{0.92}$-NKU-100, (c) $Fe_{0.16}Ni_{0.84}$-NKU-100 and (d) $Fe_{0.34}Ni_{0.66}$-NKU-100.

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