Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Construction of a hierarchically structured, NiCo-Cu-based trifunctional electrocatalyst for efficient overall water splitting and 5-hydroxymethylfurfural oxidation

Ruijuan Zheng[a], Chenhao Zhao[a], Jinhua Xiong[a], Xue Teng[b], Wuhua Chen[a], Zhibiao Hu[a] and Zuofeng Chen[b,*]

[a]Fujian Provincial Colleges and University Engineering Research Center of Solid Waste Resource Utilization (Longyan University); Fujian Provincial Key Laboratory of Clean Energy Materials, Longyan University, Longyan 364012, Fujian, China;

[b]Shanghai Key Laboratory of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China.

EXPERIMENTAL

Chemicals. Commercial copper foam (CF) with a thickness of 2 mm was performed from Kunshan Lvchuang Electronics Co. LTD. 5-Hydroxymethylfurfural (HMF, 99%), 2, 5-furandicarboxylic acid (FDCA, 98%), 2-formyl-5-furancarboxylic acid (FFCA, 98%), 2, 5-Diformylfuran (DFF, 98%) and 5-Hydroxymethyl-2-furan-carboxylic acid (HMFCA, 98%) were purchased from Aladdin. Concentrated hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 96%), potassium hydroxide

(KOH, 85%), ammonium persulfate ($(NH_4)_2S_2O_8$, 98%), cobalt chloride hexahydrate ($CoCl_2$•$6H_2O$, 99%) and nickel chloride hexahydrate ($NiCl_2$•$6H_2O$, 98%) were purchased from Sinopharm Group Co. LTD. All reagents were used directly without any further purification. Unless stated otherwise, deionized water was used in all experiments.

Apparatus. Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) elemental analysis data were obtained at Hitachi S-4800. Powder X-ray diffraction (XRD) patterns were measured by X'Pert 3 Powder. X-ray photoelectron spectroscopy (XPS) analysis for elemental compositions and valence states was conducted on a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer. The elemental contents of Ni and Co were measured by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) using the Perkin Elmer ICP-OES Optima 8300.

All electrochemical measurements were conducted on a CHI 660E electrochemical workstation (Chenhua Corp., Shanghai, China) with a typical three-electrode setup in an electrolyte solution of 1 M KOH, consisting of a $NiCo_{NSs}$/Cu NWs as the working electrode, a graphite rod as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The two-compartment cell was separated by an anion exchange membrane. Linear sweep voltammetry (LSV) measurements were conducted in 1 M KOH at a scan rate of 2 mV/s. Potentials reported were referenced to a reversible hydrogen electrode by E (RHE) = E (SCE) + 1.044 V. The electrochemical impedance spectroscopy (EIS) measurements were carried out in the range from 10^5 to 1 Hz with an amplitude of 5 mV at the open-circuit potential in 1 M KOH. The electrochemically active surface area (ECSA) was investigated by cyclic voltammetry (CV) to determine the electrochemical double-layer capacitances (C_{dl}) in 1 M KOH. All electrochemical measurements were conducted without *i*R compensation. All experiments were performed at 22 ± 2 °C.

Synthesis of $NiCo_{NSs}$/CuNWs. The $NiCo_{NSs}$/CuNWs was prepared by a facile three-step procedure. Firstly, a piece of Cu foam (1 cm × 2 cm) was immersed in 3 M HCl to remove surface oxide layer, and then cleaned with deionized water by ultrasonication for 10 min. To obtain $Cu(OH)_2$ nanowires (NWs) on Cu foam (CF), The cleaned Cu foam was immersed into aqueous solution containing 2 M NaOH and 0.1 M $(NH_4)_2S_2O_8$ for 25 min silently. The color of Cu foam surface was changed from golden yellow to blue-green. The Cu foam was taken out from the solution, rinsed with deionized water and dried in air. The electrochemical reduction of $Cu(OH)_2$ NWs to Cu NWs was achieved by applying a constant cathodic current density of 20 mA cm^{-2} in 1 M Na_2SO_4 aqueous solution, and the color of the $Cu(OH)_2$ nanowires was changed from blue-green to dark wine. The resultant Cu NWs was cleaned with deionized water for several times, then dried at 60 ºC in a vacuum drying oven.

The $NiCo_{NSs}/Cu_{NWs}$ electrode was synthesized by a simple cyclic voltammetry method in an electrolyte containing 0.1 M $CoCl_2$ and 0.1 M $NiCl_2$. The electrodeposition process was carried out in a three-electrode system using Cu NWs as the working electrode, a graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode within a potential range of −1.2 to 0.2 V at a scan rate of 10 mV/s for 25 cycles. After electrodeposition, the electrodes were carefully rinsed thoroughly with deionized water and ethanol and dried at 60 ºC in a vacuum drying oven.

Commercial 20% Pt/C (or RuO_2) with a mass loading of 3 mg cm^{-2} was dropped onto Cu NWs electrode, followed by drying in an electric oven at 60 °C.

HPLC analysis. HPLC (Shimadzu Prominence LC-2030C system) equipped with an ultraviolet-visible detector set at 265 nm and a 4.6 mm × 150 mm Shim-pack GWS 5 μm C18 column was used to analyze HMF and its oxidation products. Specifically, 10 μL of electrolyte was periodically collected during potentiostatic electrolysis and diluted with 990 mL water. The eluent solvent is a mixture aqueous solution of 5 mM ammonium formate and methanol, the ratio of ammonium formate and methanol was 7: 3. The flow rate is 0.5 ml min^{-1}, and each separation lasts for 10 minutes.

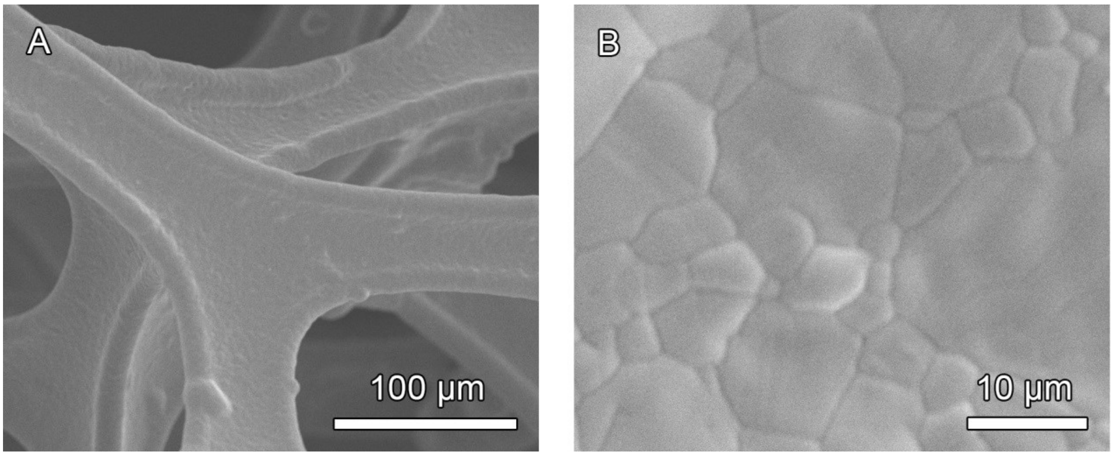

Figure S1. SEM images of Cu foam substrate of different magnifications.

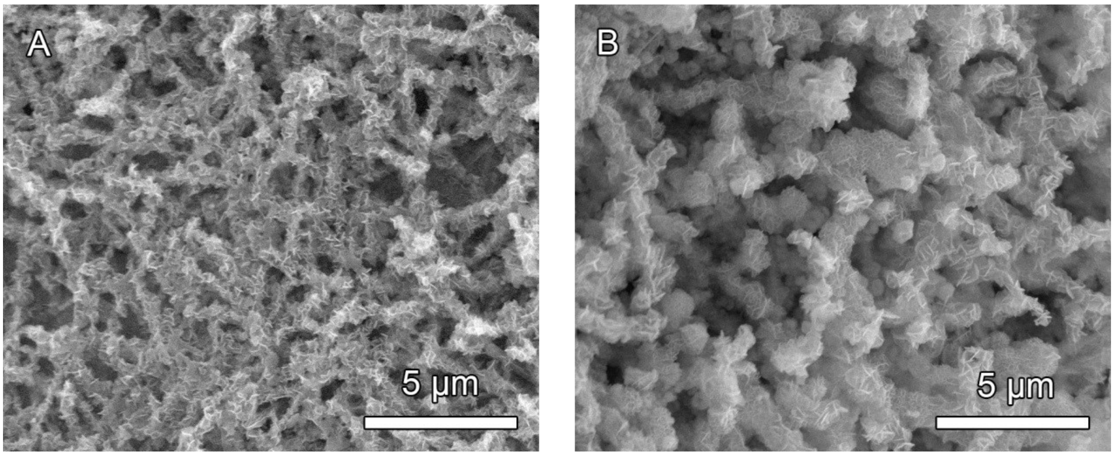

Figure S2. SEM images of Ni_{NSs}/Cu_{NWs} (A) and Co_{NSs}/Cu_{NWs} (B)

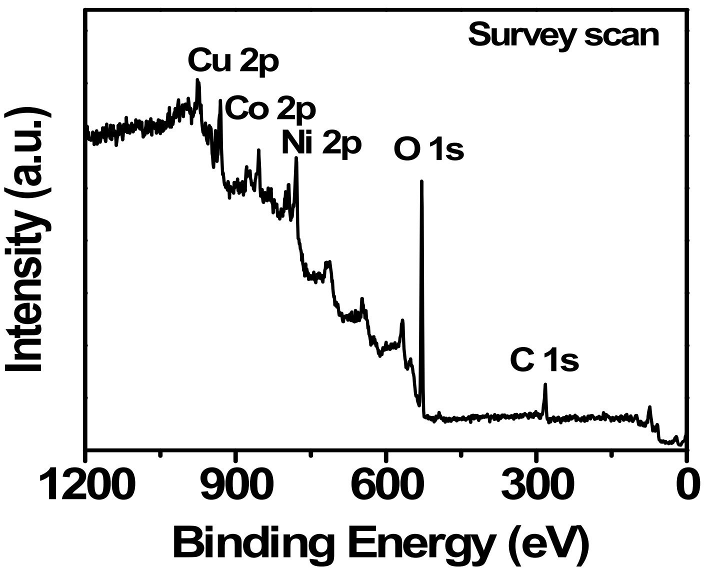

Figure S3. Survey XPS spectrum of $NiCo_{NSs}/Cu_{NWs}$.

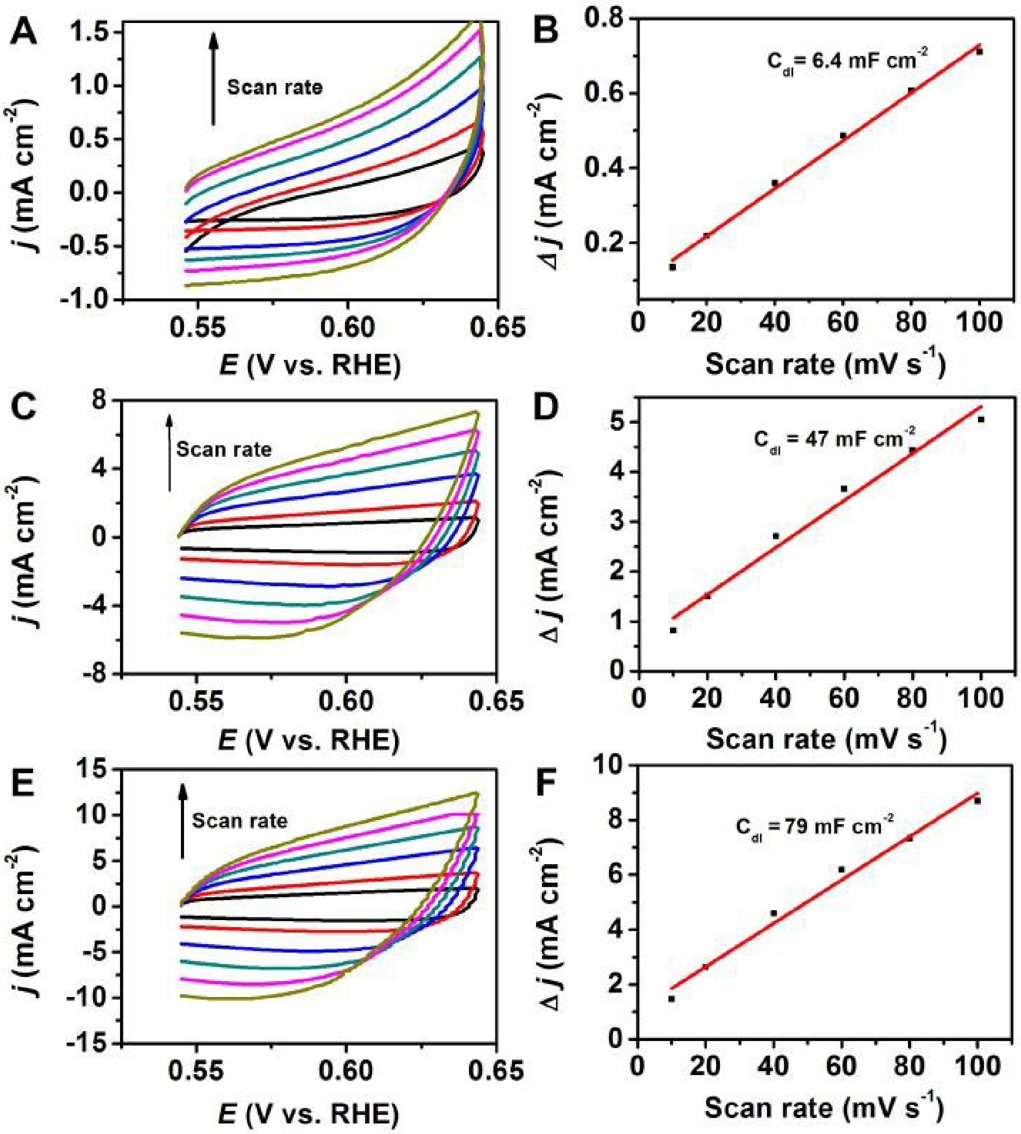

Figure S4. Cyclic voltammograms at scanning rates of 10, 20, 40, 60, 80 and 100 mV/s in the potential range of 0.545 ~ 0.645 *vs.* RHE and capacitive current at 0.595 V as a function of the scan rate for different electrodes in 1 M KOH. (A, B) Cu foam; (C, D) $Cu(OH)_2$ NWs; (E, F) Cu NWs.

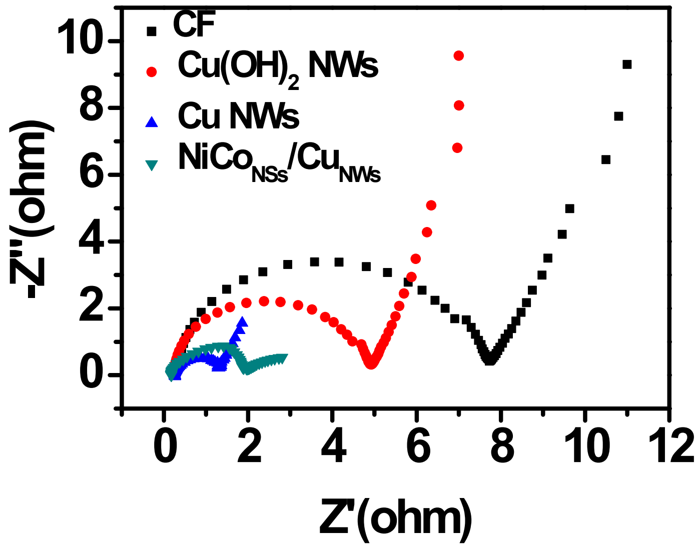

Figure S5. EIS spectra of different material samples at open circuit potentials in 1 M KOH.

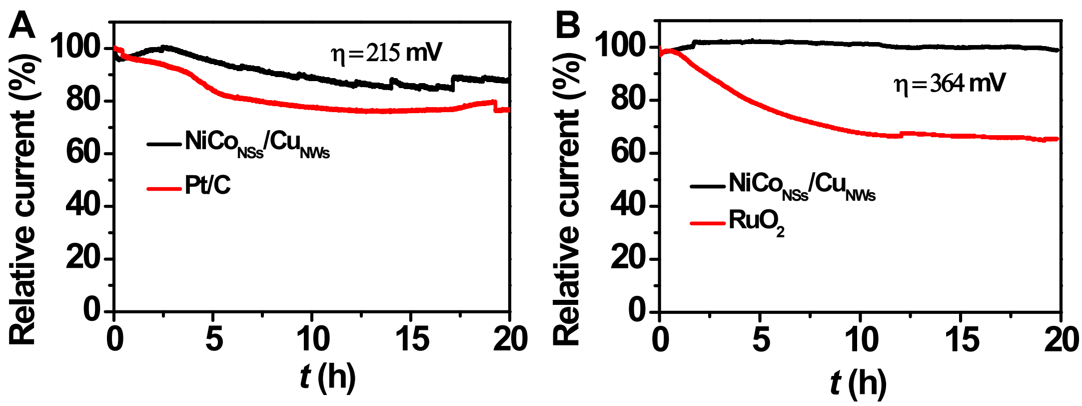

Figure S6. Comparison of electrocatalytic durability of $NiCo_{NSs}/Cu_{NWs}$ with benchmark Pt/C and RuO_2 in 1 M KOH (A) HER electrocatalytic durability of $NiCo_{NSs}/Cu_{NWs}$ and Pt/C, (B) OER electrocatalytic durability of $NiCo_{NSs}/Cu_{NWs}$ and RuO_2

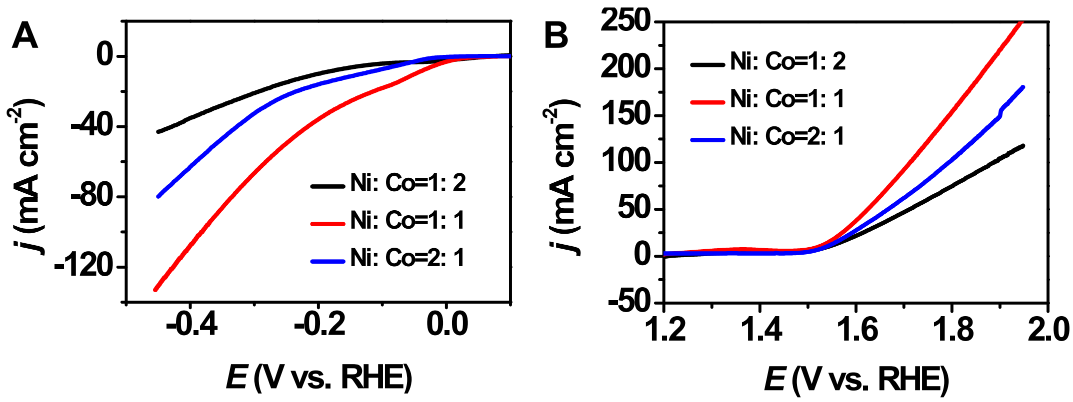

Figure S7. LSV curves for HER (A) and OER (B) at $NiCo_{NSs}/Cu_{NWs}$ prepared with different concentration ratio of $NiCl_2$ and $CoCl_2$.

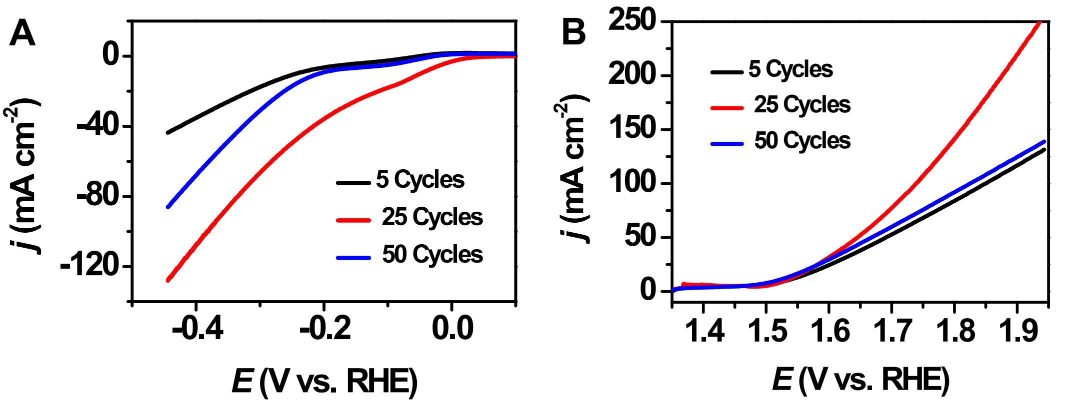

Figure S8. LSV curves for HER (A) and OER (B) at $NiCo_{NSs}/Cu_{NWs}$ prepared by different cycles of electrodeposition.

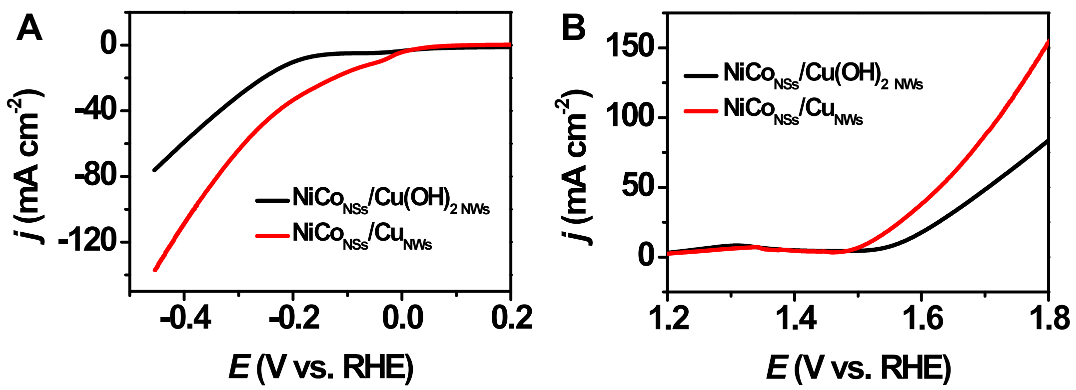

Figure S9. LSV curves for HER (A) and OER (B) at $NiCo_{NSs}/Cu(OH)_{2\ NWs}$ and $NiCo_{NSs}/Cu_{NWs}$.

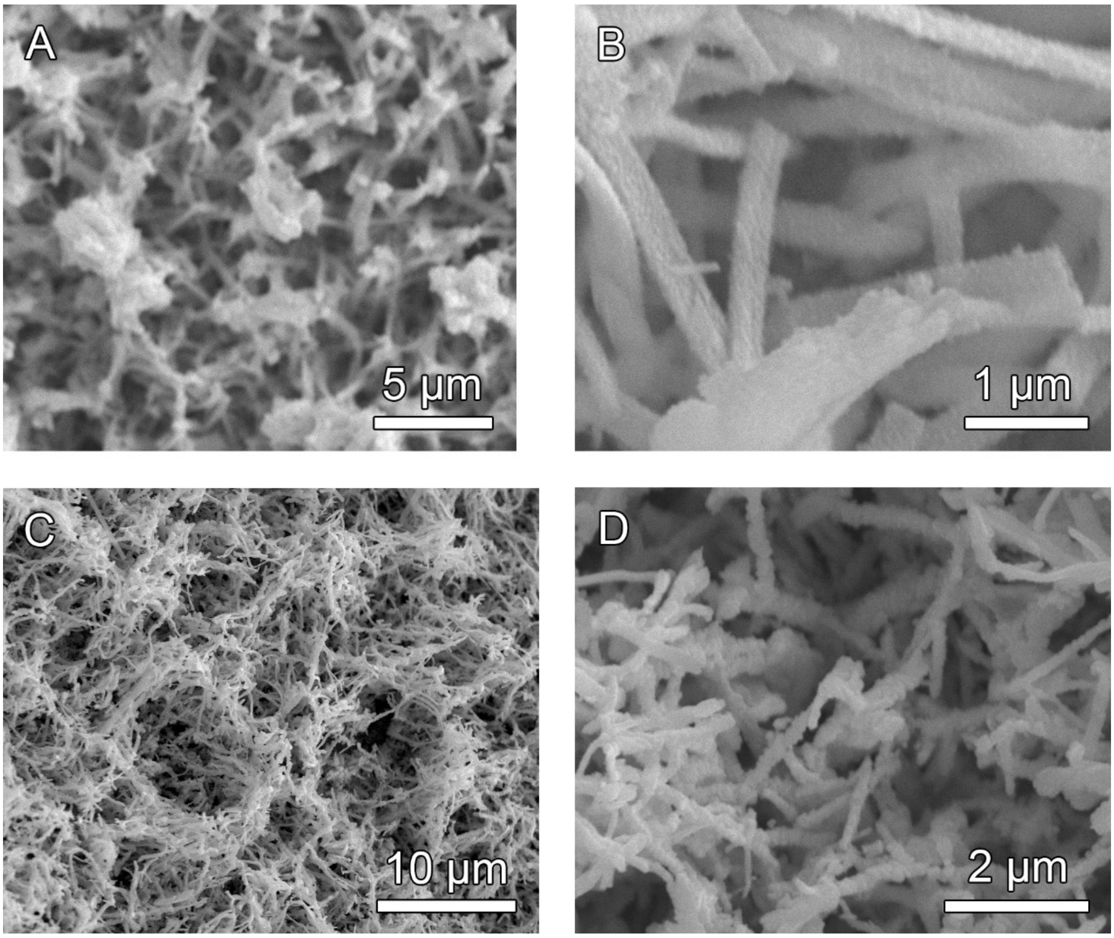

Figure S10. SEM images of $NiCo_{NSs}/Cu_{NWs}$ after overall water splitting an applied voltage of 1.78 V for 20 hours: (A, B) HER side, (C, D) OER side.

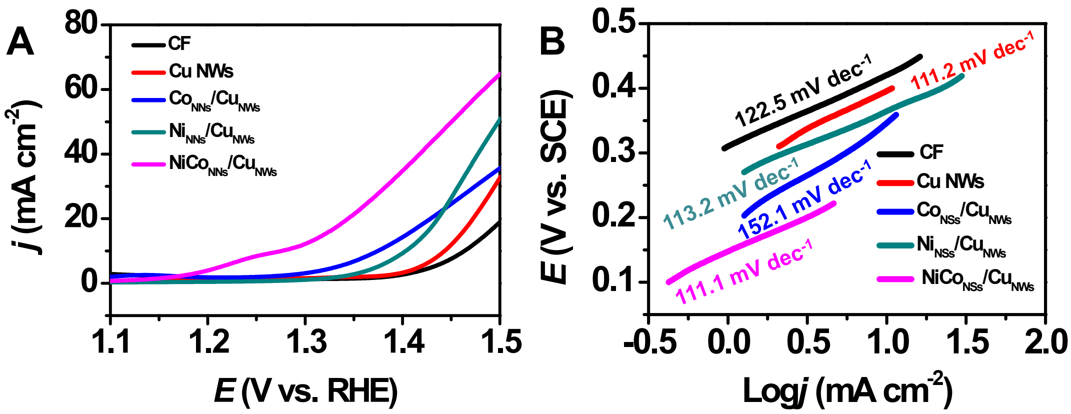

Figure S11. (A) LSV curves at a scan rate of 2 mV s^{-1} and (B) Tafel plots of $NiCo_{NSs}/Cu_{NWs}$ and other contrast samples in 1.0 M KOH with 10 mM added HMF.

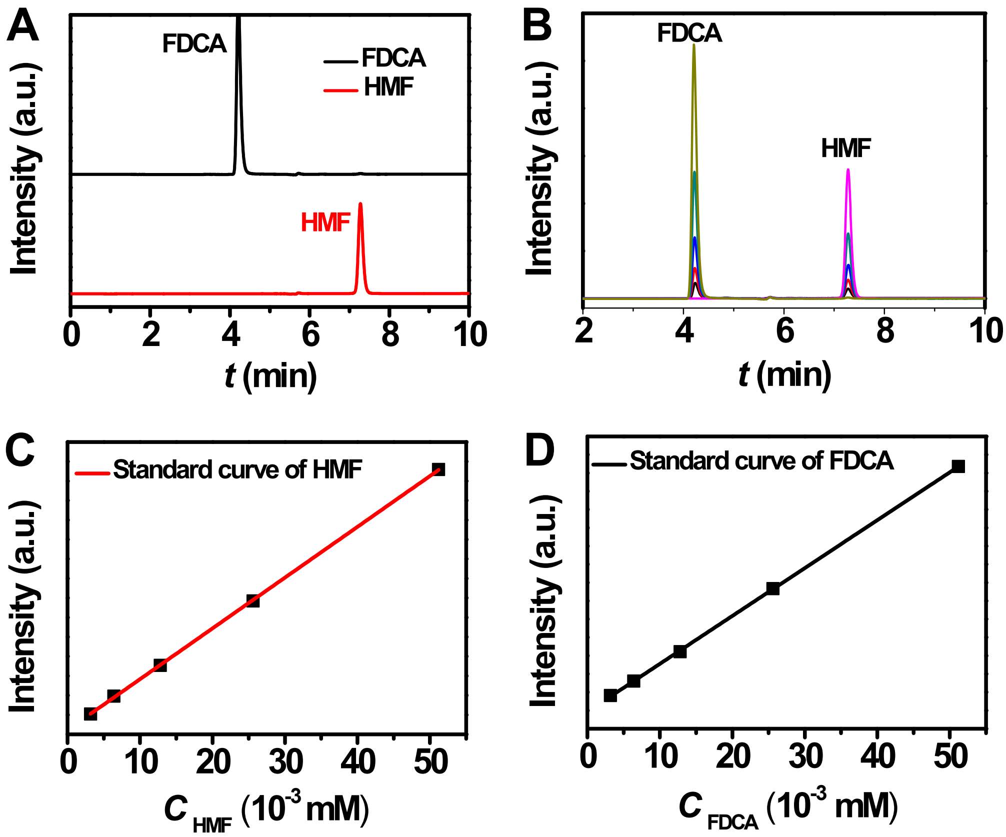

Figure S12. (A) HPLC measurements of pure HMF and FDCA. (B) HPLC chromatograms and calibration of the HPLC for (C) HMF and (D) FDCA.

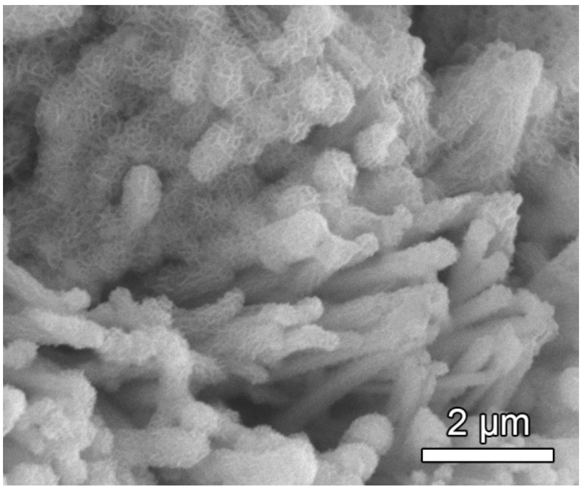

Figure S13. SEM image of $NiCo_{NSs}/Cu_{NWs}$ after 6 h electrolysis at 1.44 V vs. RHE in 1.0 M KOH with 10 mM added HMF.

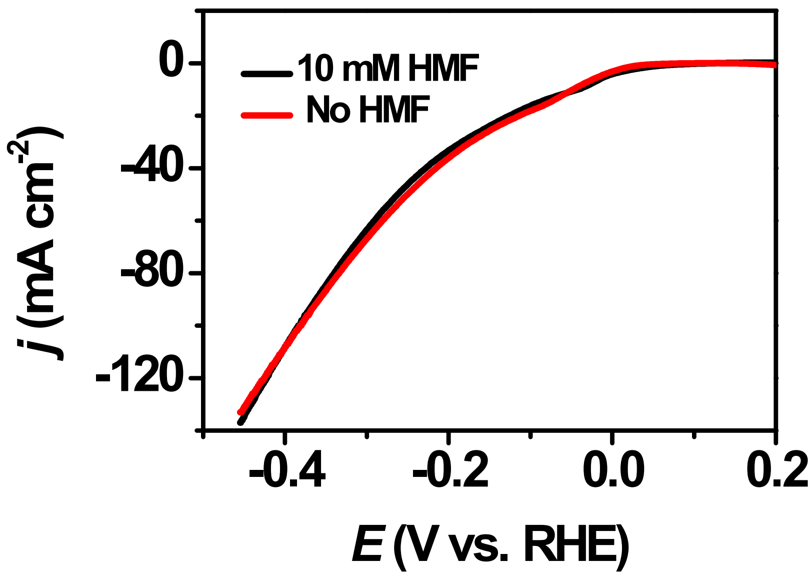

Figure S14. LSV curves for HER at $NiCo_{NSs}/Cu_{NWs}$ at a scan rate of 2 mV s^{-1} in 1.0 M KOH with and without 10 mM HMF.

Table S1. Contents of Ni and Co of $NiCo_{NSs}/Cu_{NWs}$ by ICP-AES analysis and the correlation between the Ni/Co content and HER/OER catalytic performance.

concentration ratio of Ni^{2+} and Co^{2+}	Element	mass loading (mg/cm^{-2})	HER (η@10 mA cm^{-2}) (mV)	OER (η@10 mA cm^{-2}) (mV)
1:2	Ni	0.38	201	320
	Co	0.605		
1:1	Ni	0.415	49	303
	Co	0.425		
2:1	Ni	0.64	132	308
	Co	0.312		

Table S2. Comparison of the HER performance for the $NiCo_{NSs}/Cu_{NWs}$ catalyst with other reported electrocatalysts in 1 M KOH electrolyte.

Catalysts	**Supports**	**η (10 mA cm^{-2})**	**References**
CoNi@NC	Glassy carbon	142	*Angew. Chem. Int. Ed.* **2015**, *54*, 2100
CoNi-OOH-30(40)	Titanium sheets	210	*Electrochim. Acta* **2019**, *301*, 449
CoNiBDC/CC	Carbon Cloth	135	*New J. Chem.* **2020**, *44*, 1694
$Co_{81}Ni_{19}$ nanosheet arrays	Cu foam	132	*J. Power Sources* **2019**, *427*, 184
CoNi@NC-NCNTs	Carbon cloth	85	*Appl. Surf. Sci.* **2020**, *517*, 145841
$NiCo_2O_4$/NiCoP	RDE	198	*Catal. Sci. Technol.* **2020**, *10*, 5559
$MoS_2/Co_9S_8/Ni_3S_2$	Nickel foam	113	*J. Am. Chem. Soc.* **2019**, *141*, 10417
NiCo-nitrides/$NiCo_2O_4$	Graphite fibers	71	*Adv. Sci.* **2019**, *6*, 1801829
CoP@BCN	Glassy carbon	215	*Adv. Energy Mater.* **2017**, *7*, 1601671
MoS_2/Ni_3S_2	Nickel foam	110	*Angew. Chem. Int. Ed.* **2016**, *55*, 6702
$Co(OH)_2$@P-NiCo-LDH	Carbon paper	226	*J. Colloid Interf. Sci.* **2021**, *582*, 535
$NiCo_2S_4$	Glassy carbon	345	*RSC Adv.* **2020**, *10*, 22196
NiCoP@Cu_3P	Cu foam	54	*J. Mater. Chem. A.* **2018**, *6*, 2100
$Cu_{0.50}Fe_{0.50}$	NF	158	Small **2020**, *16*, 1905884
Cu_3P@NPC	copper foam	135.45	*Sustainable Energy Fuels* **2021**, *5*, 2451
Cu_3N	NF	118	*ACS Energy Lett.* **2019**, *4*, 747
Co_2P@NPPC	glass carbon	240	*Sustainable Energy Fuels* **2021**, *5*, 2477
$NiCo_{NSs}/Cu_{NWs}$	Cu foam	50	**This work**

Table S3. Comparison of the OER performance for the $NiCo_{NSs}/Cu_{NWs}$ catalyst with other reported electrocatalysts in 1 M KOH electrolyte.

Catalysts	Supports	η (10 mAcm⁻²)	References
Ni-Co nanowire	Carbon fiber	302	*Adv. Energy Mater.* **2017**, *7*, 1601492
$CoNi(OH)_x$	Cu foil	280	*Adv. Energy Mater.* **2016**, *6*, 1501661
Exfoliate NiFe LDH	Glassy carbon	302	*Nat. Commun.* **2014**, *5*, 5477
NiCoP/C nanobox	Glassy carbon	330	*Angew. Chem. Int. Ed.* **2017**, *56*, 3897
Mo-CoOOH	Glassy carbon	305	*Nano Energy* **2018**, *48*, 73
CoNi-OOH-30(40)	Titanium sheets	279	*Electrochim. Acta* **2019**, *301*, 449
$Co\text{-}Mo_2C$ NPs	Glassy carbon	347	*Appl. Catal. B-Environ.* **2018**, *227*, 340
Co/NiMOFs@Fe	Fe foam	264	*Chemcatchem* **2019**, *18*, 6061
Ni-MOF	Carbon	346	*Chemelectrochem* **2018**, *5*, 2795
Co-Fe/Ni@HPA-MOF	Glassy carbon	320	*J. Solid State Chem.* **2019**, *272*, 32
Mo-CoOOH	Glassy carbon	305	*Nano Energy* **2018**, *48*, 73
$NiCoP@Cu_3P$	Cu foam	309	*J. Mater. Chem. A* **2018**, *6*, 2100
$Co_3S_4@MoS_2$	Glassy carbon	280	*Nano Energy* **2018**, *47*, 494
CoMnP	Glassy carbon	330	*J. Am. Chem. Soc.* **2016**, *138*, 4006
$CoNi(OH)_x$ nanotubes	Cu foil	280	*Adv. Energy Mater.* **2016**, *6*, 1501661
$NiCo_2O_4$/NiCoP	RDE	295	*Catal. Sci. Technol.* **2020**, *10*, 5559
NiCo LDH nanostructures	Carbon paper	367	*Nano Lett.* **2015**, *15*, 1421
$S\text{-}CoMn_2O_4$-MSs	FTO	300	*J. Mater. Chem. A.* **2021**, *9*, 12255
$Mn_xCo_{3-x}O_4$	Ni foam	327	*Int. J. Hydrogen Energy* **2020**, *45*, 14867
Mixed Ni-Co-Mn oxide	Glassy carbon	400	*ACS Appl. Energy Mater.* 10.1021/acsaem.0c00544
Defect-rich Cobalt oxide	Glassy carbon	369	*ChemSusChem* **2020**, *13*, 520
Co@NCNT	GCE	310	*Sustainable Energy Fuels* **2021**, *5*, 820
Co_2P@NPPC	Glassy carbon	316	*Sustainable Energy Fuels* **2021**, **5**, 2477
Co/P/N-CNP	NF	311	*Electrochim. Acta* **2020**, *337*, 135807
$NiCo_{NSs}/Cu_{NWs}$	Cu foam	303	**This work**

Table S4. Comparison of the bifunctional water splitting activity of $NiCo_{NSs}/Cu_{NWs}$ catalyst with other reported electrocatalysts in 1 M KOH electrolyte.

Catalysts	**Overall voltages (10 mAcm^{-2})**	**References**
$NiFe/NiCo_2O_4/NF$	1.67	*Adv. Funct. Mater.* **2016**, *26*, 3515
NiFe LDH/NF	1.70	*Science* **2014**, *345*, 1593
CoP/rGO	1.7	*Chem. Sci.* **2016**, *7*, 1690
$Ni_xCo_{3-X}O_4$ || NiCo/NiCoOx	1.75	*ACS Appl. Mater. Interfaces* **2016**, *8*, 4718
$NiCo_2O_4$ || $Ni_{0.33}Co_{0.67}S_2$NWs	1.73	*Adv. Energy Mater.* **2015**, *5*, 1402031
$NiCo_2O_4$	1.65	*Angew. Chem. Int. Ed.* **2016**, *55*, 6290
CoO/MoO_x	1.72	*ACS Sustain. Chem. Eng.* **2016**, *4*, 3743
Co_1Mn_1CH/NF	1.68	*J. Am. Chem. Soc.* **2017**, *139*, 832
Co–Fe oxyphosphide microtubes	1.69	*Adv. Sci.* **2019**, *6*, 1900576
CP/CTs/Co-S	1.76	*ACS nano* **2016**, *10*, 2342
CoNi-OOH-30(40)	1.76	*Electrochim. Acta* **2019**, *301*, 449
$NiCo_{NSs}/Cu_{NWs}$	1.69	**This work**