

Supporting information

Tubular Cu(OH)₂ Arrays Decorated by Nanothorny Co-Ni Bimetallic Carbonate Hydroxide Supported on Cu Foam: a 3D Hierarchical Core-shell Efficient Electrocatalyst for Oxygen Evolution Reaction

Jiahui Kang^{a, b}, Jiali Sheng^a, Jinqi Xie^a, Huangqing Ye^a, Jiahui Chen^a, Xian-Zhu Fu^{*a, c}, Guoping Du^{*b}, Rong Sun^{*a}, Ching-Ping Wong^{d, e}

^a Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China

^b School of Materials Science and Engineering, Nanchang University, Nanchang 330031, China.

^c College of Materials Science and Engineering, Shenzhen University, Shenzhen 518055, China.

^d Department of Electronics Engineering, The Chinese University of Hong Kong, Hong Kong, China

^e School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

* Corresponding authors:

Xian-Zhu Fu, E-mail address: xz.fu@szu.edu.cn;

Guoping Du, E-mail address: guopingdu@ncu.edu.cn

Rong Sun, E-mail address: rong.sun@siat.ac.cn

Tel: +86-755-86392151; Fax: +86-755-86392299

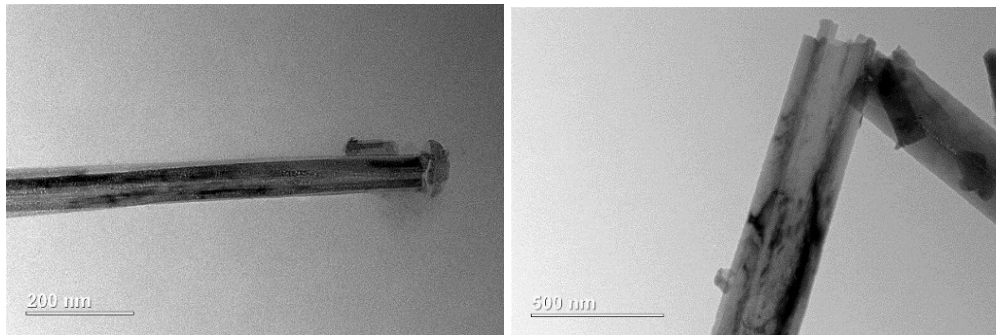


Figure S1 TEM images of Cu(OH)₂ NTs.

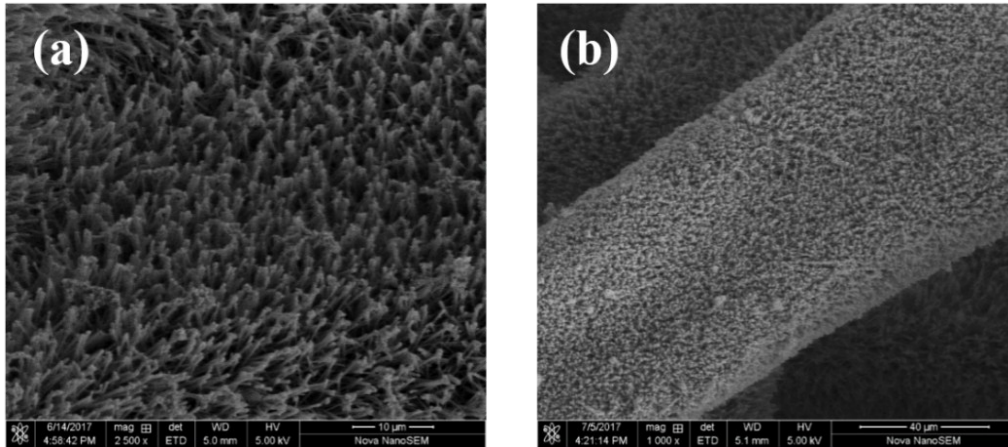


Figure S2 Low-magnification SEM of Cu(OH)₂@CoNiCH NTs/CF.

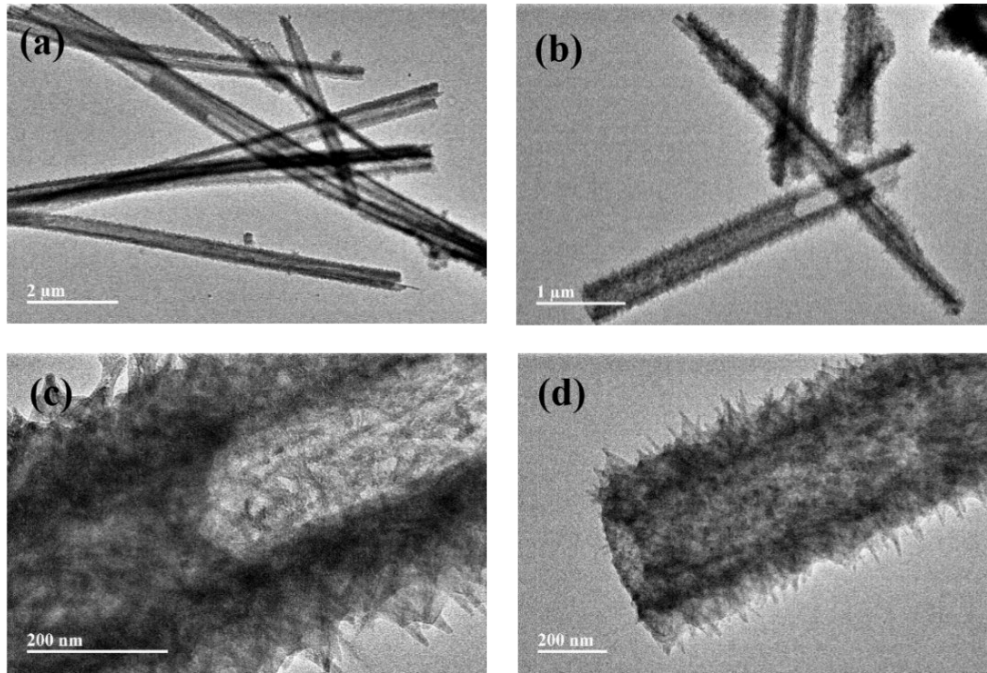


Figure S3 Low and high magnification TEM images of $\text{Cu}(\text{OH})_2@ \text{CoNiCH}$ NTs.

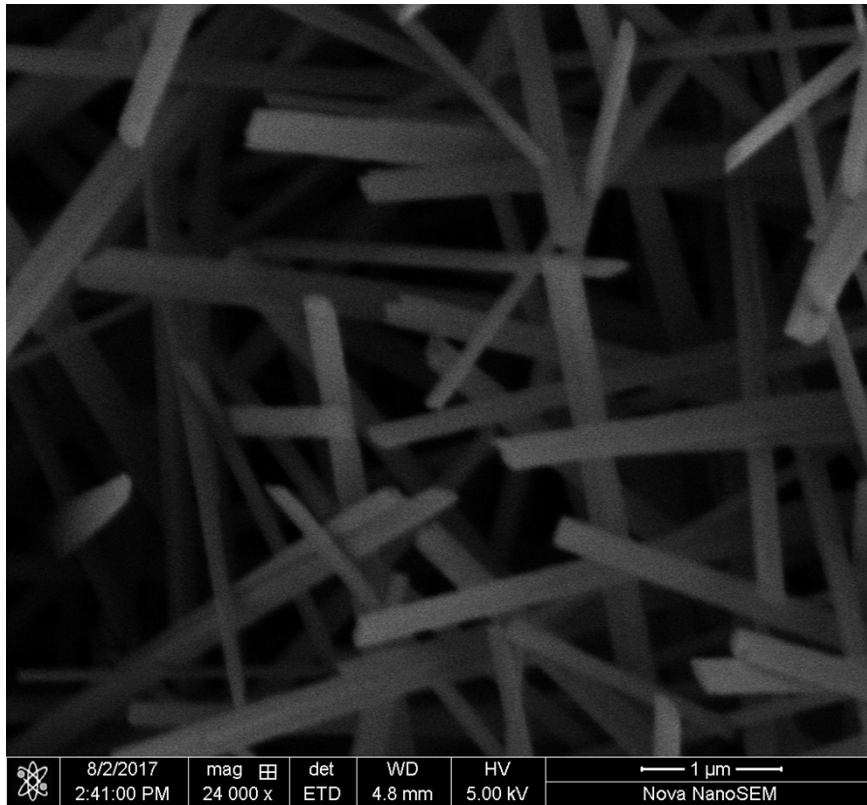


Figure S4 Low-magnification SEM of $\text{Cu}(\text{OH})_2$ NWs/CF.

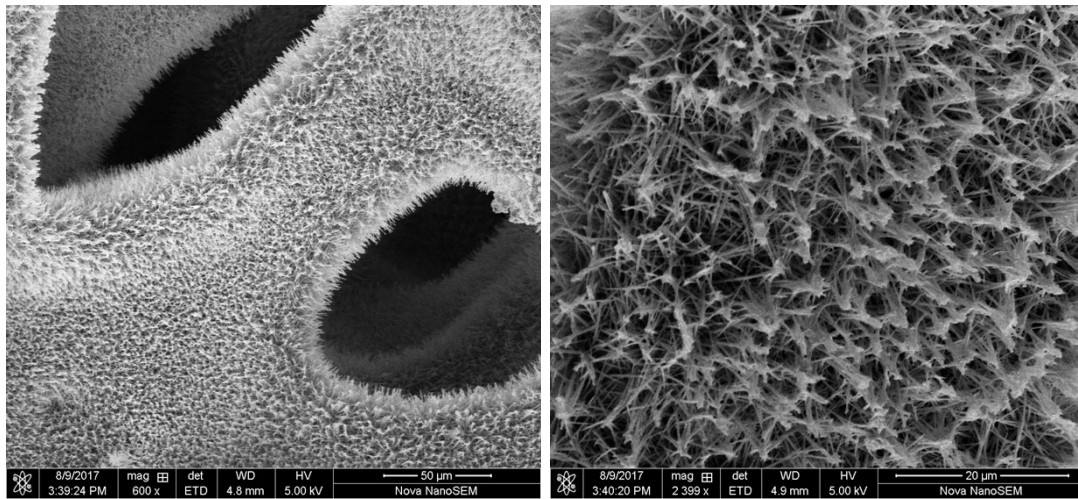


Figure S5 Low-magnification SEM of $\text{Cu}(\text{OH})_2@\text{CoNiCHNWs}/\text{CF}$.

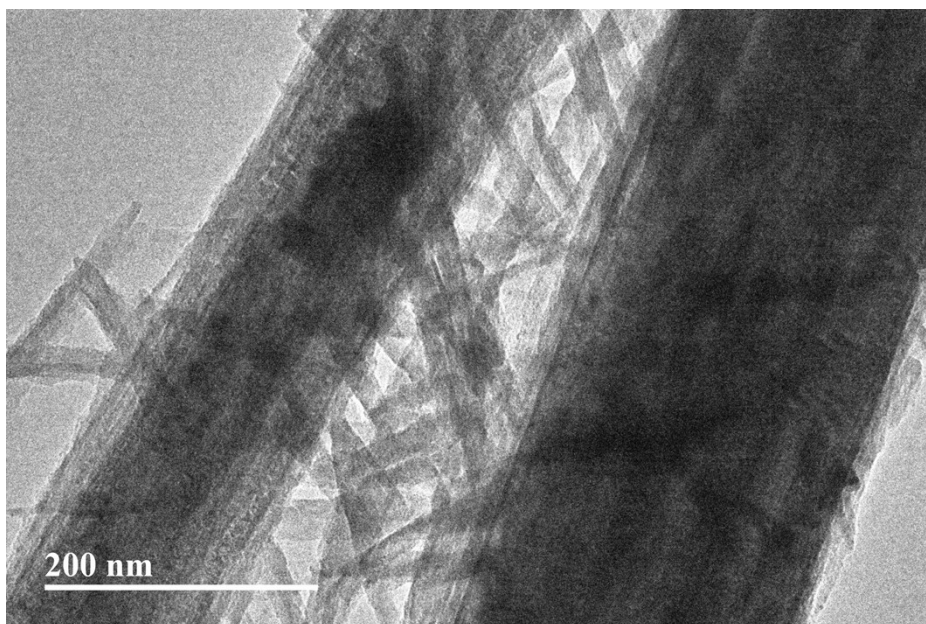


Figure S6 Low-magnification TEM of $\text{Cu}(\text{OH})_2@ \text{CoNiCH}$ NWs.

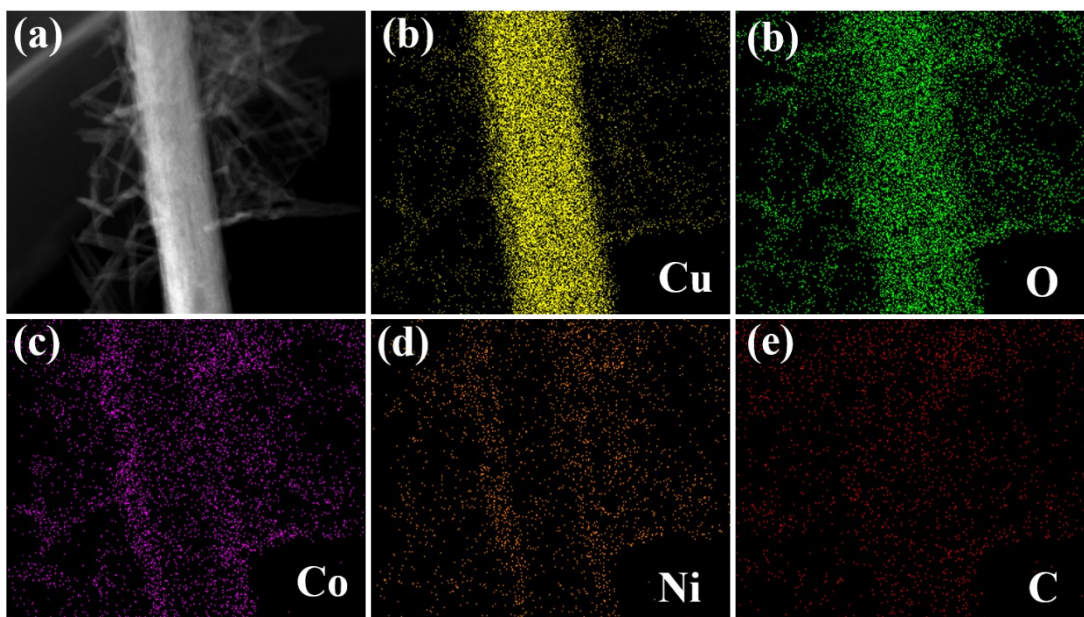


Figure S7 STEM EDS element mapping of $\text{Cu}(\text{OH})_2@ \text{CoNiCH}$ NWs: (a)HAADF image of the EDS mapping area, (b-g) element mapping of Cu, O, Co, Ni and C elements.

For comparison, Cu and O elements evenly distributing on the whole individual construction proves that the solid $\text{Cu}(\text{OH})_2$ nanowire core, and strong signals of Co and Ni in the walls mainly shows that CoNi nanothorn shell were distributed on the surface. (Figure S7)

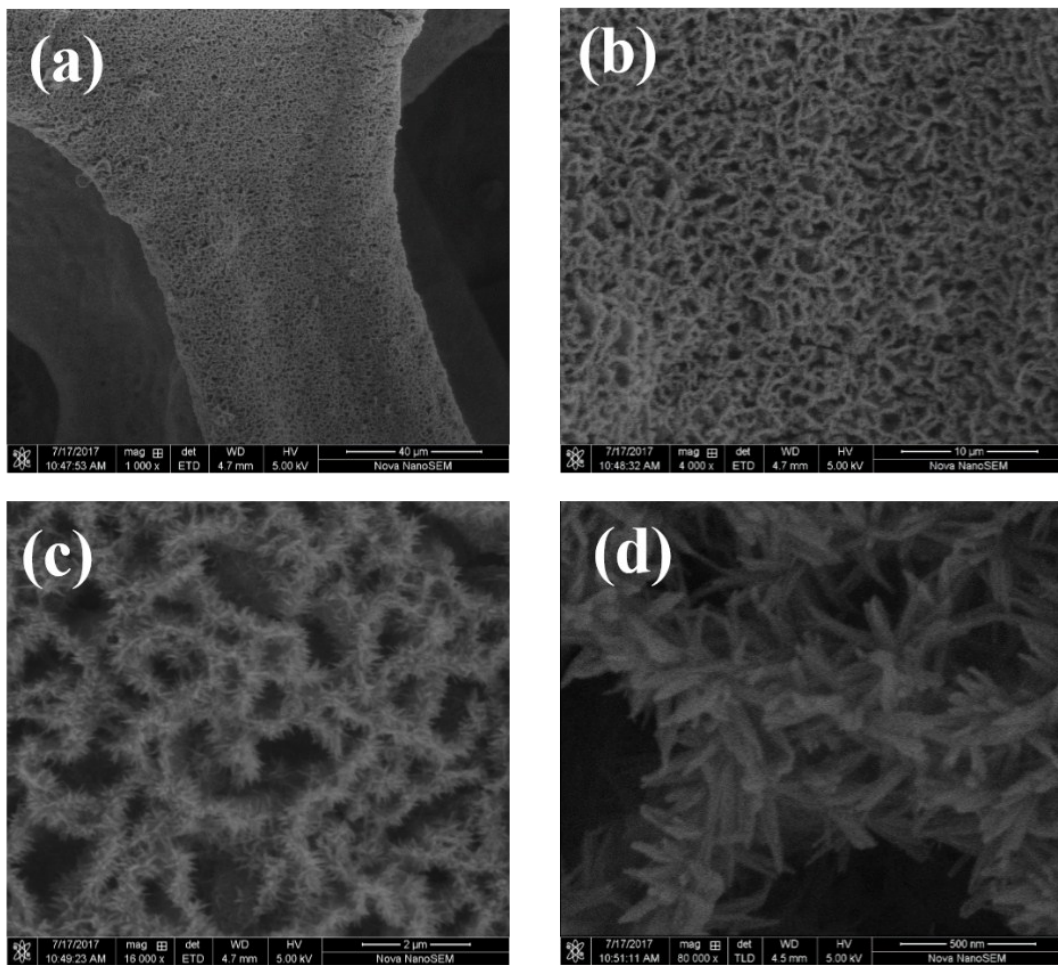


Figure S8 SEM of the CoNiCH NRs/CF.

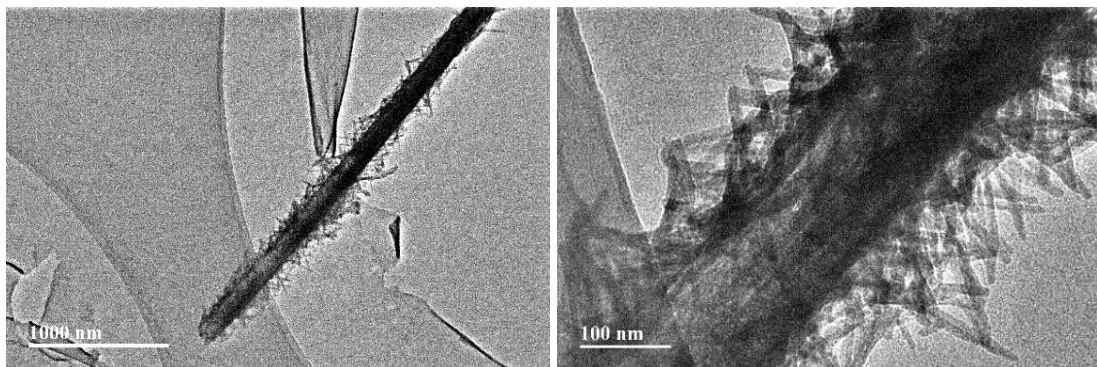


Figure S9 TEM of Cu(OH)₂@CoCH NTs.



Figure S10 EDS content of $\text{Cu}(\text{OH})_2@ \text{CoNiCH}$ NTs.

As shown in Figure S10, the atomic ratio of Co/Ni of $\text{Cu}(\text{OH})_2@ \text{CoNiCH}$ NTs is approximately 1.93 according to the EDS result.

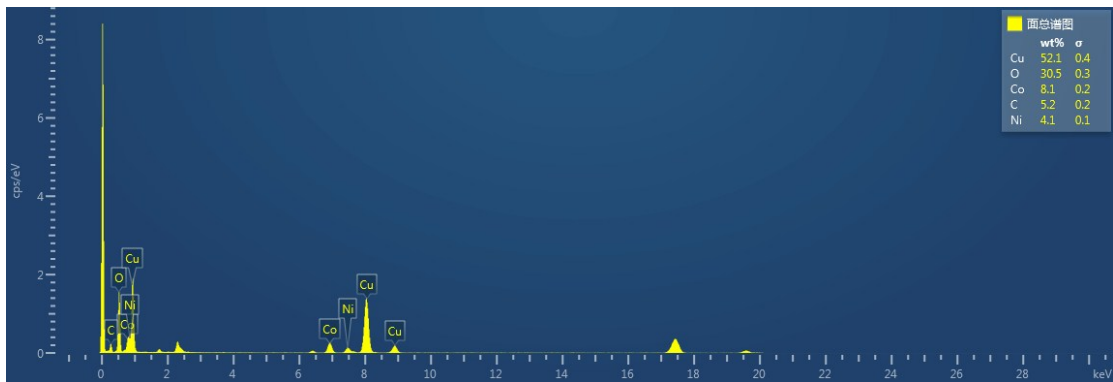


Figure S11 EDS content of $\text{Cu}(\text{OH})_2@ \text{CoNiCH}$ NWs.

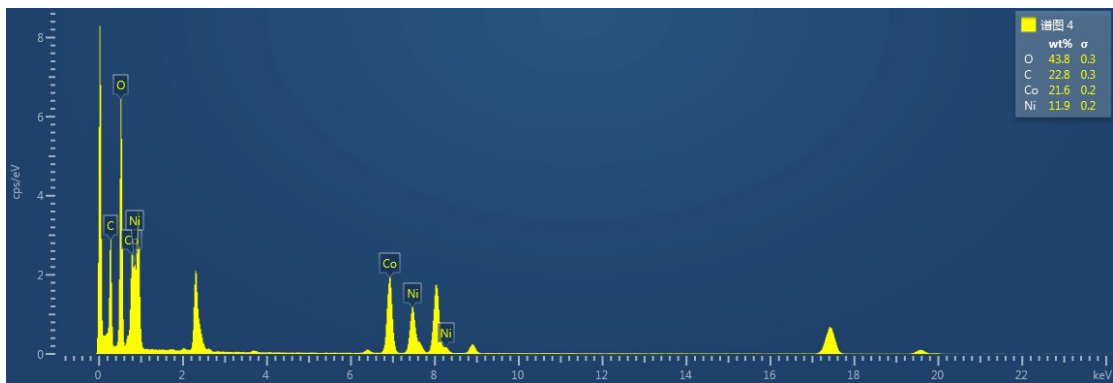


Figure S12 EDS content of CoNiCH NRs.

Table S1 The molar ratios of Co/Ni in prepared samples determined by ICP, EDS, XPS

Samples	Co/Ni molar ratios		
	ICP	EDS	XPS
Cu(OH) ₂ @CoNiCH NTs	1.90	1.93	1.91
Cu(OH) ₂ @CoNiCH NWs	1.91	1.98	1.92
CoNiCH NRs	1.89	1.82	1.91

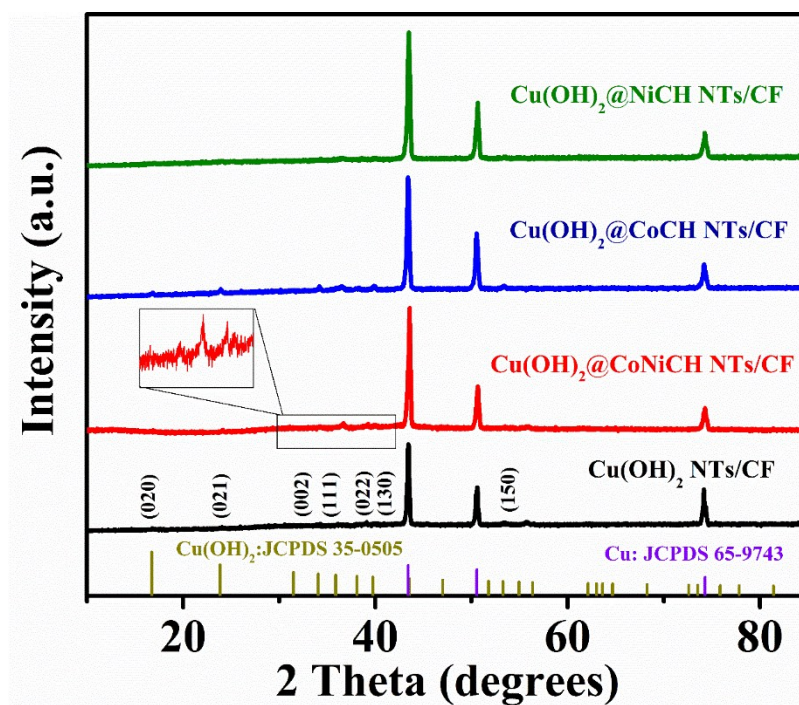


Figure S13 XRD of Cu(OH)₂@CoNiCH NTs/CF, Cu(OH)₂@CoCH NTs/CF, Cu(OH)₂@NiCH NTs/CF and Cu(OH)₂ NTs/CF.

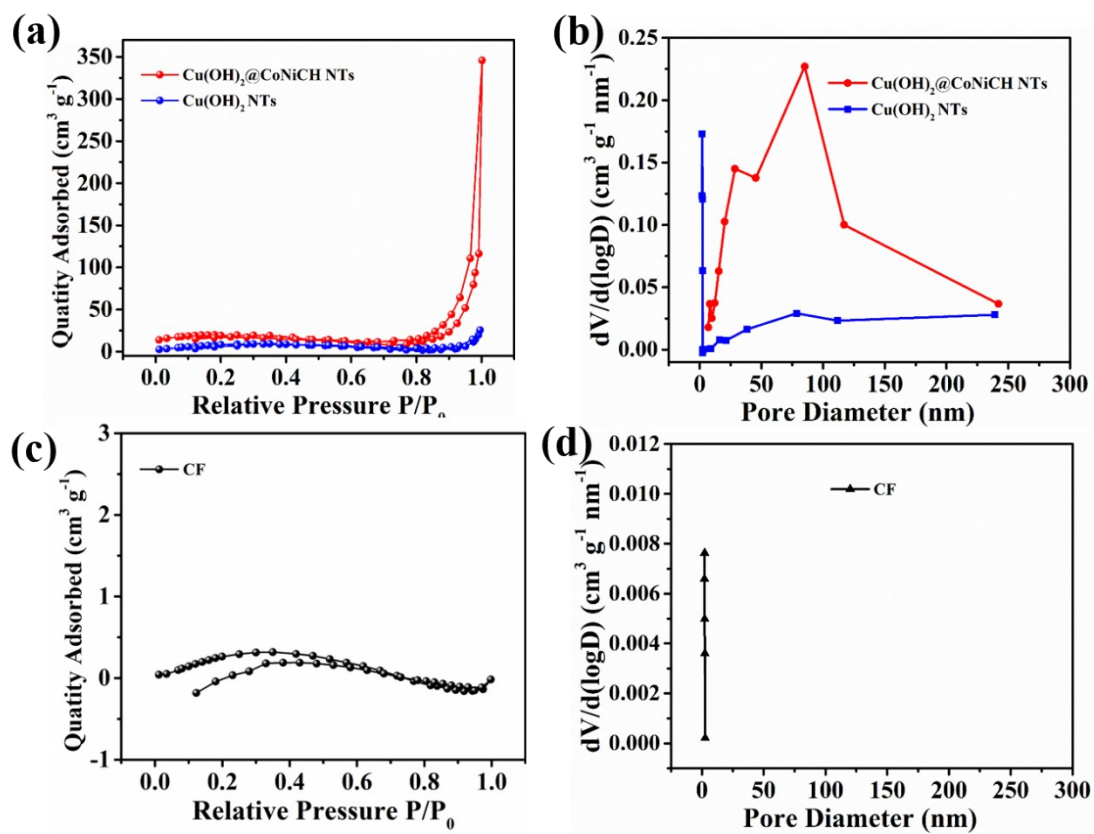


Figure S14 (a-b) BET of Cu(OH)₂@CoNiCH NTs and Cu(OH)₂ NTs, (c-d) BET of bare Cu foam.

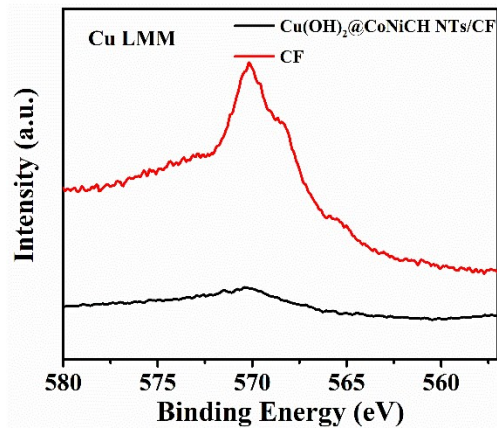


Figure S15 Cu LMM of $\text{Cu(OH)}_2@CoNiCH$ NTs/CF and bare CF.

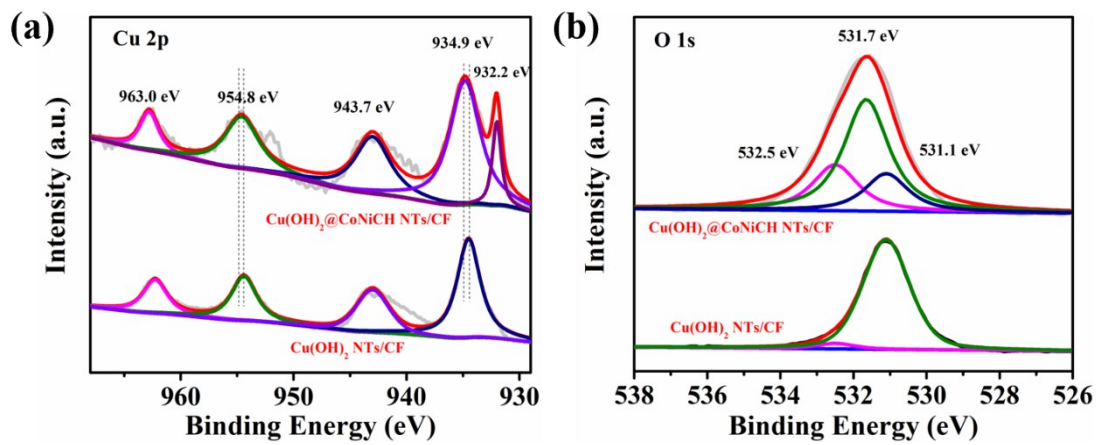


Figure S16 XPS spectra (Cu 2p and O 1s) comparison of the $\text{Cu(OH)}_2@CoNiCH$ NTs/CF and Cu(OH)_2 NTs/CF.

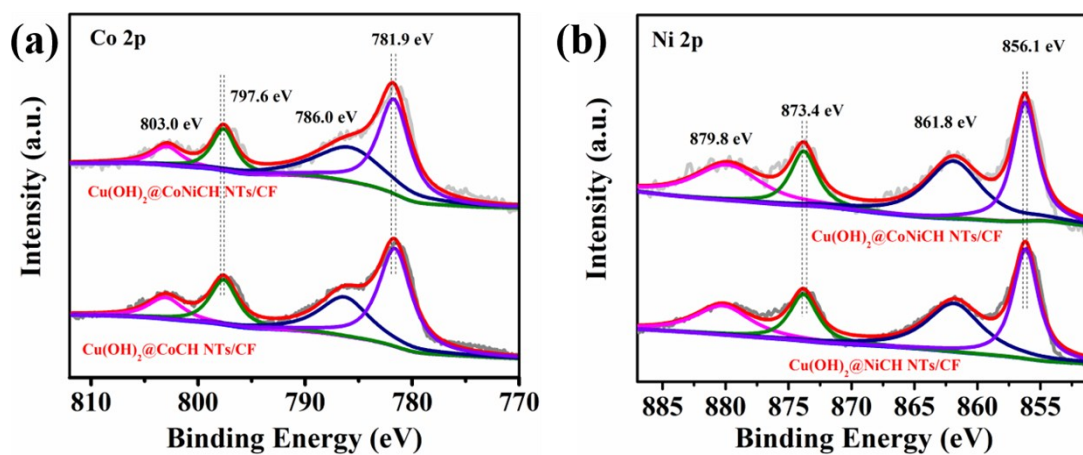


Figure S17 (a) XPS spectra (Co 2p) comparison of the $\text{Cu(OH)}_2@CoNiCH\ NTs/CF$ and $\text{Cu(OH)}_2@CoCH\ NTs/CF$, (b) XPS spectra (Ni 2p) comparison of $\text{Cu(OH)}_2@CoNiCH\ NTs/CF$ and $\text{Cu(OH)}_2@NiCH\ NTs/CF$

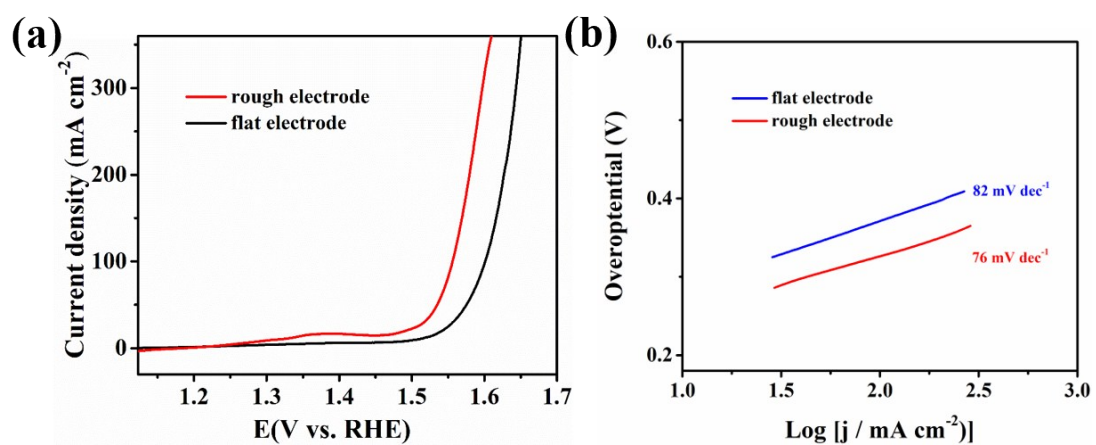


Figure S18 a) Polarization curves and b) Tafel plots of flat Cu(OH)₂@CoNiCH NTs /Cu foil and rough Cu(OH)₂@CoNiCH NTs/CF.

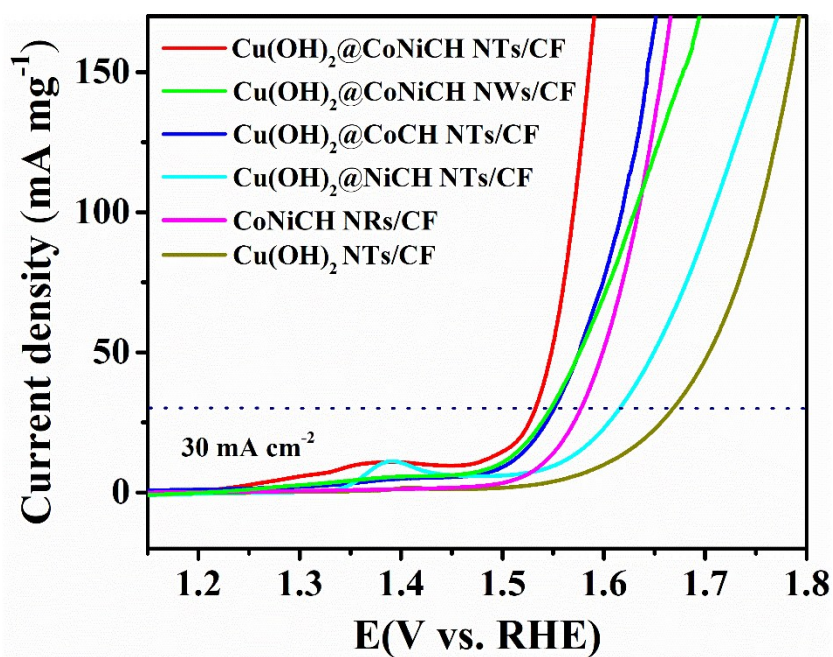


Figure S19 Mass-normalized polarization curves of the active materials loaded on CF.

Table S2 Mass-normalized overpotential of the active materials loaded on CF

Active materials	Mass (mg)	η (mV) ($j = 30 \text{ mA mg}^{-1}$)	η (mV) ($j = 100 \text{ mA mg}^{-1}$)
Cu(OH) ₂ @CoNiCH NTs/CF	1.54	303	340
Cu(OH) ₂ @CoNiCH NWs/CF	1.82	319	401
Cu(OH) ₂ @CoCH NTs/CF	1.63	321	388
Cu(OH) ₂ @NiCH NTs/CF	1.52	386	477
CoNiCH NRs/CF	0.96	349	404
Cu(OH) ₂ NTs/CF	0.64	439	524

Table S3 Comparison of the 3D Cu(OH)₂@CoNiCH NTs/CF with recently reported materials

Catalyst	Mass (mg)	Overpotential at current			Ref.
		density			
		10 mA cm ⁻²	50 mA cm ⁻²	100 mA cm ⁻²	
Cu(OH) ₂ @CoNiCH NTs/CF	1.54 mg cm ⁻²	85	305	326	This work
Co ₁ Mn ₁ carbonate hydroxide nanosheets/NF	5.6 mg cm ⁻²	-	322	349	J. Am. Chem. Soc. 2017, 139 (24), 8320-8328
CCS CoNi core-shell nanowires/carbon fiber	0.3 mg cm ⁻²	302	-	-	Adv. Energy Mater. 2017, 7 (1), 1601492
CoO–MoO ₂ Nanocages	0.5 mg cm ⁻²	312	-	-	Adv. Funct. Mater. 2017, 27 (34), 1702324
FeCoOOH/Graphene	0.2 mg cm ⁻²	330	-	-	Adv. Energy Mater. 2017, 7 (14), 1602148
NiFe LDH nanosheets/Cu nanowire	-	310	-	460	Energy Environ. Sci. , 2017, 10, 1820-1827.
Dendritic Nanostructured Copper Oxide	-	290	-	-	Angew. Chem. Int. Ed. 2017, 129 (17), 4870-4874
NiFe LDH/NF	-	240	~350	~460	Science 2014, 345, 1593
Ni(OH) ₂ -TCNQ microarray	5.6 mg cm ⁻²		322	354	ACS Catal. , 2018, 8, 651-655
CoO/Co composite	0.255 mg cm ⁻²	350	-	-	ACS Energy Lett. 2017, 2 (5), 1208–1213

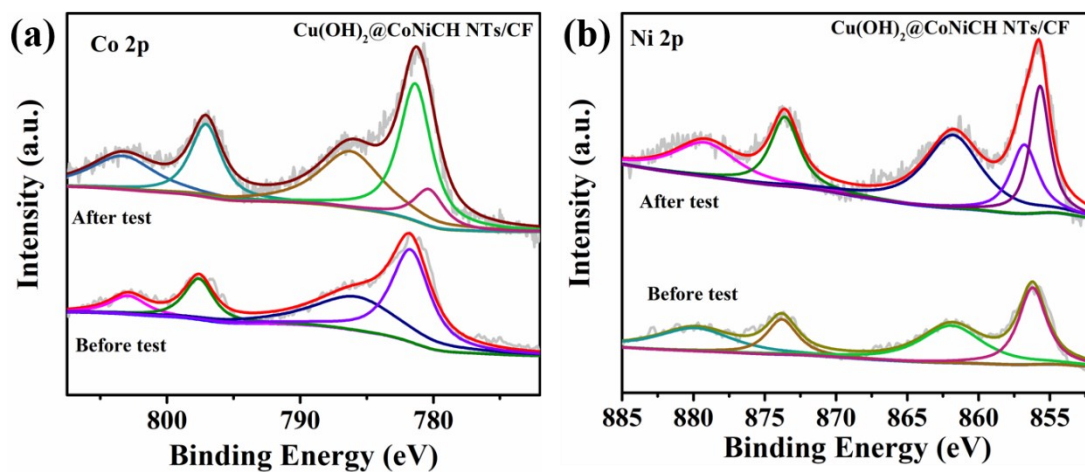


Figure S20 The XPS spectra comparison of $\text{Cu(OH)}_2@ \text{CoNiCH NTs/CF}$ before and after LSV tests.

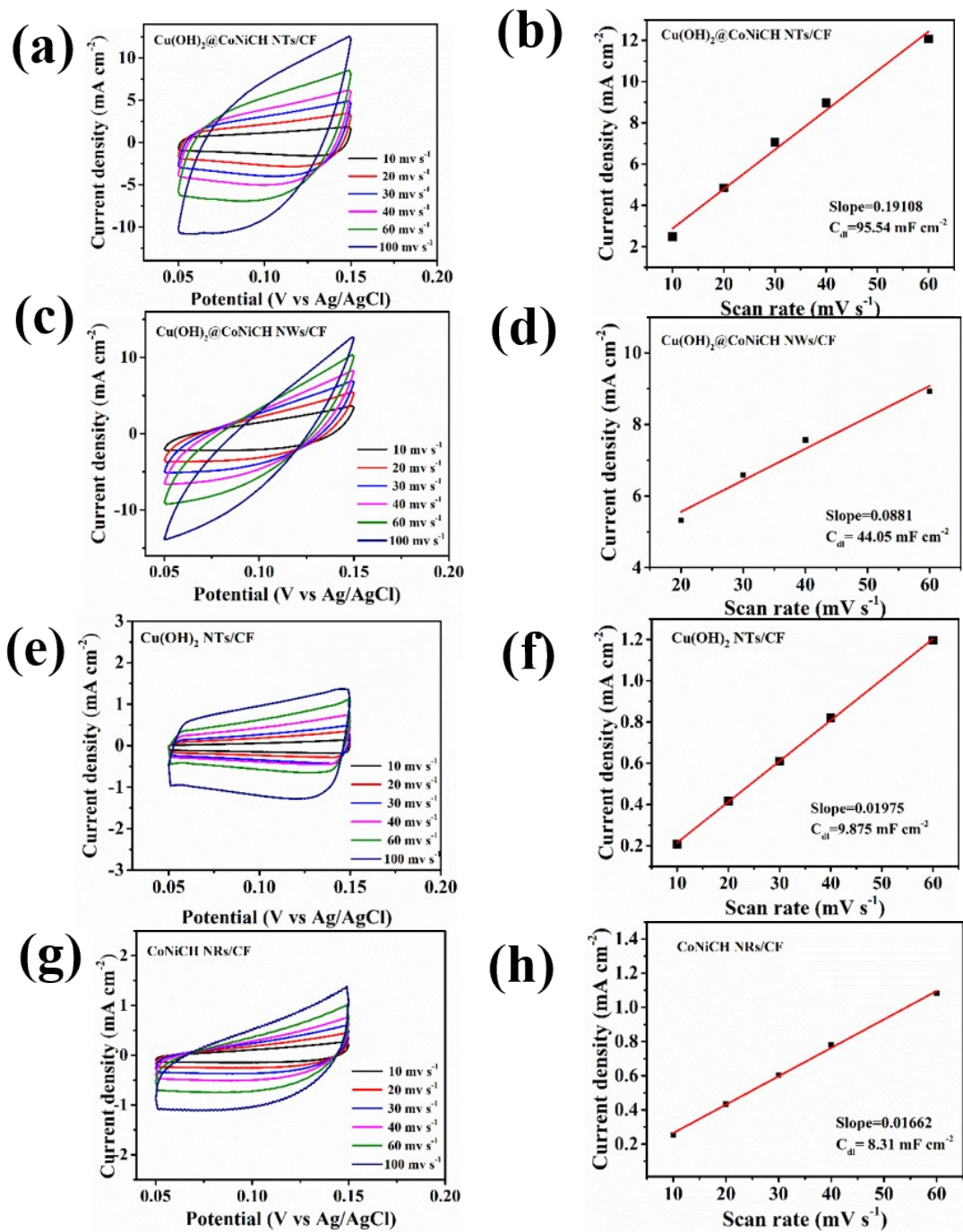


Figure S21 ECSAs and corresponding C_{dl} of the (a) $\text{Cu(OH)}_2@CoNiCH\ NTs/CF$, (b) $\text{Cu(OH)}_2@CoNiCH\ NWs/CF$, $\text{Cu(OH)}_2\ NTs/CF$, (d) $CoNiCH\ NRs/CF$.

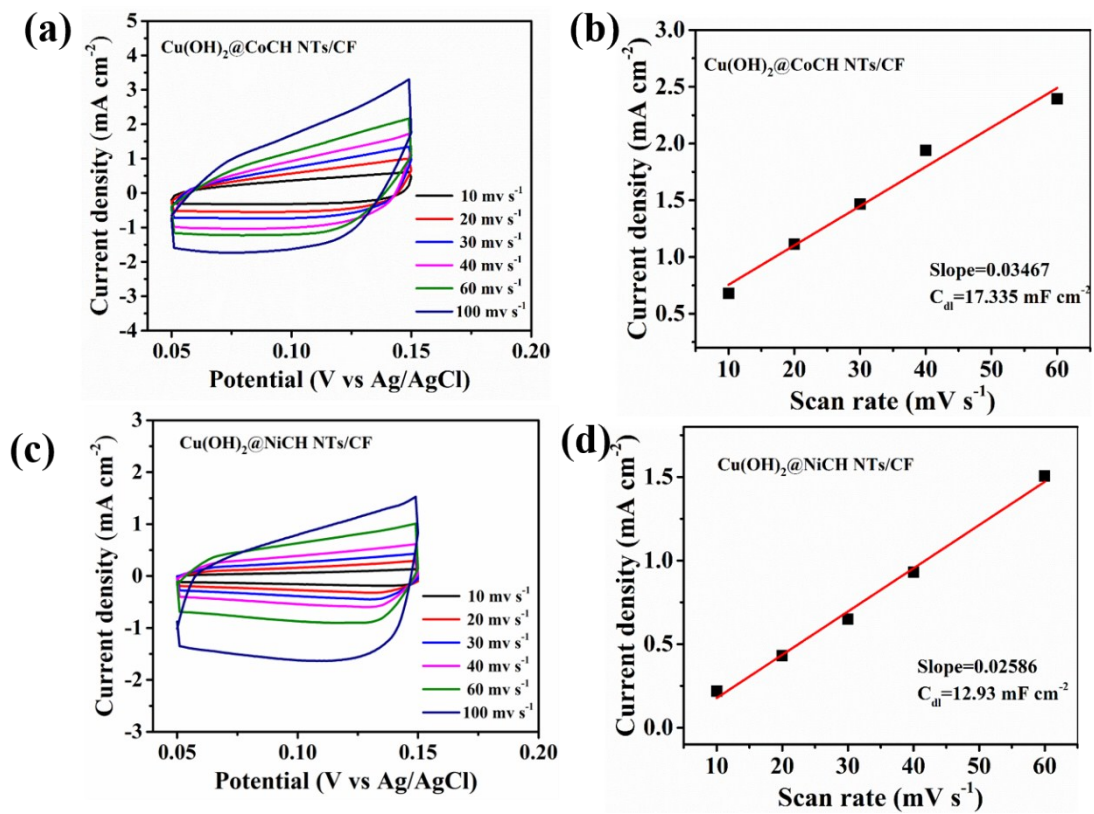


Figure S22 ECSA and corresponding C_{dl} of $\text{Cu(OH)}_2@CoCH\ NTs/CF$, $\text{Cu(OH)}_2@NiCH\ NTs/CF$

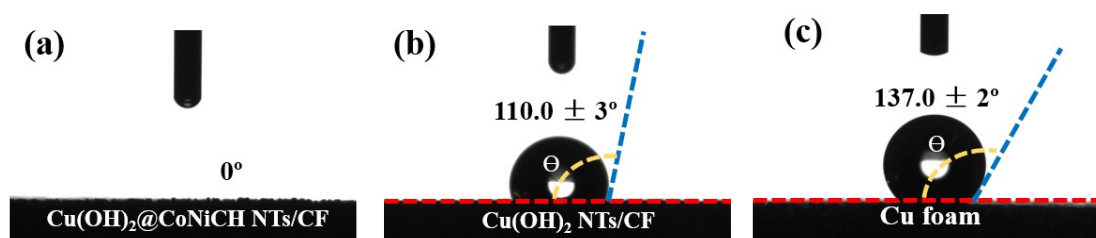


Figure S23 Contact angle images of (a) $\text{Cu(OH)}_2@CoNiCH\ NTs/CF$ (b) $\text{Cu(OH)}_2\ NTs/CF$ and (c) $Cu\ foam$