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Carbon-rich Conjugated Framework PTEB Modified Cu Nanowires for Stabilizing Lithium Metal Anode

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Experimental Section

Synthesis of Copper nanowires (CuNW) grown on Cu Foam

0.445 g of ammonium persulfate ($(NH_4)_2S_2O_8$) and 1.602 g of sodium hydroxide (NaOH) were dissolved in 15 mL of deionized water, respectively. After completely dissolved, the two solution were mixed evenly, and then the Cu foam with 12 mm diameter was placed in the mixed solution for 10 min. Take the Cu foam out and rinse it with deionized water for 3 times, and finally put it into the oven at 60℃ to dry. The Cu foam was first calcined at 400 ℃ in Ar atmosphere for 2 h at a heating rate of 5 ℃ min^{-1}, and then calcined at 200 ℃ in hydrogen atmosphere for 4 h at a heating rate of 2 ℃ min^{-1}. The copper nanowires grown on the Cu foam were obtained.

Synthesis of CuNW modified by carbon-rich conjugated skeleton (CuNW@PT)

5 mg of 1, 3, 5-triacetylene benzene ($C_{12}H_6$) and 28 mg of N-methyl iodide and butylpyridine were mixed into the glass bottle, then 10 mL of pyridine solution was added into the glass bottle, the CuNW was put into the glass bottle and sealed, Afterwards, the glass bottle was put into a 60 ℃ oven for 24 h. After the reaction, the CuNW was washed with pyridine, dichloroethane and methanol solutions, respectively. Finally, the washed CuNW sample was placed in tubular furnace and dried with N_2 atmosphere. Then the sample was calcined at 300 ℃ in a N_2 atmosphere for 2 h at a heating rate of 2 ℃ min^{-1}. Finally, CuNW modified by carbon-rich conjugated skeleton (defined as CuNW@PT) as 3D host structure

materials was obtained. The areal loading of PT in CuNW@PT is about 2 mg cm^{-2}.

Materials Characterizations

The morphology of all samples was characterized by SEM (FEI Nova Nano-SEM 460). X-ray diffraction (XRD Brucker D2 Advance diffractometer) was used to detect the pahse structure. X-ray photoelectron spectroscopy (XPS) analysis was carried out by using ESCALAB 250 instrument with Al Kα radiation. Raman spectra were collected using a Jobin Yvon Lab RAM HR800 with a 632.8 nm He-Ne laser. ATR-FTIR spectra was recorded on Nicolet iS5 iD7 ATR spectrometer.

Electrochemical measurements

The electrochemical performance of Cu, CuNW, and CuNW@PT as 3D host structure were assessed via assembling CR2032 coin cell in the Ar-filled glovebox. The 3D host were cut into piece with a diameter of 12 mm as the current collector. Half cells were assembled with 1 m lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in dioxolane (DOL)/ dimethoxyethane (DME) (1:1 by volume) with 3wt% of $LiNO_3$ as the electrolyte to test CE. For the symmetrical cells test, 5 mAh cm^{-2} of Lithium was first deposited onto the 3D host structure at current density of 0.5 mA cm^{-2}, then the cells were cycled at 1 mA cm^{-1} for 1 mAh cm^{-2} and 2 mA cm^{-2} for 3 mAh cm^{-2}, respectively. $LiFePO_4$ was used as cathode with 1.0 M $LiPF_6$ in EC/DEC (v/v = 1/1). The Li-Cu, Li-CuNW, and Li-CuNW@PT with area capacity of 5 mAh cm^{-2} and 12 mm in diameter were used as anode in the full cells. The areal loading and size of LFP are 2-2.5 mg cm^{-2} and 10 mm in diameter. The diameter of separator is 16 mm. The amount of electrolyte is 50 μL in a full cell

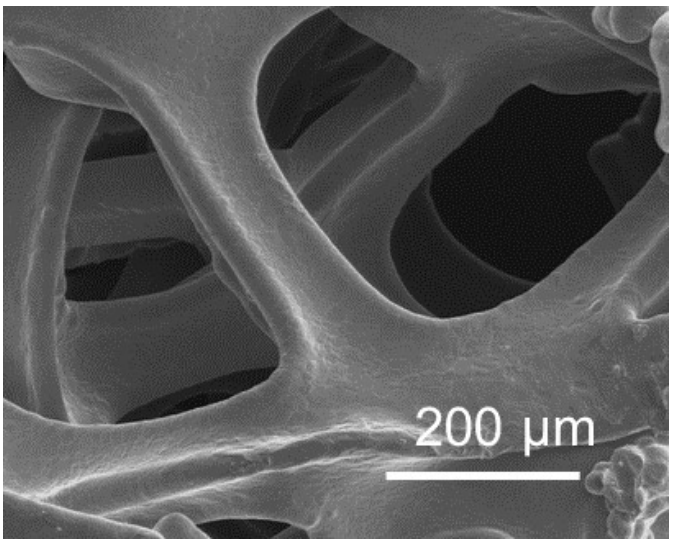

Fig S1. SEM of bare Cu foam.

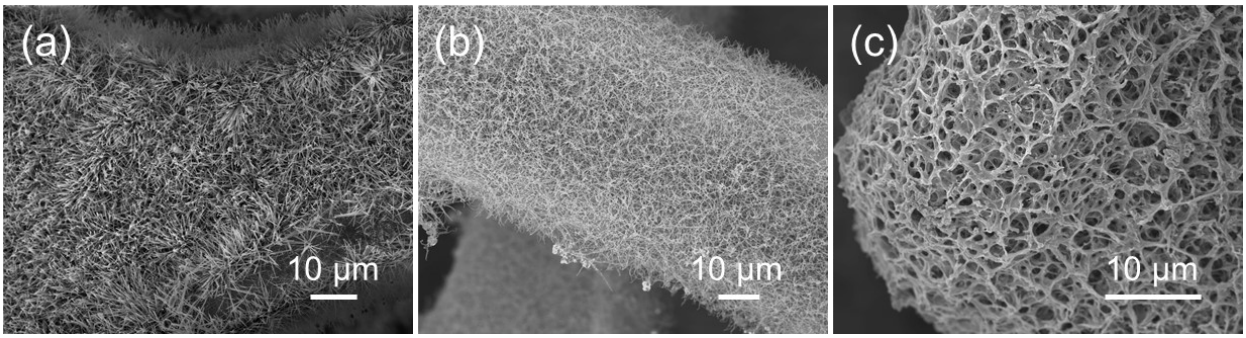

Fig S2. SEM images of $Cu(OH)_2$ NWs (b), CuNW (c), and CuNW@PT.

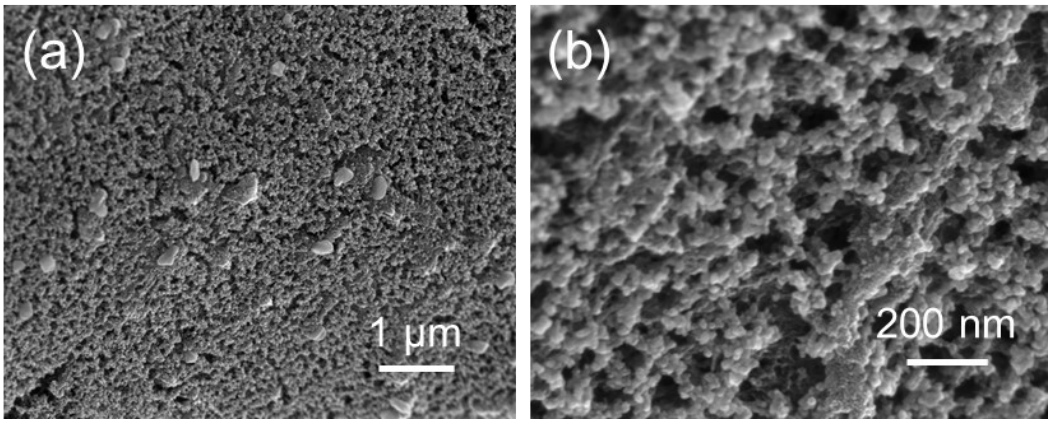

Fig S3. SEM of Cu foam@PT.

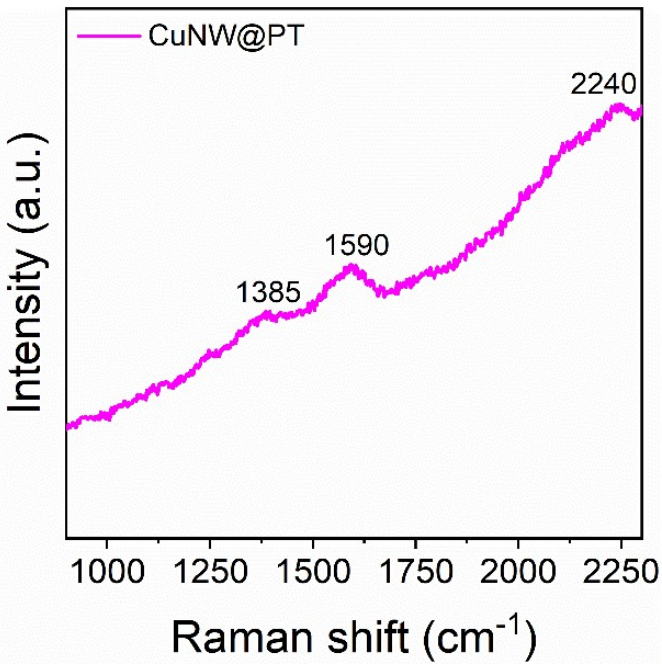

Fig S4. Raman of CuNW@PT.

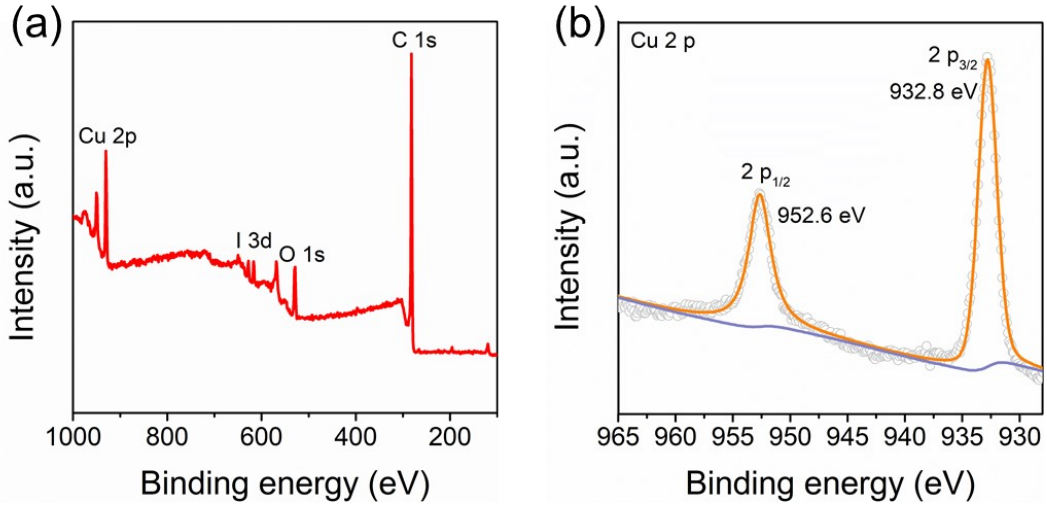

Fig S5. (a) XPS of CuNW@PT. (b) High-resolution C 1s spectrum of CuNW@PT.

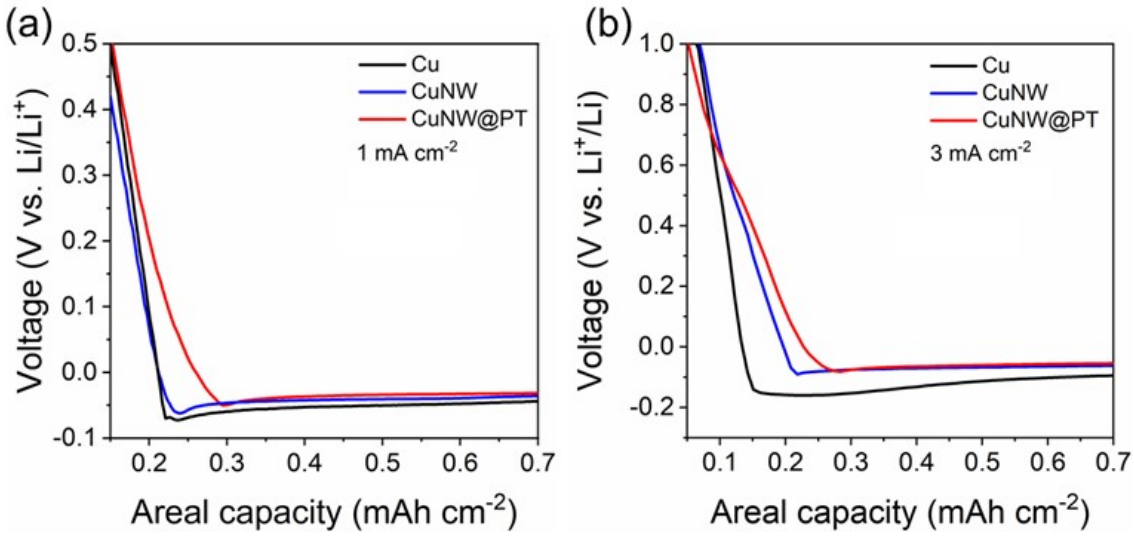

Fig S6. Voltage profiles for Cu, CuNW, CuNW@PT at (a) 1 mA cm^{-2} and (b) 3 mA cm^{-2} with specific areal capacity of 1 mAh cm^{-2}, respectively.

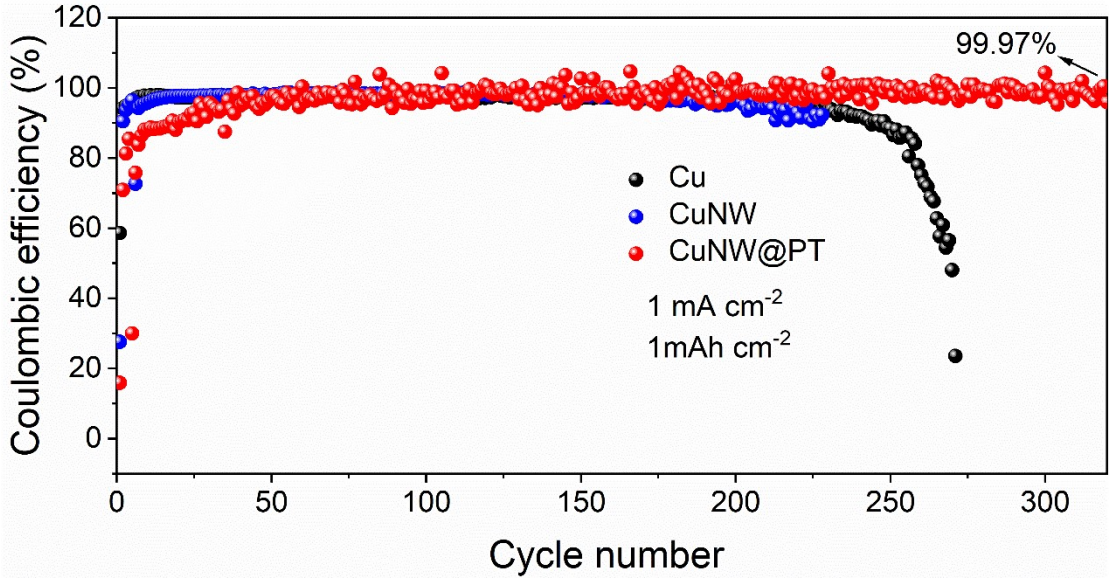

Fig S7. Coulombic efficiency of Cu, CuNW, CuNW@PT with specific areal capacity 1 mAh cm^{-2} at 1 mA cm^{-2}, respectively.

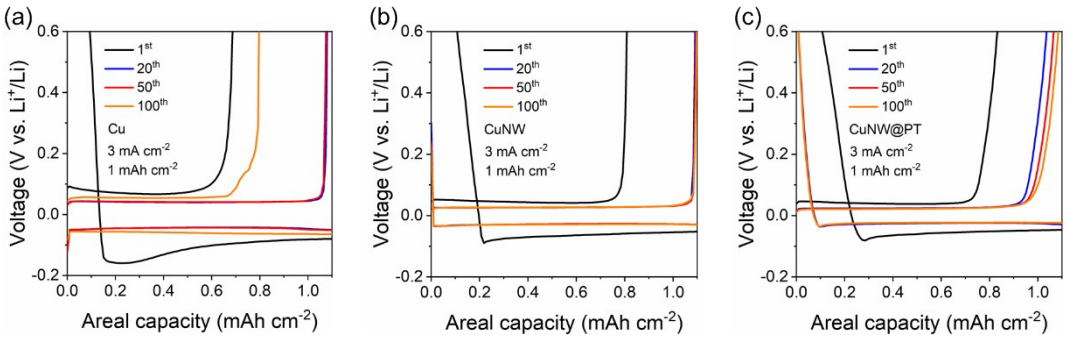

Fig S8. Voltage profiles of Cu (a), CuNW (b), CuNW@PT (c) at the 1st, 20th, 50th, and 100th, respectively.

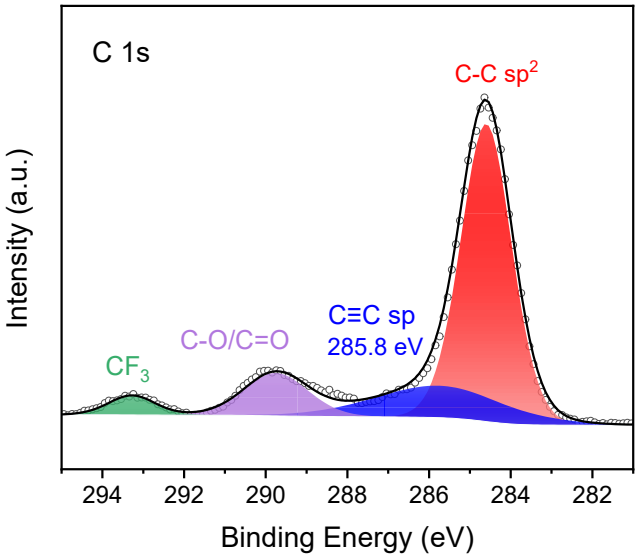

Fig S9. High-resolution C 1s spectrum of CuNW@PT after the 1st cycle.

To identify whether the acetylene bonds will remain, XPS of Li-CuNW@PT electrode after the 1st cycle was measured, and the C 1s spectrum is shown Fig S9. It can be clearly observed that acetylene bonds located at 285.8 eV shift to the higher binding energy compared to Fig. 2C, which can be ascribed to the affiliative bonding between in-plane acetylene bonds and Li^+ during the Li plating/stripping process. Therefore, the specific lithiophilic site in this work is the lithiated acetylene bonds, which act as the active sites and induce uniform Li deposition.

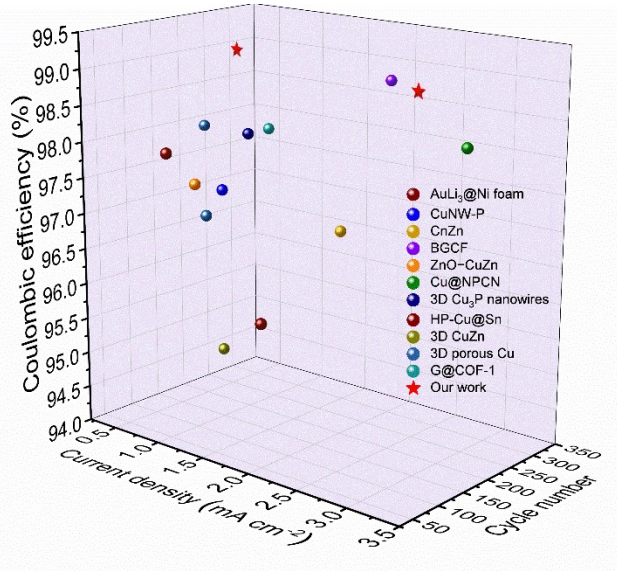

Fig S10. Comparison in Coulombic efficiency of CuNW@PT and other 3D host structure previously reported.

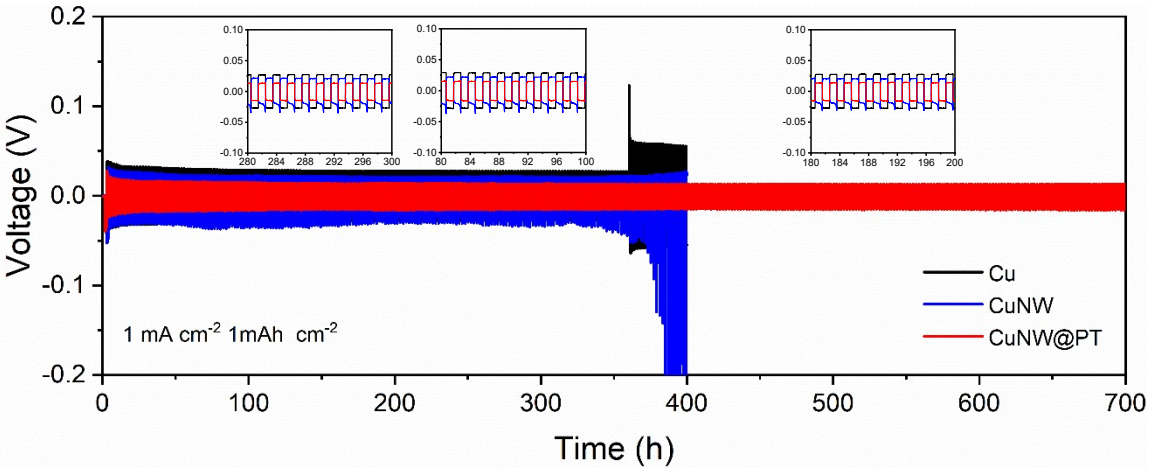

Fig S11. Voltage-time curves of Cu, CuNW, CuNW@PT in symmetric cell at 1 mA cm^{-2} for 1 mAh cm^{-2}.

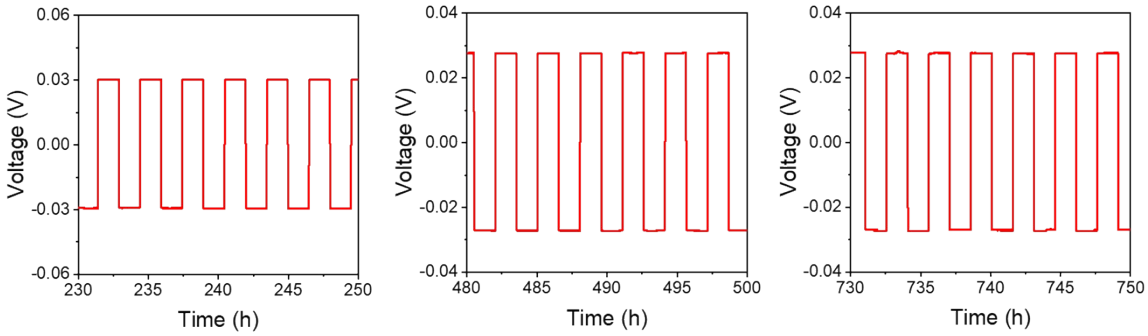

Fig S12. The voltage-time profile of symmetric cell using CuNW@PT electrode at different time.

Table S1. Electrochemical performance comparison between CuNW@PT and the reported representative 3D host structure for lithium metal batteries.

	Coulombic efficiency	Lifespan	Voltage hysteresis	literature	
CuNW@PT	99.2% at 1 mA cm^{-2} over 180 cycles 99.1% at 3 mA cm^{-2} over 150 cycles	700 h at 1 mA cm^{-2} 800 h at 2 mA cm^{-2}	13 mV at 1 mA cm^{-2} 27 mV at 3 mA cm^{-2}	-	This work
$AuLi_3$@Ni foam	98% at 1 mA cm^{-2} over 50 cycles 96% at 2 mA cm^{-2} over 50 cycles	740 h at 0.5 mA cm^{-2}	22 mV at 0.5 mA cm^{-2}	*Energy Sto. Mater.*	SI
CNF@Ni	~100% at 2 mA cm^{-2} over 200 cycles	300 h at 1 mA cm^{-2}	50 mV at 1 mA cm^{-2}	*Adv. Funct. Mater.*	S2
Rimous Cu foam (RCF)	99% at 1 mA cm^{-2} over 660 cycles	1200 h at 1 mA cm^{-2} 200 h at 3 mA cm^{-2}	22 mV at 1 mA cm^{-2} 65 mV at 3 mA cm^{-2}	*Energy Sto. Mater.*	S3
CuNW-P	97.3% at 1 mA cm^{-2} over 150 cycles	1000 h at 1 mA cm^{-2} 300 h at 2 mA cm^{-2}	18 mV at 1 mA cm^{-2}	*Adv. Mater.*	S4
CnZn	98.6% at 0.5 mA cm^{-2} over 800 cycles 96.9% at 2 mA cm^{-2} over 200 cycles	Over 500 h at 0.5 mA cm^{-2}	53 mV at 0.5 mA cm^{-2}	*Nano Lett.*	S5
BGCF	98.8% at 2 mA cm^{-2} over 300 cycles	850 h at 1 mA cm^{-2}	<15 mV at 1 mA cm^{-2}	*J. Am. Chem. Soc.*	S6
ZnO−CuZn	97.48% at 1 mA cm^{-2} over 100 cycles	1200 h at 1 mA cm^{-2}	-	*Nano Lett.*	S7
Cu@NPCN	98.2 % at 3 mA cm^{-2} over 250 cycles	1200 h at 1 mA cm^{-2}	30 mV at 0.5 mA cm^{-2}	*ACS Nano*	S8
3D Cu_3P nanowires	98 % at 1 mA cm^{-2} over 200 cycles	1000 h at 1 mA cm^{-2}	30 mV at 1 mA cm^{-2}	*Adv. Energy Mater.*	S9
HP-Cu@Sn	98 % at 1 mA cm^{-2} over 240 cycles	800 h at 1 mA cm^{-2}	<20 mV at 1 mA cm^{-2}	*Energy Sto. Mater.*	S10

3D CuZn	95 % at 1 mA cm^{-2} over 150 cycles	450 h at 1 mA cm^{-2}	25 mV at 1 mA cm^{-2}	*ACS Energy Lett.*	S11
3D porous Cu	98% at 0.5 mA cm^{-2} over 200 cycles 97% at 1 mA cm^{-2} over 120 cycles	700 h at 0.5 mA cm^{-2} 200 h at 1 mA cm^{-2}	<20 mV at 0.5 mA cm^{-2} 15 mV at 1 mA cm^{-2}	*J. Mater. Chem. A*	S12
G@COF-1	98% at 1 mA cm^{-2} over 240 cycles	300 h at 1 mA cm^{-2}	~30 mV at 0.5 mA cm^{-2}	*Matter*	S13

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