Supplementary Information for

Cu Nanowires Shelled with NiFe Layered Double Hydroxide Nanosheets as Bifunctional Electrocatalysts for Overall Water Splitting

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Experimental methods

Chemicals. Hydrochloric acid (HCl, AR, MACRON), ethanol (C_2H_5OH, Decon Labs, Lnc.), sodium hydroxide (NaOH, AR, MACRON), ammonium persulfate [$(NH_4)_2S_2O_8$, 98%, Sigma-Aldrich], potassium bicarbonate ($KHCO_3$, 99.7%, Sigma-Aldrich), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98%, Sigma-Aldrich), iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, ≥99.95%, Sigma-Aldrich), nafion 117 solution (5%, Sigma-Aldrich), iridium oxide powder (IrO_2, 99%, Alfa Aesar), potassium hydroxide (KOH, 50% w/v, Alfa Aesar), and Cu foam (thickness: 1.5 mm) were used as received. Deionized water (18.3 MΩ·cm resistivity) was used for the preparation of all aqueous solutions.

Fabrication of Cu@NiFe LDH on Cu foam. Firstly, $Cu(OH)_2$ NWs were synthesized through a chemical oxidation method, and a typical process was as follows. A piece of Cu foam with a size of 2 × 5 cm^2 was cleaned in hydrochloric acid (37%) and then cleaned ultrasonically in ethanol and deionized water for 15 min sequentially. The cleaned Cu foam was then immersed into 80 mL of an aqueous solution containing 2.5 M NaOH and 0.125 M $(NH_4)_2S_2O_8$ for 20 min. Finally, the Cu foil with a light blue color was taken out from the solution, rinsed with deionized water, and dried in air. Afterward, the prepared $Cu(OH)_2$ NWs were calcined at 180 ℃ in the air for 1 h to obtain CuO NWs. The electrochemical reduction of CuO to Cu was conducted in Ar purged $KHCO_3$ solution at -0.4 V (vs. reversible hydrogen electrode, RHE). When the cathodic current reached to steady and near-zero, the reduction was complete. The electrodepostion of NiFe LDH was carried out in a three-electrode configuration, by using as-prepared Cu NWs/Cu foam, Pt net and saturated calomel electrode (SCE) as the working, counter and reference electrode, respectively. The electrolyte was obtained by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ (0.15 M) and $FeSO_4 \cdot 7H_2O$ (0.15 M) in 100 mL water with a continuous Ar flow to prevent the oxidation of Fe^{2+}. The applied potential was -1.0 V vs. SCE, and different electrodeposition time with 60, 90 and 120 s were used to control the amount of the NiFe LDH, which were labeled with Cu@NiFe LDH-60, Cu@NiFe LDH-90, and Cu@NiFe LDH-120, respectively. The samples were then washed with deionized water and dried in air. For comparison, pure NiFe LDH was synthesized on Cu foam by the same method for 90 s.

Preparation of IrO_2 electrode on Cu foam. To prepare the IrO_2 electrode, 40 mg IrO_2 and 60 μL Nafion, 540 μL ethanol and 400 μL deionized water were ultrasonicated for 30 min to obtain a homogeneous dispersion. Then, the dispersion was coated onto a cleaned Cu foam, which was then dried in air overnight at room temperature. The loading of IrO_2 catalyst on Cu foam is ~ 2.2 mg cm^{-2}, just the same with that of Cu@NiFe LDH.

Materials characterization. The morphology and crystal structure of the samples were detected with scanning electron microscopy (SEM, LEO 1525) and transmission electron microscope (TEM, JEOL 2010F) coupled with energy dispersive X-ray spectroscopy (EDS). The phase composition of the samples was characterized by X-ray diffraction (PANalytical X' pert PRO diffractometer with a Cu Ka radiation source). X-ray photoelecton spectroscopy (XPS) (PHI Quantera XPS) was performed using a PHI Quantera SXM Scanning X-ray Microprobe.

Electrochemical Tests. Electrochemical measurements were carried out on an electrochemical station (Bio-logic SP 150) in a standard three-electrode system with the prepared samples as the working electrode, a Pt net as the counter electrode, and a standard Hg/HgO electrode as the reference. The OER activity was evaluated using linear sweep voltammetry (LSV) with a sweep rate of 2 mV s^{-1} and chronopotentiometry at constant current densities of 10 and 100 mA cm^{-2} in O_2-saturated 1 M KOH solution. The HER tests were performed in Ar-saturated 1 M KOH solution with a sweep rate of 2 mV s^{-1}. Cyclic voltammetry (CV) curves were collected at different scan rates in the potentials from 1.025 V to 1.125 V vs RHE to evaluate the double-layer capacitance values. Electrochemical impedance spectroscopy (EIS) was measured at an overpotential of 250 mV from 0.1 Hz to 100 kHz with an amplitude of 10 mV. The overall water splitting performance was evaluated in 1 M KOH using a two-electrode configuration, and the polarization curve was recorded at a scan rate of 2 mV s^{-1}. All the measured potentials vs. the Hg/HgO were converted to RHE by the Nernst equation ($E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.0591\ \mathrm{pH} + 0.098$). All the curves were reported with iR compensation.

Supplementary Figures

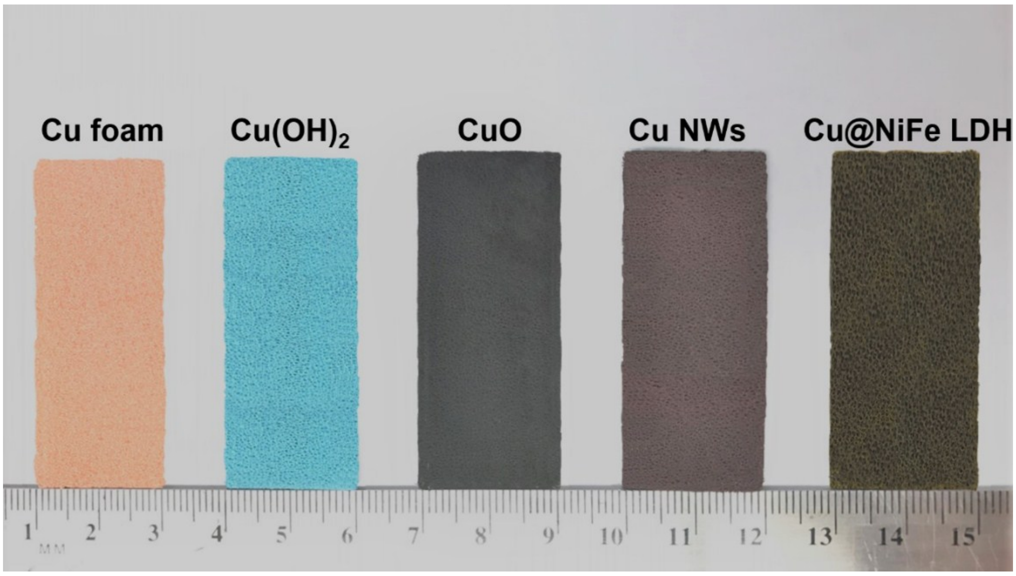

Figure S1. Optical pictures of as-prepared samples.

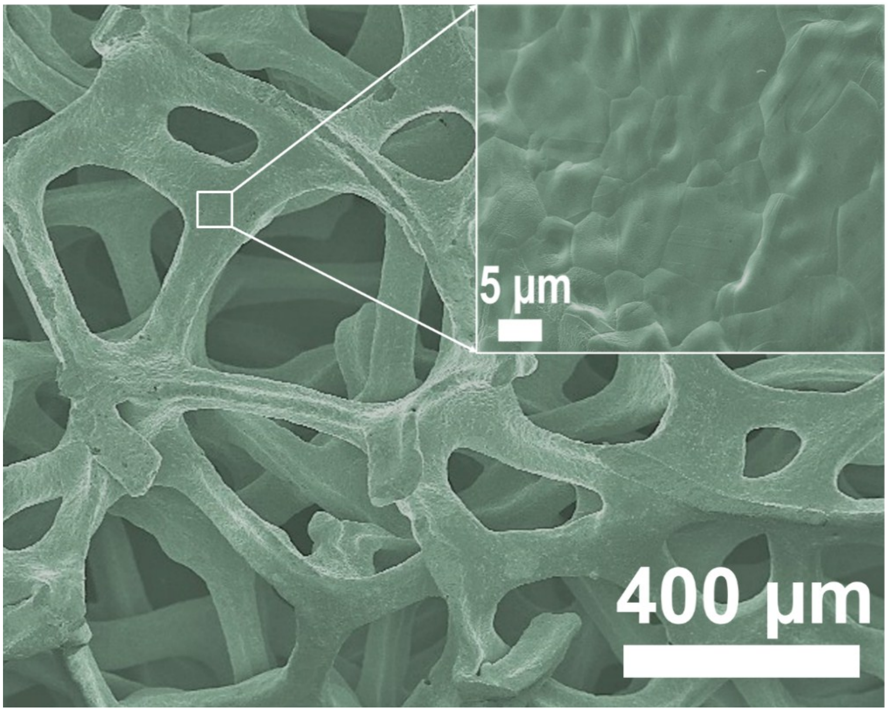

Figure S2. Typical SEM images of the starting Cu foam.

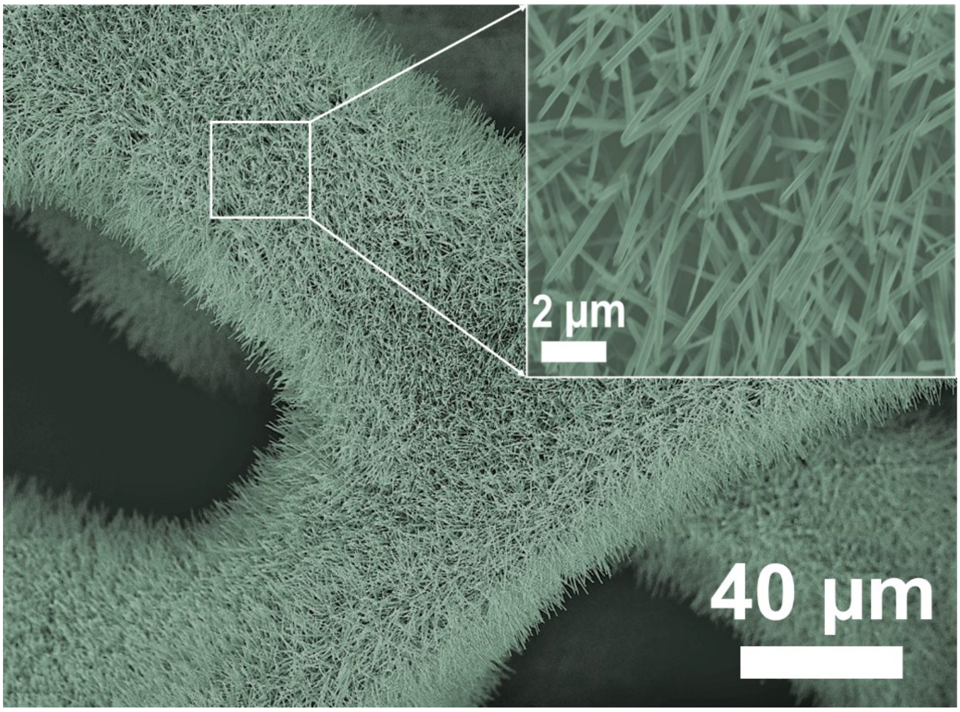

Figure S3. SEM images of $Cu(OH)_2$ NRs.

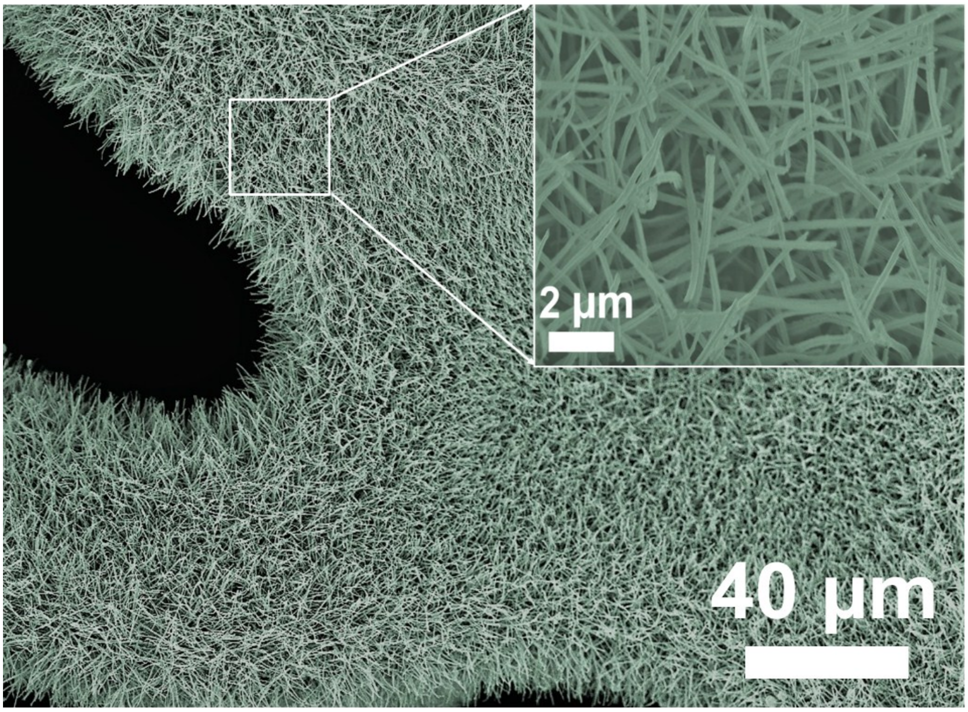

Figure S4. SEM images of CuO NWs.

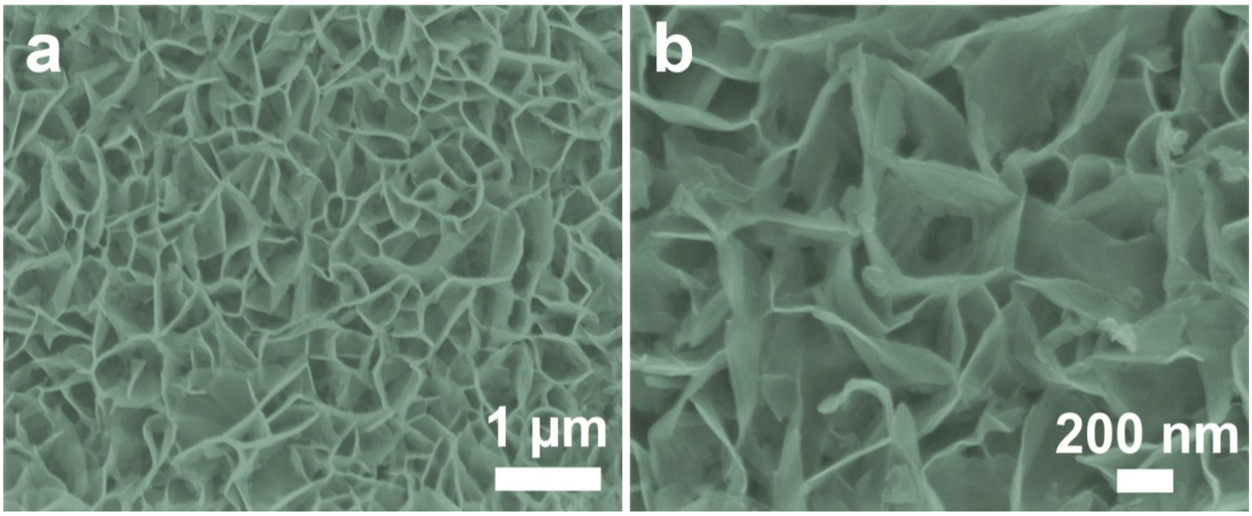

Figure S5. SEM images of pure NiFe LDH on Cu foam in different magnifications.

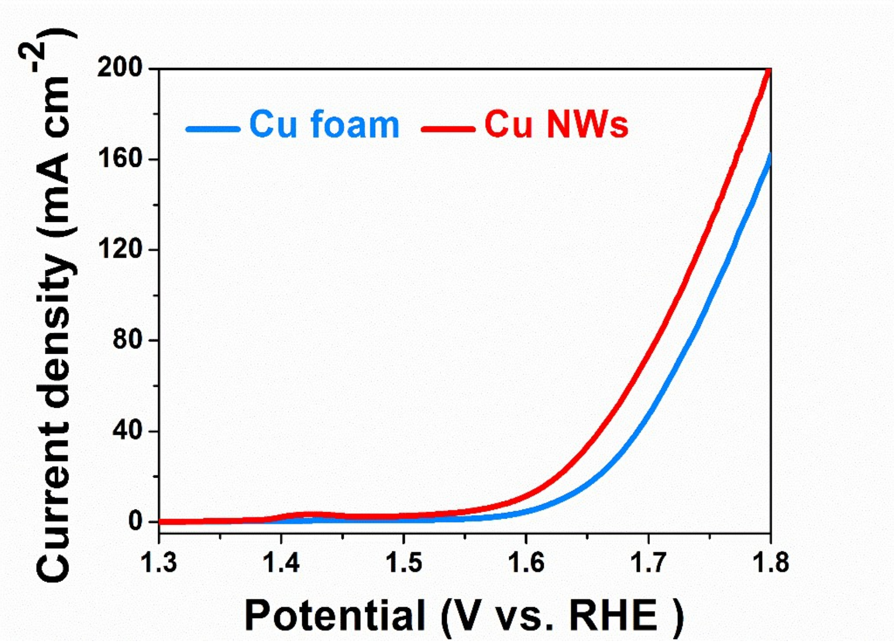

Figure S6. OER polarization curves of Cu foam and Cu NWs tested in 1 M KOH electrolyte.

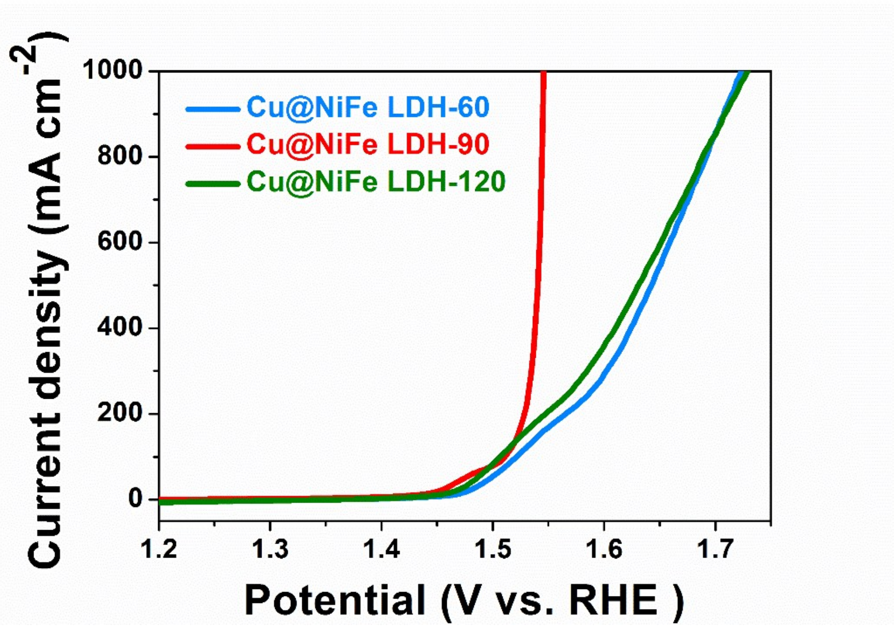

Figure S7. OER polarization curves of Cu@NiFe LDH with different electrodeposition time of NiFe LDH tested in 1 M KOH electrolyte. (Cu@NiFe LDH-90 is the sample used in the manscript.)

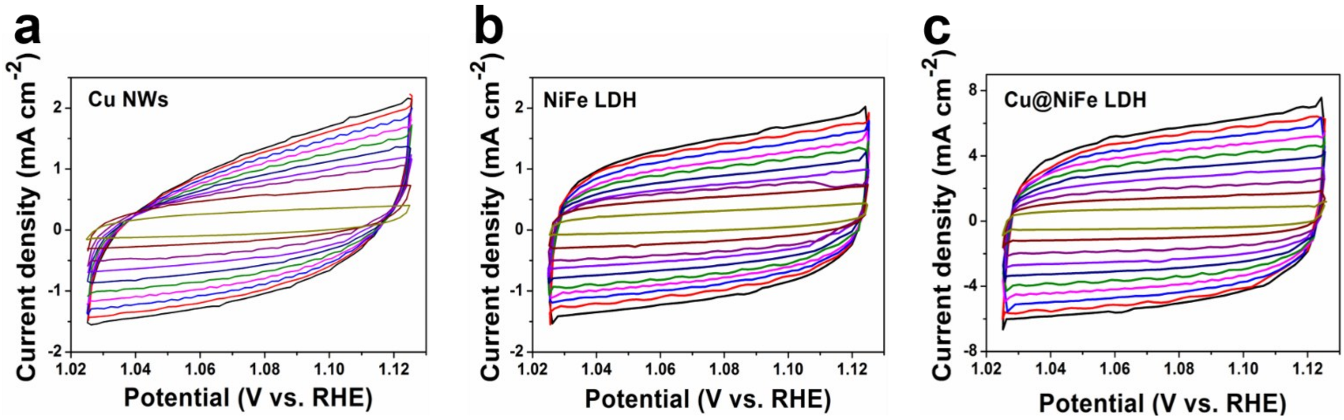

Figure S8. Typical cyclic voltammograms at different scan rates. (a) Cu NWs, (b) NiFe LDH, and (c) Cu@LDH with scan rates ranging from 10 mV/s to 100 mV/s with an interval point of 10 mV/s. The scanning potential range is from 1.025 V to 1.125 V vs RHE.

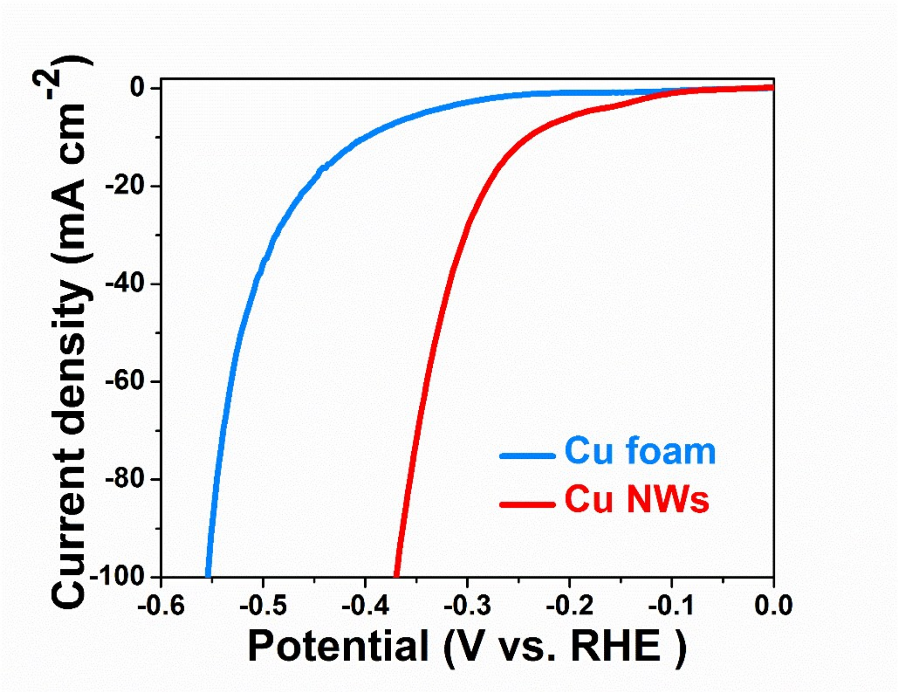

Figure S9. HER polarization curves of Cu foam and Cu NWs tested in 1 M KOH electrolyte.

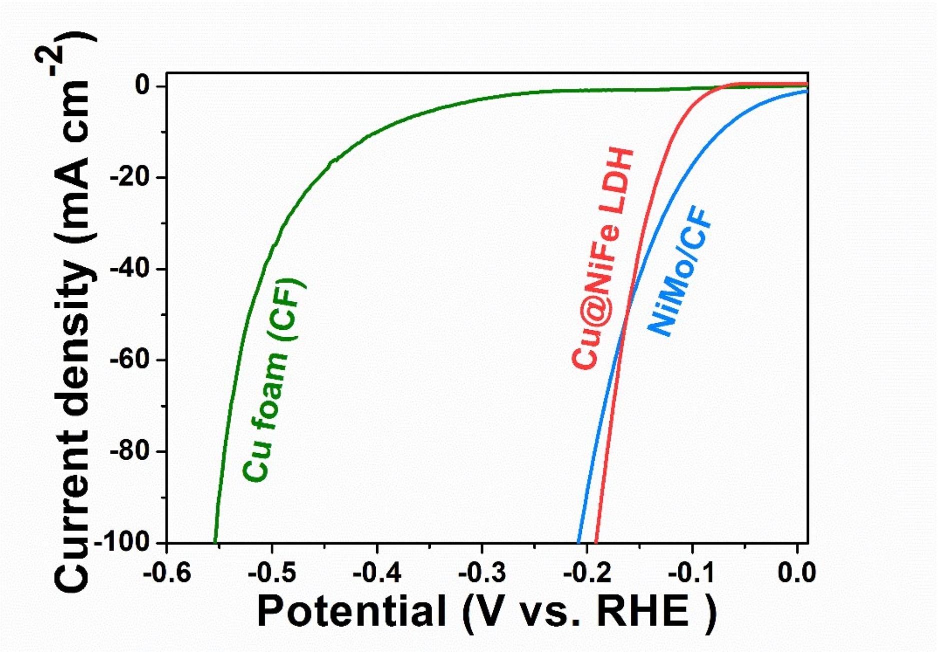

Figure S10. HER polarization curves of Cu@NiFe LDH in 1 M KOH in comparison with NiMo/CF.

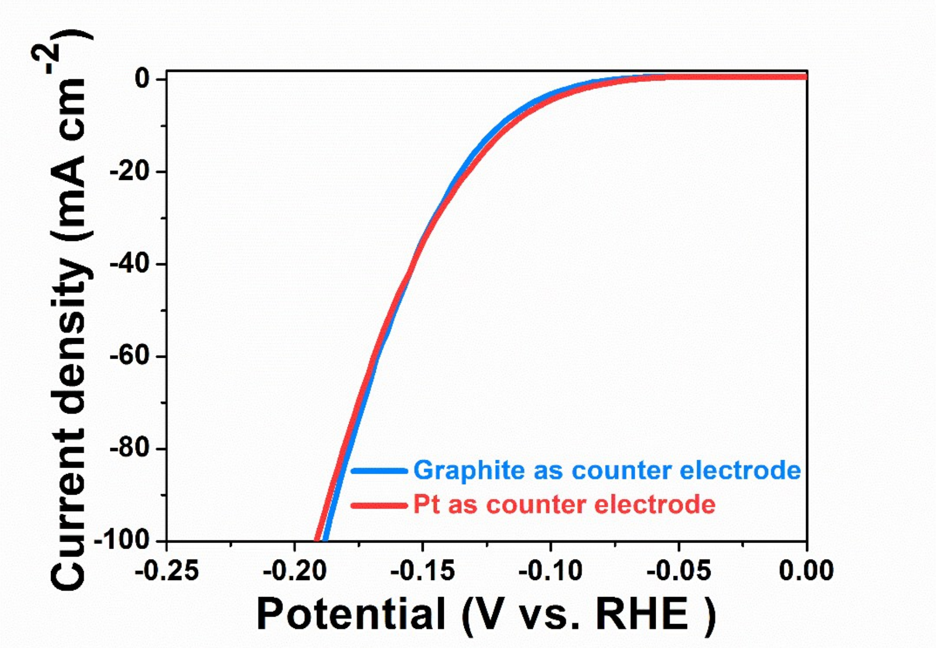

Figure S11. HER polarization curves of Cu@NiFe LDH in 1 M KOH with graphite rod and Pt net as the counter electrode.

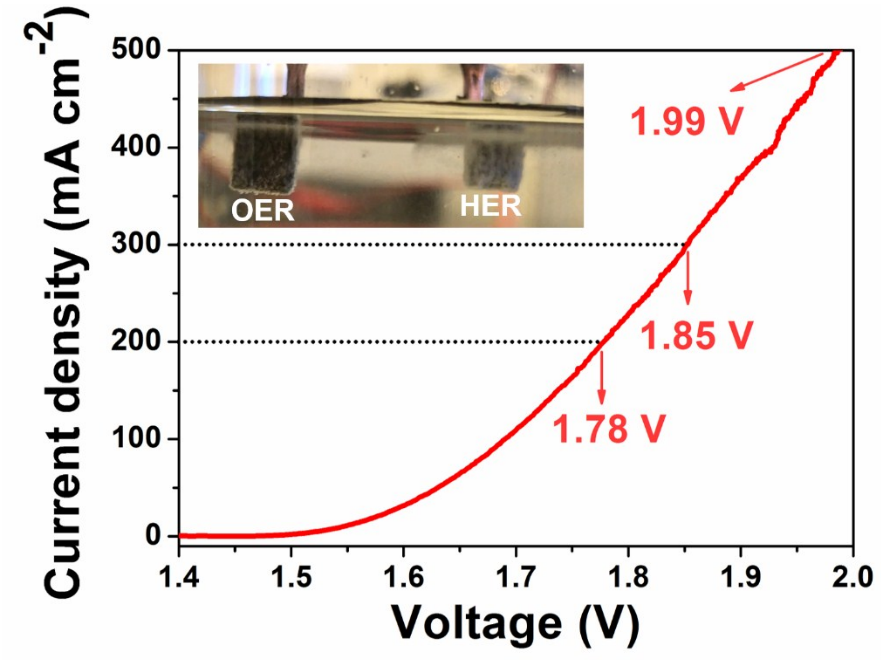

Figure S12. Polarization curve for overall water splitting of Cu@NiFe LDH to show the high current density performance. (The inset is the optical photograph showing the strong generation of H_2 and O_2 bubbles on the electrodes.)

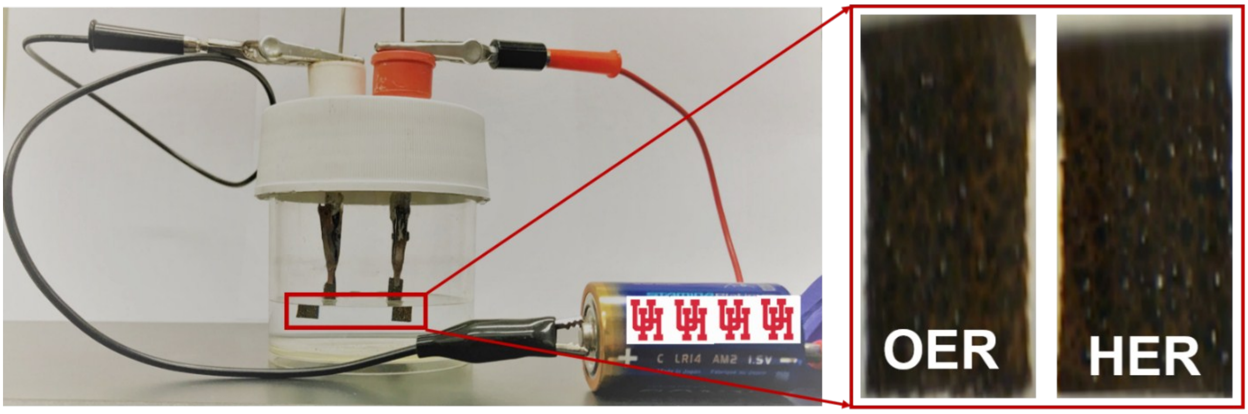

Figure S13. Optical photograph of overall water splitting with Cu@NiFe LDH as the bifunctional catalysts powered by a 1.5 V battery.

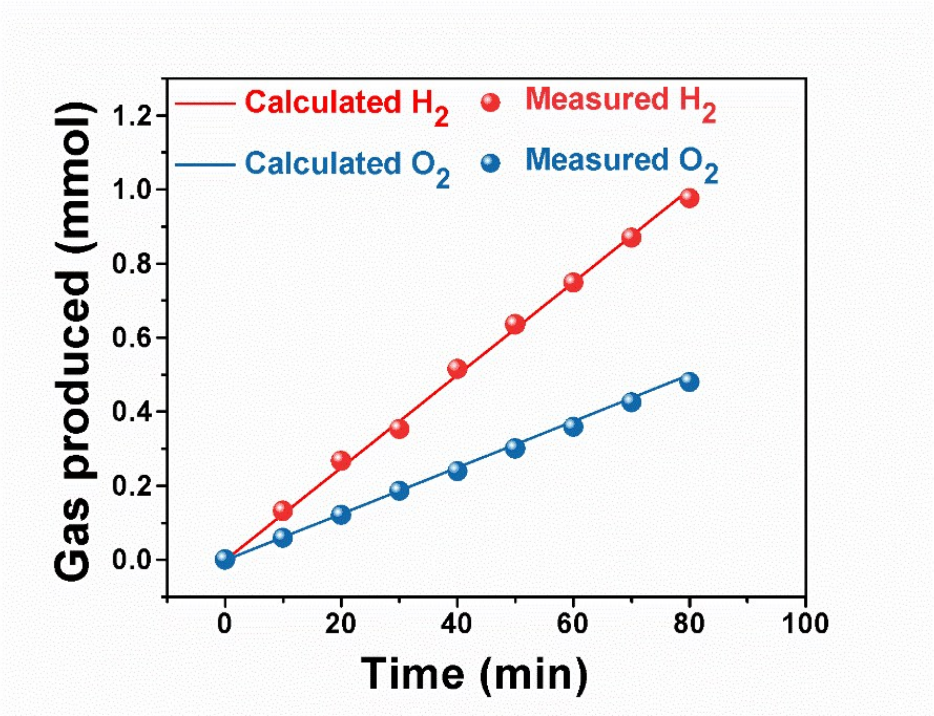

Figure S14. Experimental and theoretical amounts of H_2 and O_2 by the Cu@NiFe LDH electrode at a fixed current density of 40 mA cm^{-2}.

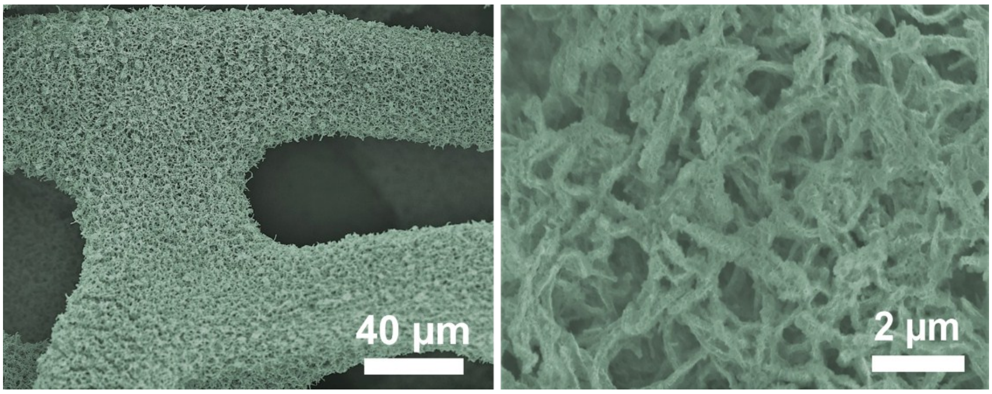

Figure S15. SEM images of Cu@NiFe LDH after OER stability test in different magnifications.

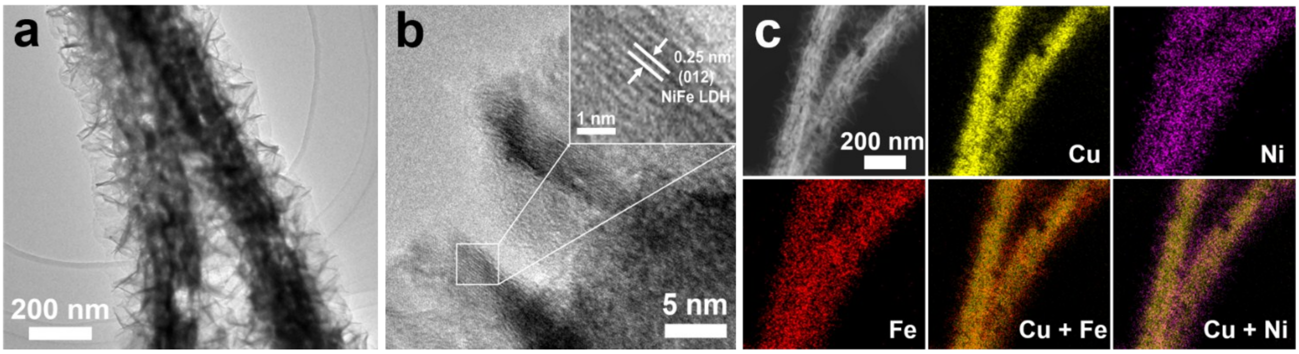

Figure S16. (a) TEM, (b) HRTEM, and (c) EDS elemental mapping of the Cu@NiFe LDH after overall water splitting stability test (cathode for HER).

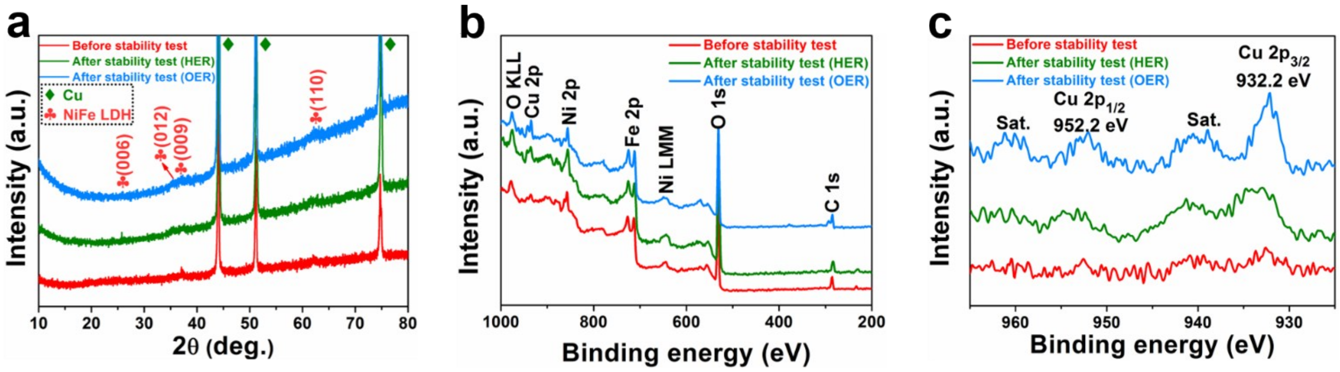

Figure S17. XRD and XPS characterizations of Cu@NiFe LDH before and after stability tests. (a) XRD patterns, (b) XPS survey, and (c) high-resolution XPS spectra of Cu 2p.

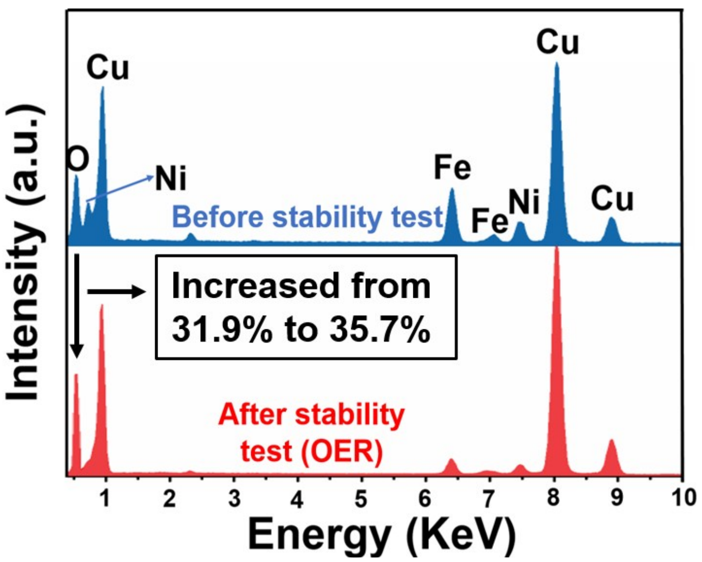

Figure S18. EDS characterizations of Cu@NiFe LDH before and after OER stability tests.

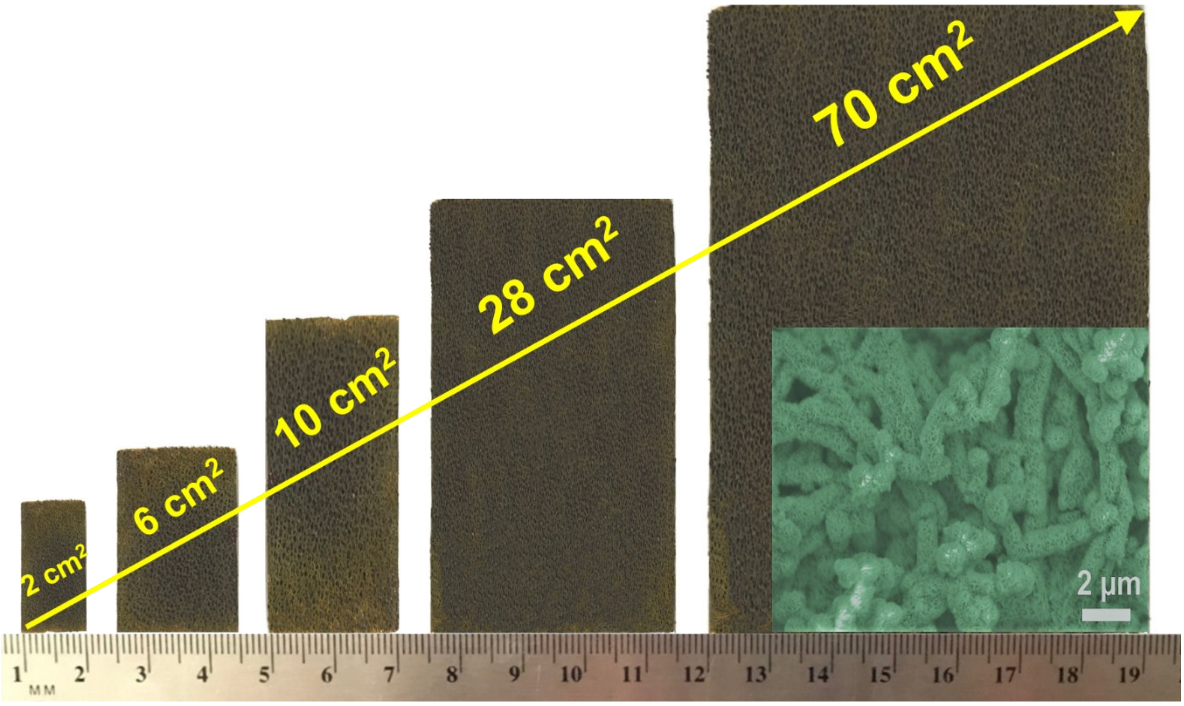

Figure S19. Optical photographs of Cu@NiFe LDH synthesized on Cu foam at various scales (inset: SEM image of Cu@NiFe LDH on the 70 cm^2 substrate).

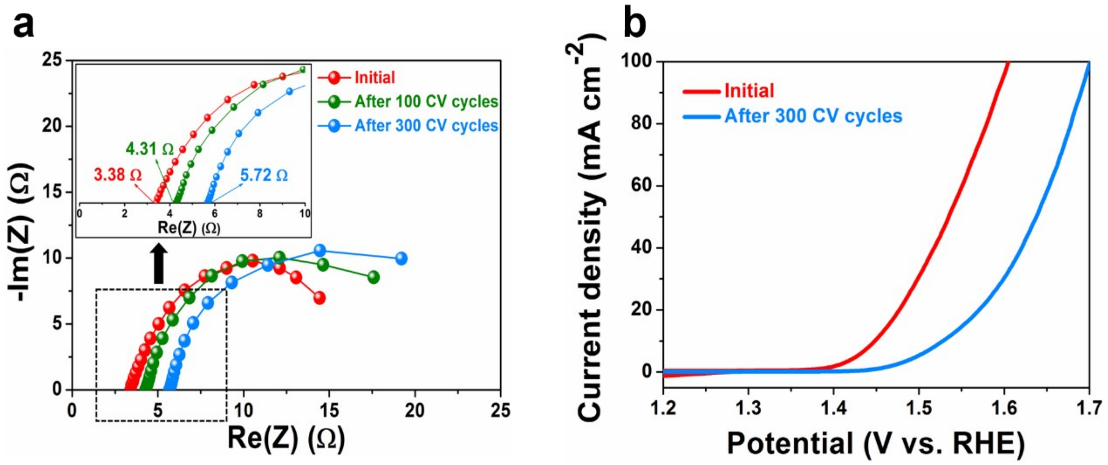

Figure S20. (a) EIS Nyquist plots, and (b) OER polarization curves of IrO_2/Cu foam before and CV cycles (CV range: 1.3 ~ 1.5 V vs. RHE).

Supplementary Discussion

Why the voltage of IrO_2(+)//Pt(-) at 10 mA cm^{-2} (1.63 V) is larger than the overpotential sums of IrO_2 for OER and Pt for HER?

Our samples used for overall water splitting are the same samples after HER and OER tests. Normally, the voltage for two-electrode cell (V_{overall}) at a certain current density can be described as: $\boldsymbol{V_{\text{overall}} = 1.23\ \text{V} + \eta_{\text{HER}} + \eta_{\text{OER}} + \eta_{\text{other}}}$ (η_{HER}, η_{OER}, and η_{other} correspond to the overpotentials of HER, OER, and overpotential caused by other factors.) We think the voltage difference mainly originated from the η_{OER} and η_{other} as illustrated below.

First, IrO_2 is not very stable in alkaline solution, and it can be transformed to IrO_4^{2-} (*J. Am. Chem. Soc.* 2015, **137**, 4347-4357.), which will reduce the activity for overall water splitting. This phenomenon can also be found in other papers: *Adv. Energy Mater.*, 2017, **7**, 1602643-1602652; *Angew. Chem. Int. Ed.*, 2017, **56**, 1324-1328; *Adv. Mater.*, 2017, **29**, 1606200-1606207; *Adv. Funct. Mater.*, 2016, **26**, 4839-4847. Second, the contact between IrO_2 and Cu foam is not good as NiFe LDH with Cu foam, which is related to the preparation method. The contact resistance will increase after catalytic reactions. This can be verified by the EIS Nyquist plots. As shown in Figure S20a, the series resistances (R_s) after CV cycles increased obviously, suggesting the electrical contacts to the substrate became worse. And this will increase the η_{OER} (Figure S20b) and η_{other}. Third, the IrO_2 powder were not uniformly dispersed on the Cu foam, which makes the inner Cu easily oxidized compared with that of Cu@NiFe LDH, thus increasing the η_{OER}. Fourth, we speculate the combination of IrO_2 (or RuO_2) and Pt in two-electrode cell will somehow increase the η_{other} due to their asymmetry, since quite a few papers reported similar results that $\boldsymbol{V_{\text{overall}} > 1.23\ \text{V} + \eta_{\text{HER}} + \eta_{\text{OER}}}$. (*ACS Nano*, 2016, **10**, 2342-2348; *ACS Nano*, 2016, **10**, 8738-8745.)

Supplementary Tables

Table S1. Comparison of the OER performance for the Cu@NiFe LDH catalyst in this work with other reported electrocatalysts in 1 M alkaline electrolytes (KOH or NaOH). Here η_{10}, η_{100}, and η_{500} correspond to the overpotentials at current densities of 10, 100, and 500 mA cm^{-2} in the OER, respectively.

Catalyst	**Support**	**Tafel slope (mV dec^{-1})**	**η_{10} (mV)**	**η_{100} (mV)**	**η_{500} (mV)**	**Reference**
Cu@NiFe LDH	Cu foam	27.8	199	281	311	This work
Exfoliated NiFe LDH/ defective graphene	Glassy carbon	52	210	325*	NA	*Adv. Mater.* **29**, 1700017-1700024 (2017)
CoSe/NiFe LDH	Exfoliated graphene foil	57	250	294*	NA	*Energy Environ. Sci.* **9**, 478-483 (2016)
Exfoliated NiFe LDH	Glassy carbon	40	302	NA	NA	*Nat. Commun.* **5**, 5477-5485 (2014)
NiFe LDH	Ni foam	NA	240	450*	NA	*Science* **345**, 1593-1596 (2014)
NiFe-OH/NiFeP	Ni foam	39	199	245	NA	*ACS Energy Lett.* **2**, 1035-1042 (2017)
Fe doped CoP	Ti foil	67	230	310	NA	*Adv. Mater*. **29**, 1602441-1602449 (2017)
Fe(PO$_3$)$_2$	Ni foam	51.9	177	NA	265	*Proc. Natl Acad. Sci. USA* (2017) DOI: 10.1073/pnas.1701562114.
Fe$_x$N	Graphene/Ni foam	44.5	238	290*	NA	*ACS Catal.* **7**, 2052-2057 (2017)
Ni-Co nanowire	Carbon fiber	43.6	302	310*	NA	*Adv. Energy Mater.* **7**, 1601492-1601502 (2017)
NiPS$_3$/NiOOH	Glassy carbon	NA	225*	320*	NA	*ACS Catal.* **7**, 229-237 (2017)
Gelled FeCoW	Au foam	37	190	NA	NA	*Science* **352**, 333-337 (2016)
NiS$_x$	Ni foam	96	180	210*	320*	*Adv. Energy Mater*. **6**, 1502333-1502339 (2016)
CoFePO	Ni foam	51.7	274	400*	870*	*ACS Nano* **10**, 8738-8745 (2016)
CoMnP	Glassy carbon	61	330	NA	NA	*J. Am. Chem. Soc.* **138**, 4006-4009 (2016)
CoNi(OH)$_x$	Cu foil	77	280	340*	425*	*Adv. Energy Mater*. **6**, 1501661-1501667 (2016)
FeOOH/Co/FeOOH	Ni foam	32	NA	308*	NA	*Angew. Chem., Int. Ed.* **55**, 3694-3698 (2016)

* The value is calculated from the curves shown in the literatures.

Table S2. Comparison of the HER performance for Cu@NiFe LDH catalyst with other reported electrocatalysts in 1 M alkaline electrolytes (KOH or NaOH). Here η_{-10} and η_{-100} correspond to the overpotentials at current densities of 10 and 100 mA cm^{-2} in the HER, respectively.

Catalyst	**Support**	**Tafel slope (mV dec^{-1})**	**η_{-10} (mV)**	**η_{-100} (mV)**	**Reference**
Cu@NiFe LDH	Cu foam	58.9	116	192	This work
Exfoliated NiFe LDH/ defective graphene	Glassy carbon	110	210	NA	*Adv. Mater.* **29**, 1700017-1700024 (2017)
$NiCo_2O_4$/NiFe LDH	Ni foam	59	192	440*	*ACS Appl. Mater. Interfaces.* **9**, 1488-1495 (2017)
CoSe/NiFe LDH	Exfoliated graphene foil	NA	260	NA	*Energy Environ. Sci.* **9**, 478-483 (2016)
NiFe/$NiCo_2O_4$	Ni foam	88	105	202*	*Adv. Funct. Mater.* **26**, 3515-3523 (2016)
$Cu_{0.3}Co_{2.7}P$	Glassy carbon	122	220	445*	*Adv. Energy Mater*. **7**, 1601555-1601563 (2017)
Ni/Mo_2C/porous C	Glassy carbon	101	179	NA	*Chem. Sci.* **8**, 968-973 (2017)
Janus Co/CoP	N doped C membranes	64	135	NA	*ACS Nano* **11**, 4358-4364 (2017)
Janus Co/CoP	Ni foam	73.8	193	NA	*Adv. Energy Mater.* 1602355-1602361 (2017)
$Ni_{12}P_5$	Ni foam	NA	170	290	*ACS Catal.* **7**, 103-109 (2017)
Cu/CoS_x	Cu foam	NA	134	267	*Adv. Mater.* **29**, 1606200-1606207 (2017)
Co_3O_4 microtube	Ni foam	98	170*	285*	*Angew. Chem., Int. Ed.* **56**, 1324-1328 (2017)
VOOH hollow nanosphere	Ni foam	104	164	270*	*Angew. Chem., Int. Ed.* **56**, 573-577 (2017)
CoS/carbon nanotube	Carbon paper	131	190	NA	*ACS Nano* **10**, 2342-2348 (2016)
$NiCo_2S_4$ nanowire	Ni foam	58.9	210	350	*Adv. Funct. Mater.* **26**, 4661-4672 (2016)
MoC/Mo_2C	Glassy carbon	42	120	NA	*Chem. Sci.* **7**, 3399-3405 (2016)
CoO_x/N doped C	Glassy carbon	NA	232	NA	*J. Am. Chem. Soc.* **137**, 2688-2694 (2015)

* The value is calculated from the curves shown in the literatures.

Table S3. Comparison of the bifunctional water splitting activity of the Cu@NiFe LDH catalyst with other recently reported bifunctional electrocatalysts in 1 M alkaline electrolytes.

Catalyst	Support	Current densities (J, mA cm^{-2})	Voltage at the corresponding J (V)	Reference
Cu@NiFe LDH	Cu foam	10	1.54	This work
		100	1.69	
		200	1.78	
Exfoliated NiFe LDH/ defective graphene	Glassy carbon	20	1.5	*Adv. Mater.* **29**, 1700017-1700024 (2017)
		60	1.7*	
$NiCo_2O_4$/NiFe LDH	Ni foam	10	1.6	*ACS Appl. Mater. Interfaces*. **9**, 1488-1495 (2017)
		60	1.84*	
Fe doped CoP	Ti foil	10	1.6	*Adv. Mater*. **29**, 1602441-1602449 (2017)
		60	1.73*	
Cu/CoS_x	Cu foam	10	1.5	*Adv. Mater.* **29**, 1606200-1606207 (2017)
		100	1.8*	
Co-N-P doped carbon	Exfoliated graphene foil	10	1.6	*Adv. Mater.* **29**, 1604480-1604486 (2017)
		30	1.67*	
Janus Co/CoP	Ni foam	10	1.45	*Adv. Energy Mater.* 1602355-1602361 (2017)
		20	1.66	
$Ni_xCo_{3-x}S_4/Ni_3S_2$	Ni foam	10	1.53	*Nano Energy* **35**, 161-170 (2017)
		100	1.8	
MoS_2/Ni_3S_2	Ni foam	10	1.5	*ACS Catal.* **7**, 2357-2366 (2017)
		90	1.63*	
NiOS hollow nanospheres	Ni foam	10	1.55	Small **13**, 1602637-1602642 (2017)
		50	1.78*	
Ni-Mo alloy	Cu foil	10	1.59	*J. Mater. Chem. A* **5**, 5797-5805 (2017)
		100	1.9*	
NiCoP	Ni foam	10	1.58	*Nano Lett.* **16**, 7718-7725 (2016)
		100	1.82	
		200	1.98	

* The value is calculated from the curves shown in the literatures.