NiFe LDH/CuO nanosheets: a sheet on sheet strategy for efficient and durable oxygen evolution reaction

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Experimentals

1. Chemicals

Sodium hydroxide (NaOH), Ethylenediamine (C$_2$H$_8$N$_2$), Hydrazine hydrate (N$_2$H$_4$·H$_2$O), Copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O), Nickel(II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O), Iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as-received. Deionized water (DI water, 18.2 MΩ at 25 °C) was used in all processes.

2. Catalysts preparation

(1) Synthesis of Cu nanowires

20 mL Cu(NO$_3$)$_2$·3H$_2$O (0.1 M) was slowly added into a three-neck flask containing 200 mL of NaOH (15 M) with agitation, then the solution was kept at 80 °C and agitated for 20 min for the formation of Cu nanowires (CuNWs). After that, the solution was cooled down rapidly to 10 °C in an ice bath, following the filtration and rinsing with plenty of DI water, the CuNWs was freeze dried.

(2) Synthesis of CuO nanosheets/Cu nanowires

120 mg of CuNWs and 800 mg of NaOH were dispersed in 200 mL of ethylene glycol in a three-neck flask and stirred for 3 h under N$_2$ atmosphere. After filtration and rinsing with plenty of DI water, the paste was kept at 200 °C for 3 h.

(3) Synthesis of NiFe LDH/CuO nanosheets

The prepared CuO nanosheets/Cu nanowires, 129.0 mg of Fe(NO$_3$)$_3$·6H$_2$O, and 361.9 mg of Ni(NO$_3$)$_3$·6H$_2$O were dispersed in 40 mL of DI water and stirred at 80 °C under N$_2$. The Ni:Fe atomic ratio was kept constantly at 4:1. 1 mL of ammonia was

added drop wise. After vigorous agitation for 3 h, filtration, and rinsing with plenty of DI water, the paste was freeze-dried. The final products, NiFe LDH/CuO nanosheets (NiFe LDH/CuO NS) were ready for tests.

A control experiment, adding different amount of NiFe precursors, was carried out for morphology comparison. 96.75 mg of $Fe(NO_3)_3 \cdot 6H_2O$ and 271.43 mg of $Ni(NO_3)_3 \cdot 6H_2O$, 64.50 mg of $Fe(NO_3)_3 \cdot 6H_2O$ and 181.0 mg of $Ni(NO_3)_3 \cdot 6H_2O$, were added to prepare NiFe LDH-L/CuO NS and NiFe LDH-M/CuO NS.

(4) Synthesis of NiFe LDH/CuNWs

120 mg of CuNWs, different amounts of $Fe(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_3 \cdot 6H_2O$ were dispersed in 40 mL of DI water and stirred at 80 °C under N_2. The Ni:Fe atomic ratio was kept constantly at 4:1. 2 mL of ammonia was added drop wise. After vigorous agitation for 3 h, filtration, and rinsing with plenty of DI water, the paste was freeze-dried.

The dosages of $Fe(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_3 \cdot 6H_2O$ are listed in table below:

| Sample	$Fe(NO_3)_3 \cdot 6H_2O$ (mg)	$Ni(NO_3)_3 \cdot 6H_2O$ (mg)	Labelled as
1	258.0	723.7	NiFe LDH/CuNWs-L
2	386.8	1085.6	NiFe LDH/CuNWs
3	515.8	1447.4	NiFe LDH/CuNWs-H

3. Characterizations

The morphologies of as-prepared catalysts were observed by s scansmission electron

microscope (SEM) (TECNAI G2F20, FEI) equipped with Energy Dispersive X-Ray Spectroscopy (EDX). X-ray diffraction (XRD) was carried out on Ultima III (Rigaku) in the scanning 2θ range of 20-90° with Cu kα (λ=0.15406 nm) as radiation source. X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB 250 (Thermo Scientific).

3.2 Electrochemical tests

The ink was prepared by ultrasonically dispersing 4 mg of sample f in a solution containing 1 mL of DI water, 1 mL of Isopropanol, and 20 μL of 5% Nafion. OER was performed on CHI660 with a conventional three-electrode system. Glassy carbon (ϕ = 5 mm), platinum wire (ϕ = 1 mm), and Ag/AgCl were used as working electrode (WE), counter electrode, and reference electrode, respectively. Before used, WE was polished with Al_2O_3 ($\leq$ 50 nm) slurry to a mirror-like surface and rinsed with plenty of DI water. Pipetted 10 μL of ink onto the WE surface and dried under ambient condition, the WE was ready for electrochemical tests.
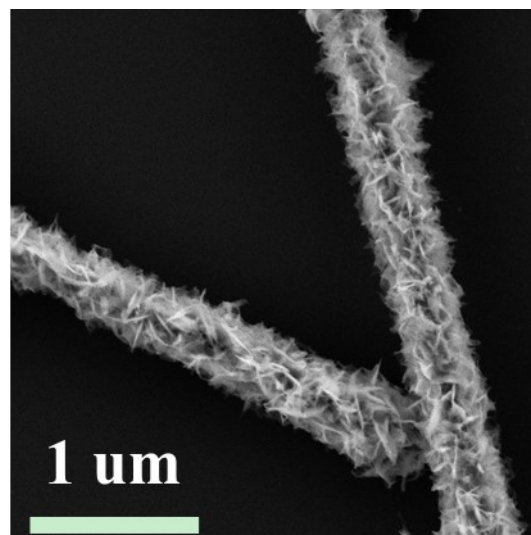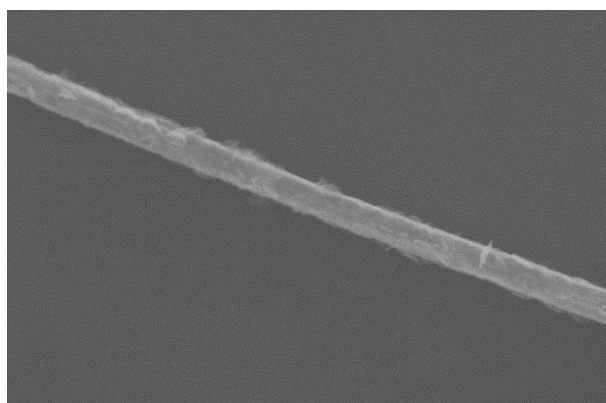
A

B

10 um

C

1 um
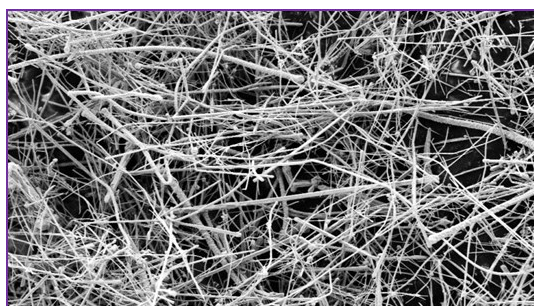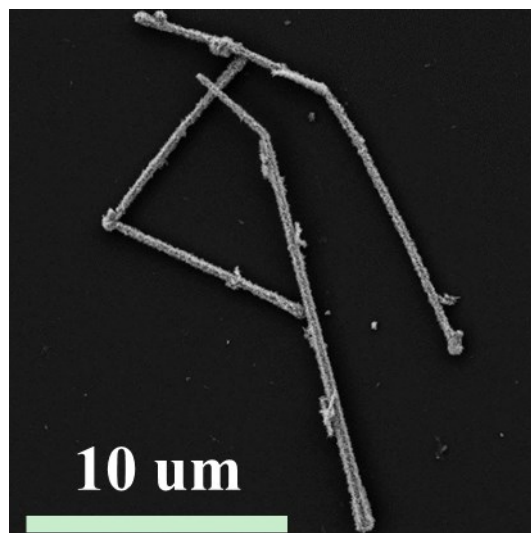
Figure S1 The SEM images of CuNWs (A), CuO NS/Cu NWs at low (B) and high (C)

solutions.

A

B

| EHT = 5.00 kV | Signal A = SE2 | 200 nm | ZEISS |
| WD = 4.8 mm | Mag = 50.00 K X | | |

C

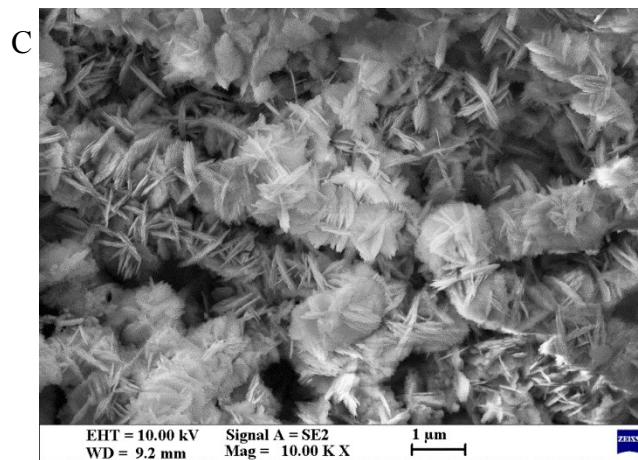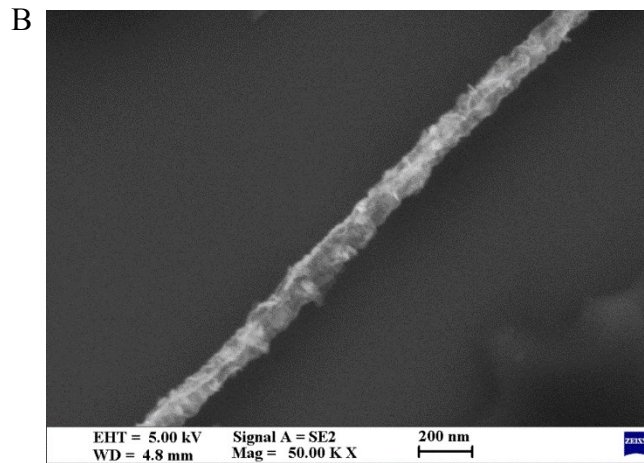| EHT = 10.00 kV | Signal A = SE2 | 1 µm | ZEISS |
| WD = 9.2 mm | Mag = 10.00 K X | | |

Figure S2 The SEM images of NiFe LDH/CuNWs with different density of NiFe
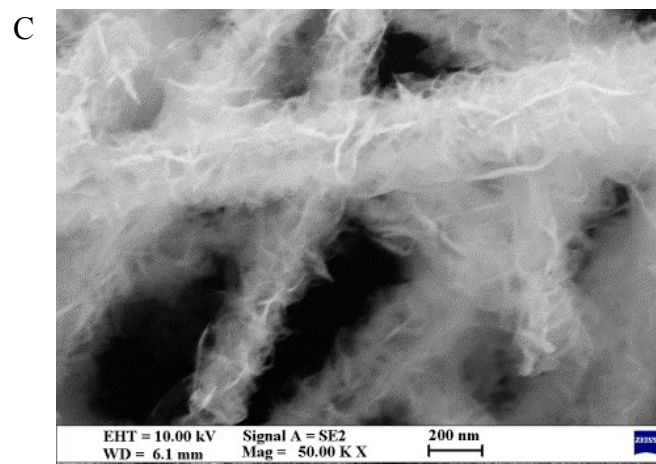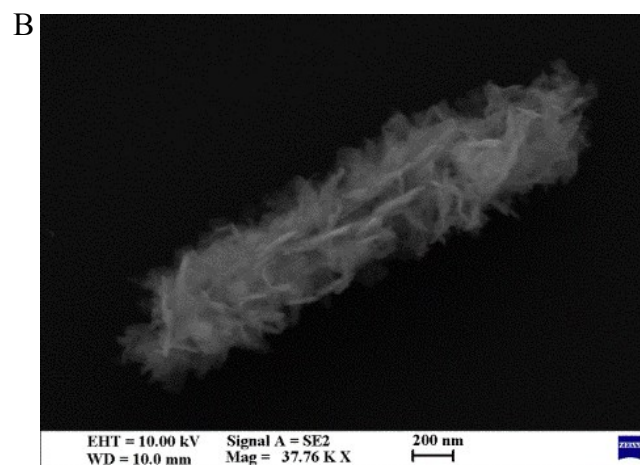
LDHs.

A

B

C

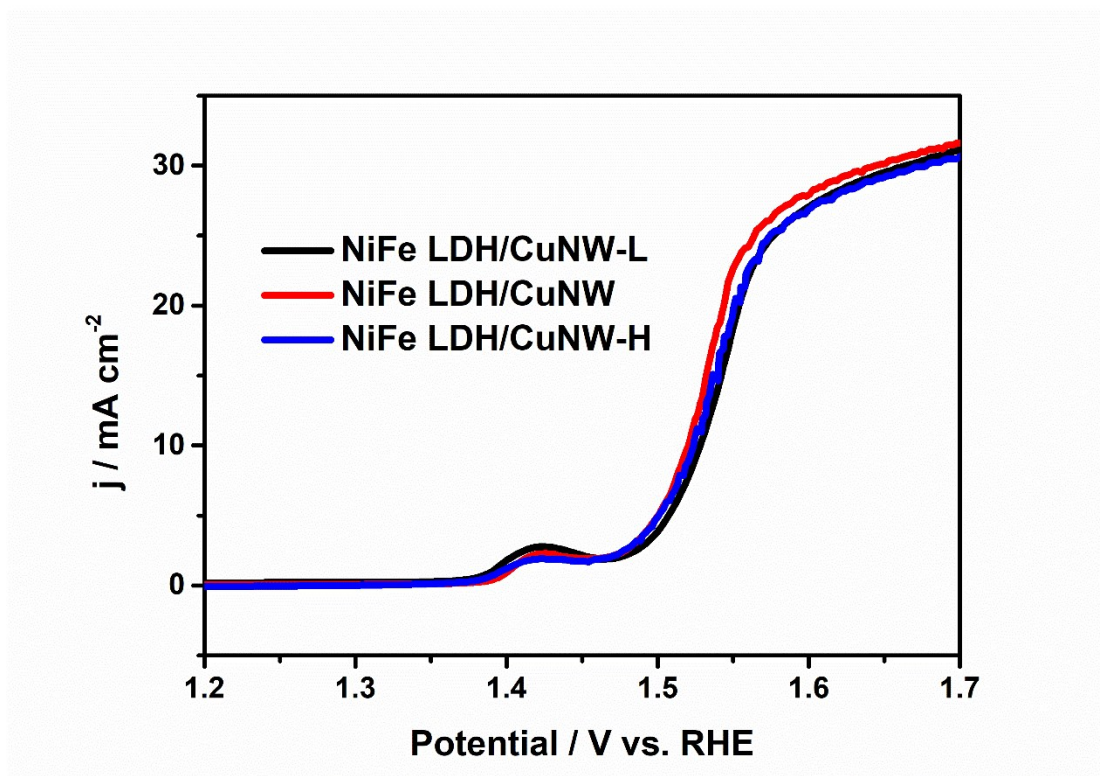Figure S3 The SEM images of NiFe LDH-L/CuO NS and NiFe LDH-M/CuO NS.

Figure S4 The LSV of NiFe LDH/CuNWs with different density of NiFe LDHs at the

scanning rate of 5 mV s^{-1} in 1 M KOH.

Table S1 the elemental compositions of NiFe LDH/CuO NS detected by EDS.

Elements	wt%
O	4.44
Fe	4.11
Ni	17.55
Cu	73.91
total	100.00

Table S2 The overpotentials and Tafel slopes of catalysts reported in literatures

Catalyst	Overpotential (mV)	Tafel slope (mV dec^{-1})	Ref.
NiFe LDH/AgNWs	265 mV at 10 mA cm^{-2} (1M KOH)	122	[1]
NiFe LDH/CuO nanorods	290 mV at 50 mA cm^{-2} (1M KOH)	60	[2]
NiFe LDH/NiCoP nanoarrey	220 mV at 10 mA cm^{-2} (1M KOH)	Not given	[3]
NiFe oxyfluoride holey film	295 mV at 10 mA cm^{-2} (1M KOH)	38	[4]
NiO/NiFe LDH	205 mV at 30 mA cm^{-2} (1M KOH)	30	[5]
NiFeV LDHs	195 mV at 20 mA cm^{-2} (1M KOH)	42	[6]
NiCe@NiFe/NF-N	254 mV at 100 mA cm^{-2} (1M KOH)	59.9	[7]
Single atom Au/ NiFe LDH	263 mV at 10 mA cm^{-2} (1M KOH)	Not given	[8]
Cu@NiFe LDH	199 mV at 10 mA cm^{-2} (1M KOH)	27.8	[9]
V-Ni$_3$S$_2$@NiFe LDH	209 mV at 10 mA cm^{-2} (1M KOH)	32.5	[10]

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