

Electronic supplementary information

Experimental section

Chemicals: Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99-100%) was purchased from Xiya Reagent; sodium salicylate ($\text{C}_7\text{H}_5\text{O}_3\text{Na}$), sodium hydroxide (NaOH), potassium hydroxide (KOH) were purchased from Tianjin Fuchen Chemical Reagent; ethanol ($\text{C}_2\text{H}_5\text{OH}$) was purchased from Beijing Chemical Works; Nafion solution (5 wt.%) was purchased from Sigma-Aldrich. All chemicals were analytical grade and used as received without further purification.

Synthesis of $\text{Cu}(\text{OH})(\text{Hsal}) \cdot \text{H}_2\text{O}$ precursor: The precursor was prepared by a simple coprecipitation method. In a typical procedure, the $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.02 mol) and $\text{C}_7\text{H}_5\text{O}_3\text{Na}$ (0.04 mol) were mixed in the 250 mL deionized water in a four-necked flask. To control the pH at 5.5, 1 M NaOH solution was added into the flask drop by drop through the dropping funnel and the mixture was stirred at 90 °C for 24 h. Thereafter, the precipitates were separated by centrifugation, washed repeatedly, and dried in a vacuum oven overnight at 50 °C.

Synthesis of $\text{Cu}@C$ nanofiber: The as-obtained $\text{Cu}(\text{OH})(\text{Hsal}) \cdot \text{H}_2\text{O}$ precursor loaded in a ceramic boat were placed at the center of a tube-furnace under continuous flow (40 $\text{mL cm}^{-2} \cdot \text{min}^{-1}$) of N_2 gas. The furnace temperature was raised at a ramping rate of 5 °C min^{-1} and then kept at 800 °C for 2 h.

Electrocatalytic HER and OER measurements: All the electrochemical measurements were carried out on a CHI 660E electrochemical station (Shanghai Chenhua, China) with a conventional three-electrode configuration at room temperature. Rotating disk electrode (RDE, 0.07069 cm^2 for the geometric surface area) was used as the working electrode, and an Ag/AgCl electrode (3 M KCl) and a platinum carbon electrode serve as the reference and counter electrodes, respectively. The catalyst inks (5 mg mL^{-1}) were prepared by dispersing the prepared samples in a mixed solution ($V_{\text{water}}: V_{\text{EtOH}}: V_{\text{Nafion}} = 7: 12: 1$) under ultrasonication for at least 60 min (The

total volume of the solution is 1 ml). Prior to fabricating the working electrode, a glassy carbon (GC) RDE electrode was polished by alumina powder and then sonicated in ethanol and deionized water to obtain a mirror-like finish surface. Then, 4 μL of the as-prepared ink was dropped onto the surface of RDE and dried naturally with the loading density of 0.283 mg cm^{-1} . With this prepared glassy carbon disk as the working electrode, electrochemical measurements were performed in 1M KOH aqueous solution. Linear sweep voltammetry (LSV) was measured at 1600 rpm (to remove the in situ-formed H_2 or O_2 bubbles on the RDE) with a sweep rate of 5 mV s^{-1} . All of the measured LSV curves were corrected with 95% iR-compensation. For comparison, the commercial 20 wt% Pt/C was measured under the same experimental conditions. The following potential ranges were scanned at a scan rate of 5 mV s^{-1} ; OER: 0.20 to 1.80 V (vs. Ag/AgCl) and HER: -0.20 to -2.00 V (vs. Ag/AgCl). Prior to the OER and HER measurements, the working electrode was first “activated” by running 20 consecutive CVs in the potential range of -0.70 - 0 V (vs. Ag/AgCl) for HER and 0 - 0.50 V (vs. Ag/AgCl) for OER at 50 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were carried out with a frequency range from 0.1 Hz to 1 MHz and an amplitude potential of 5 mV at an overpotential of 0.457 V (OER) and -1.223 V (HER) in 1 M KOH electrolyte. The potential was held at -1.26 V (vs. Ag/AgCl) during the chronoamperometric measurement. A galvanostatic measurement with an applied current density of 10 mA cm^{-2} for 10 h was run to assess the stability of the highest performing OER catalyst. All the measured potentials against the Ag/AgCl reference were converted to a reversible hydrogen electrode (RHE) scale according to the equation of $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.1976 \text{ V} + 0.0591 \times \text{pH}$. The Tafel slope can be calculated according to the equation as follows:

$$\eta = b \log j + a \quad (1)$$

$$\eta = E \text{ vs. RHE} - 1.23 \text{ V} \quad (2)$$

in which j , b and η represent the current density, Tafel slope and overpotential, respectively.

Overall water splitting tests: The overall water splitting tests were carried out in a two-electrode system using a CHI 660E electrochemical workstation (Shanghai Chenhua, China) controlled at room temperature. The Cu@C electrocatalysts were deposited on Ni foam (1 cm², catalyst loading 1 mg) and then used as the cathode and anode electrodes, respectively. Before used, Ni foam was cleaned by diluted HNO₃, deionized water, and acetone with ultrasonication for 5 min in each step. LSV curves were obtained at a sweep rate of 5 mV s⁻¹ in 1.0 M KOH aqueous solution. The long-term durability test was performed by continuous chronoamperometry at the potential of 1.645 V for 10 h. Additionally, bare Ni foam was used for overall water splitting tests to avoid the possible activity contribution from the Ni foam substrate during water splitting process.

Characterizations: X-ray diffraction (XRD) was carried out on a RIGAKU XRD-6000A diffractometer at 40 kV and 100 mA with copper filtered K α radiation ($\lambda = 1.5406 \text{ \AA}$). The Fourier Transform Infrared Spectra (FT-IR) of samples were recorded at room temperature by Bruker Vector 22. N₂ adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2460 system at liquid N₂ temperature. Before measurements, the samples were outgassed at 110 °C for 6 h. The specific surface area was calculated by using Brunauer–Emmett–Teller (BET) method. The morphology of the samples was obtained with Zeiss Supra 55 scanning electron microscope (SEM). High resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-2100 transmission electron microscope (Tokyo, Japan). Scanning transmission electron microscopy (STEM) images and corresponding energy dispersive X-ray spectroscopy (EDX) mappings were recorded on a FEI Tecnai F20 microscopy. X-ray photoelectron spectroscopy (XPS) was measured on an VG Escalab 2201 XL X-ray electron spectrometer using Al K α radiation. Raman spectroscopy was used Jobin Yvon Horiba type Raman microscope, regulating an excitation wavelength of 633 nm to characterize and analyze the carbon element properties in nanofibers. Thermogravimetric analysis was carried out using a Rigaku TG-8120 instrument in the temperature range 25-800 at a heating rate of 10 °C min⁻¹ under a nitrogen flow.

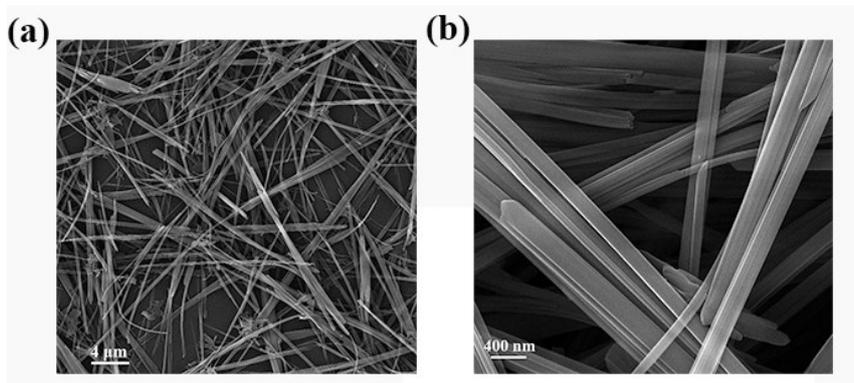


Fig. S1 (a) Low-resolution and (b) high-resolution SEM images of $\text{Cu(OH)(Hsal)·H}_2\text{O}$.

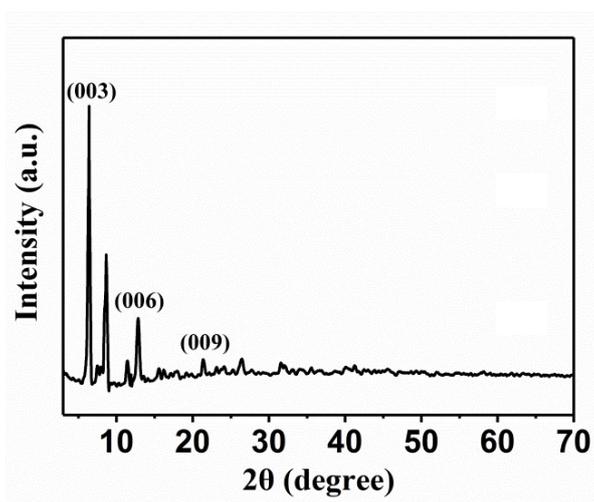


Fig. S2 The XRD pattern of $\text{Cu(OH)(Hsal)·H}_2\text{O}$.

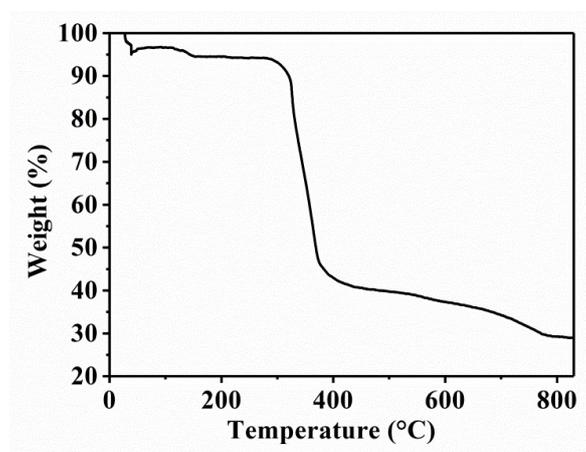


Fig. S3 Thermogravimetry analysis of $\text{Cu(OH)(Hsal)·H}_2\text{O}$ in nitrogen atmosphere.

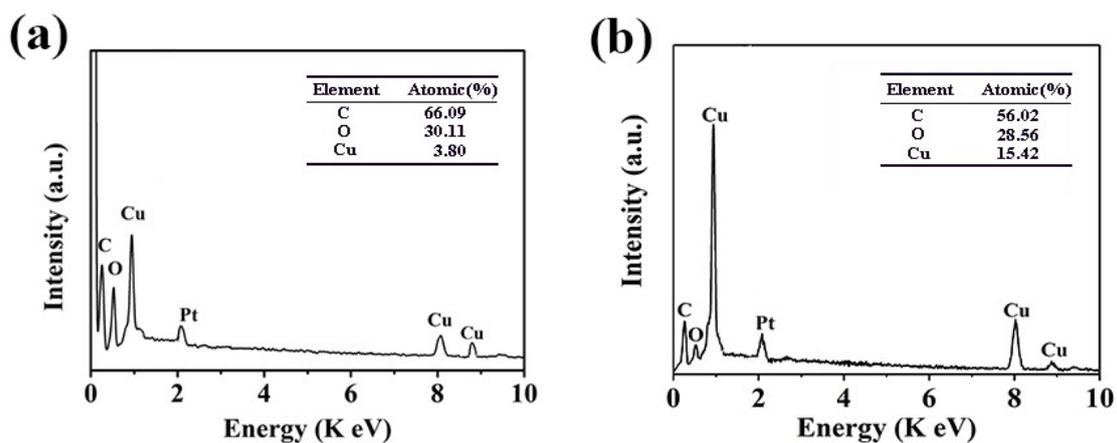


Fig. S4 EDX spectra of (a) $\text{Cu(OH)(Hsal)} \cdot \text{H}_2\text{O}$, (b) Cu@C (inset: element atomic percentage of C/O/Cu).

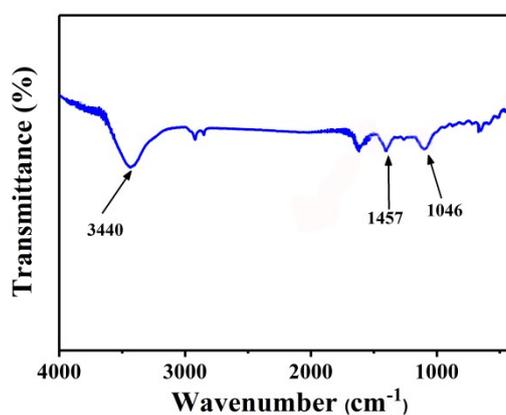


Fig. S5 FT-IR spectrum of Cu@C .

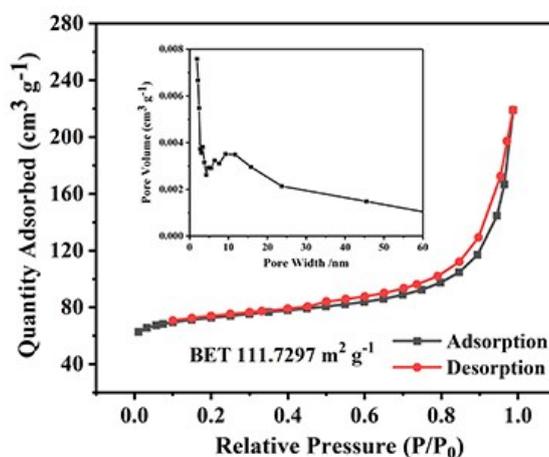


Fig. S6 N_2 adsorption/desorption isotherms and pore size distributions of Cu@C .

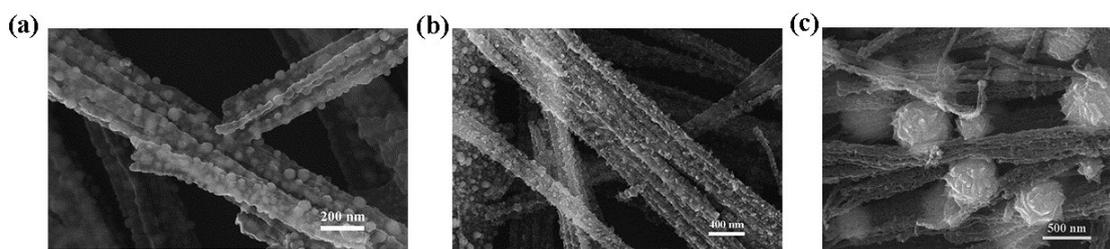


Fig. S7 SEM images of (a) Cu@C-400, (b) Cu@C-600 and (c) Cu@C-1000.

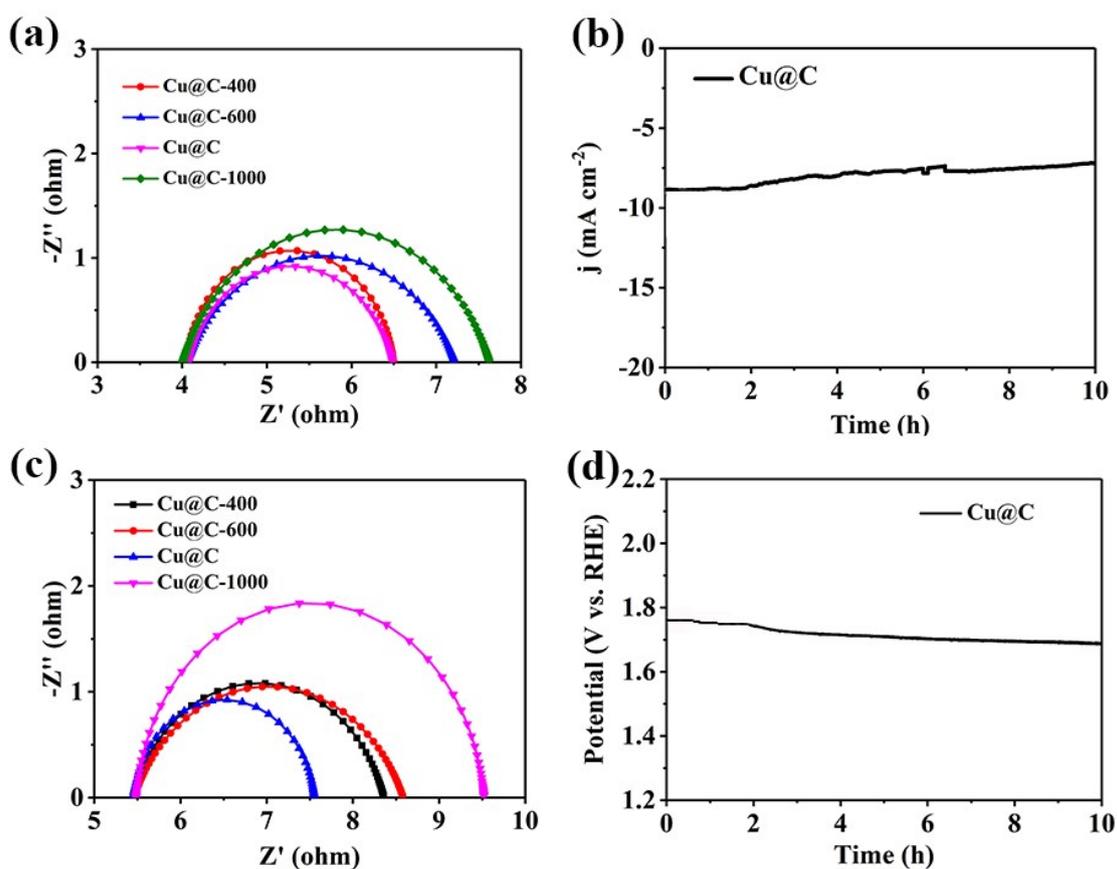


Fig. S8 Electrocatalytic performance of Cu@C nanofibers and reference samples in 1.0 M KOH solution. (a) Nyquist plots of different materials for HER, (b) Chronoamperometric responses recorded on Cu@C nanofibers for HER at a constant potential of -1.26 V (vs. Ag/AgCl), (c) Nyquist plots of different materials for OER. (d) Chronopotentiometric curves of Cu@C nanofibers for OER at constant current densities of 10 mA cm^{-2} in 1.0 M KOH.

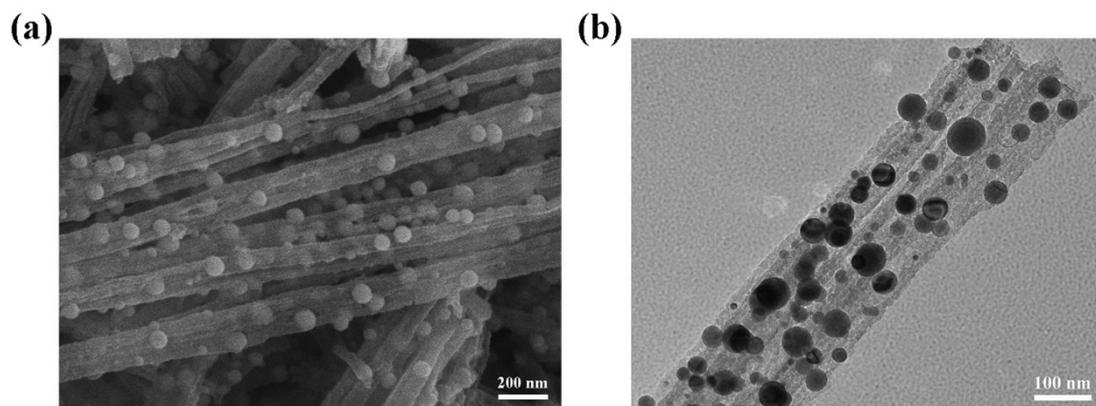


Fig. S9 SEM (a) and TEM (b) images of Cu@C after catalysis.

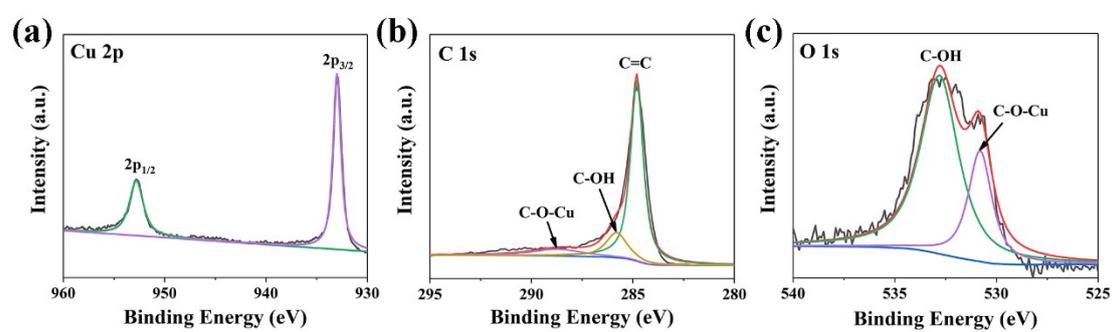


Fig. S10 High-resolution XPS spectra of Cu 2p (a), C 1s (b) and O 1s (c) of Cu@C nanofibers after catalysis.

Table S1. Comparison of cell voltage for overall water splitting of various Cu based catalysts in 1.0 M KOH electrolyte

| Catalyst | Support | Cell Voltage (V) | j (mA cm ⁻²) | References |
|--------------------------------------|--------------|------------------|--------------------------|--|
| Cu@C | Ni foam | 1.645 | 10 | This work |
| Cu ₃ N/NF | Ni foam | 1.60 | 10 | <i>ACS Energy Lett.</i> , 2019 , 4, 747. |
| Cu@CoSx | Cu foam | 1.50 | 10 | <i>Adv. Mater.</i> , 2017 , 29, 1606200. |
| NC@CoN/Cu ₃ N/CF | Cu foam | 1.62 | 10 | <i>Inorg. Chem. Front.</i> , 2018 , 5, 2906-2913 |
| CuCo ₂ O ₄ /NF | Ni foam | 1.61 | 10 | <i>Adv. Funct. Mater.</i> , 2016 , 26, 8555-8561. |
| Ni ₄ Cu ₂ @C | Carbon paper | 1.49 | 15 | <i>Mater. Chem. Front.</i> , 2020 , 4, 996-1005 |

Table S2. Comparison of cell voltage for overall water splitting of various non-precious catalysts in 1.0 M KOH electrolyte

| Catalyst | Support | Cell Voltage (V) | j (mA cm ⁻²) | References |
|--|--------------|------------------|--------------------------|--|
| Cu@C | Ni foam | 1.645 | 10 | This work |
| Ni/Mo ₂ C-NCNFs | Ni foam | 1.64 | 10 | <i>Adv. Energy Mater.</i> , 2019 , 9, 1803185. |
| PO-Ni/Ni-N-CNFs | Ni foam | 1.69 | 10 | <i>Nano Energy</i> , 2018 , 51, 286. |
| NiS | Carbon cloth | 1.74 | 10 | <i>Nanoscale</i> , 2019 , 11, 5646-5654. |
| α-NiOOH | Ni foam | 1.66 | 10 | <i>ACS Sustain. Chem. Eng.</i> , 2017 , 5, 3808. |
| NiCo ₂ O ₄ @C | Ni foam | 1.608 | 10 | <i>J. Power Sources</i> , 2018 , 372, 46-53. |
| Ni/Mo ₂ C-PC | Ni foam | 1.66 | 10 | <i>Chem. Sci.</i> , 2017 , 8, 968-973. |
| Co-NC@ Mo ₂ C | GCE | 1.685 | 10 | <i>Nano Energy</i> , 2019 , 57, 746. |
| Co-Mo ₂ C@NCNT | Ti plate | 1.628 | 10 | <i>ACS Sustain. Chem. Eng.</i> , 2018 , 6, 9912-9920. |
| CNTs@CoS _x Se _{2(1-x)} | Carbon cloth | 1.74 | 10 | <i>ChemSusChem</i> , 2019 , 12, 1 – 10 |
| Ni ₅ P ₄ | Ni foil | 1.7 | 10 | <i>Angew. Chem. Int. Ed.</i> , 2015 , 54, 12361. |