Electronic Supplementary Information

Experimental section

Materials: Ammonium persulfate (APS) and sodium hydroxide (NaOH) were purchased from Aladdin Ltd. (Shanghai, China). Copper foam (CF) was supplied by Jiangsu Yijiasheng Foamed Metal Plant. All reagents were used as received without further purification. Ultrapure water was utilized to prepare all solutions.

Synthesis of $Cu(OH)_2$ NA/CF: The precursor was prepared according to previous reports.[1,2] A piece of CF (2 cm × 3 cm) was cleaned by hydrochloric acid, ethanol and deionized water several times to remove the surface oxides and impurities. Then the substrate was immediately immersed in 30 mL solution containing 4 mmol APS and 80 mmol NaOH at room temperature for 20 min. After that, the CF was taken out and washed by deionized water for several times. Finally, the as-made $Cu(OH)_2$ NA/CF was dry at 60 °C for 12 h.

Synthesis of Cu_3N NA/CF: The precursor was placed in the furnace and heated to 350 °C with a heating speed of 2 °C/min under a flowing NH_3 atmosphere for 3 h. The system was allowed to cool down to room temperature (25 °C) naturally still under a flowing NH_3 atmosphere.

Preparation of RuO_2/CF electrode: The RuO_2 was prepared according to a previous report.[3] Briefly, 1.0 mL NaOH (1.0 M) and 2.61 g $RuCl_3 \cdot 3H_2O$ were added into 100mL ultrapure water and ultrasound for 30 min at 373 K. The precipitates were collected by centrifugation and washed with water for three times. The obtained solids were dried at 353 K. Finally, the product was annealed at 573 K for 3 h under air atmosphere. The as-prepared RuO_2 powder (50 mg) was dispersed into a solution of Nafion, ethanol and water with a volume ratio of 20/280/70 via sonication, and deposited onto copper foam with a loading of 2.0 mg cm^{-2}.

Characterizations: The X-ray diffraction (XRD) patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40kV, 30mA) of wavelength 0.154 nm (SHIMADZU, Japan). Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an

accelerating voltage of 20 kV. The structures of the samples were determined by Transmission electron microscopy (TEM) images on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data of the samples was collected on an ESCALABMK II x- ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. Cu_3P-CoP/CC, graphite plate and Hg/HgO was used as the working electrode, the counter electrode and reference electrode, respectively. All tests were carried out in 1.0 M KOH at room temperature. The potentials reported in this work were calibrated to reversible hydrogen electrode (RHE) other than especially explained and the reference electrode was calibrated to RHE scale in all measurements using the following equation: E (RHE) = E (Hg/HgO) + (0.059 pH + 0.098) V.

Tafel plots calculation: The Tafel plots are employed to evaluate the OER catalytic kinetics and fitted with the following equation:

$$\eta = b \log j + a$$

Where j is the current density and b is the Tafel slope.

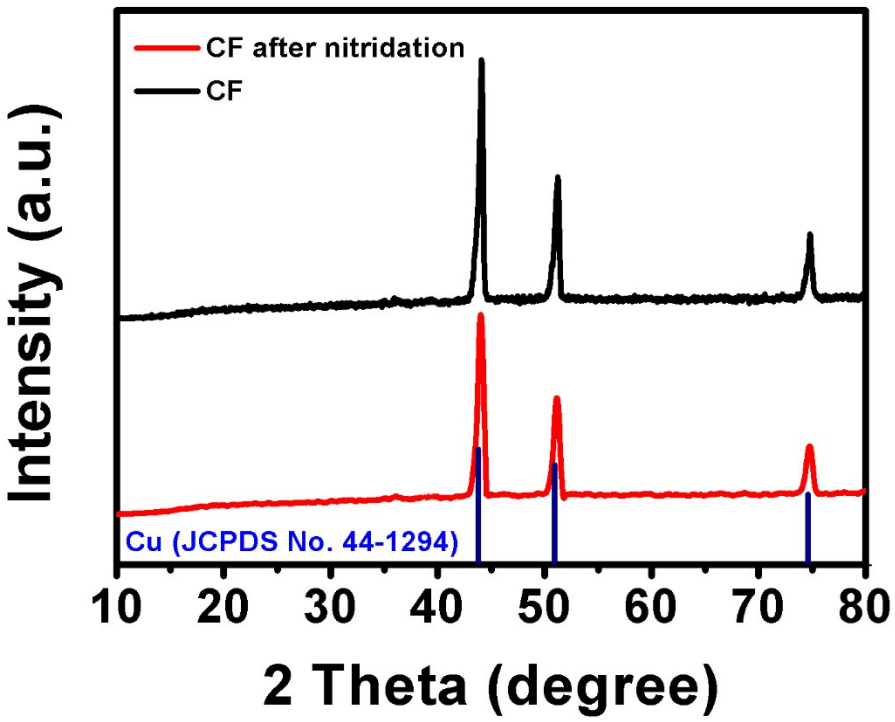

Fig. S1. XRD patterns of copper foam before (black line) and after (red line) nitridation process.

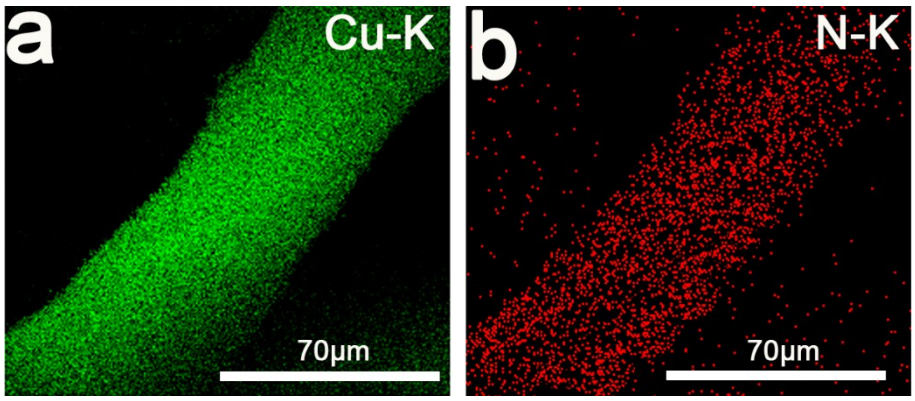

Fig. S2. EDX elemental mapping images of Cu and N elements for Cu_3N NA/CF.

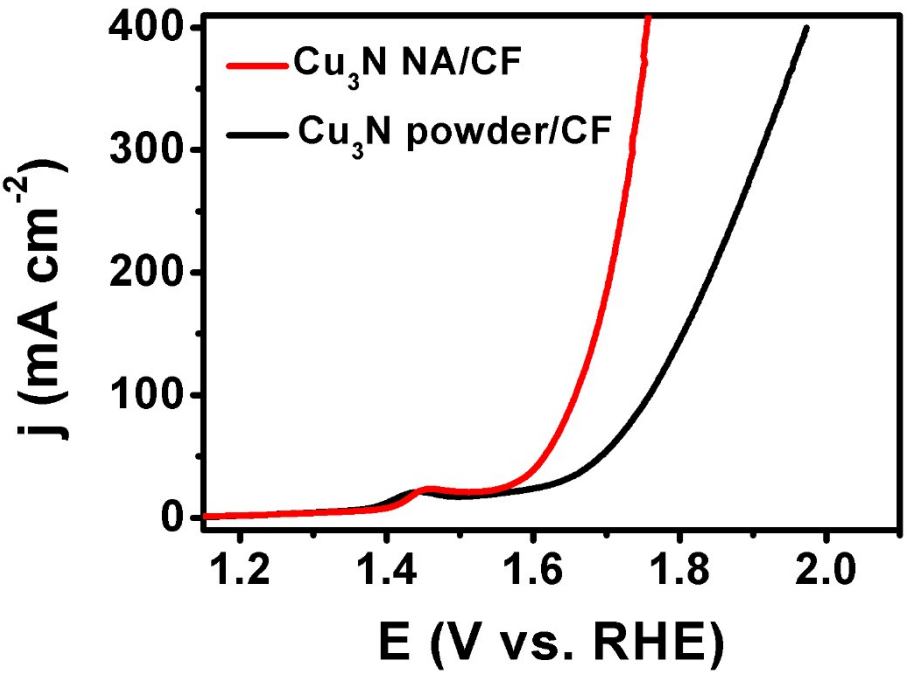

Fig. S3. LVS curves for Cu_3N NA/CF and Cu_3N powder.

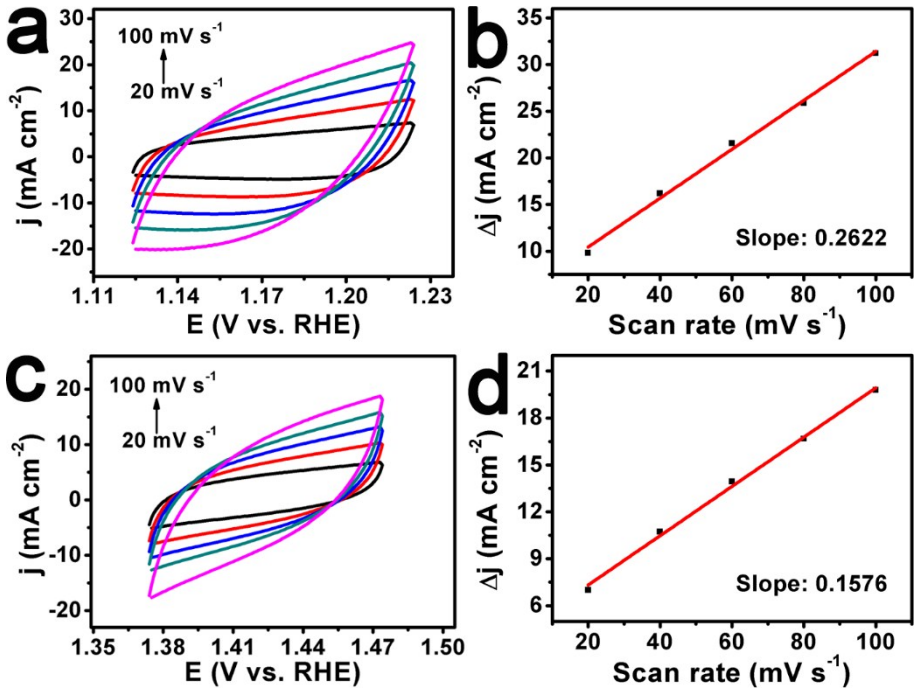

Fig. S4. CV curves at various scan rates (20, 40, 60, 80 and 100 mV s^{-1}) for (a) Cu_3N NA/CF and (c) $Cu(OH)_2$ NA/CF in 1.0 M KOH. The differences (Δj) between capacitive currents at the center of selected potential window as a function of scan rate for (b) Cu_3N NA/CF and (d) $Cu(OH)_2$ NA/CF in 1.0 M KOH. The slope is twice of C_{dl}.

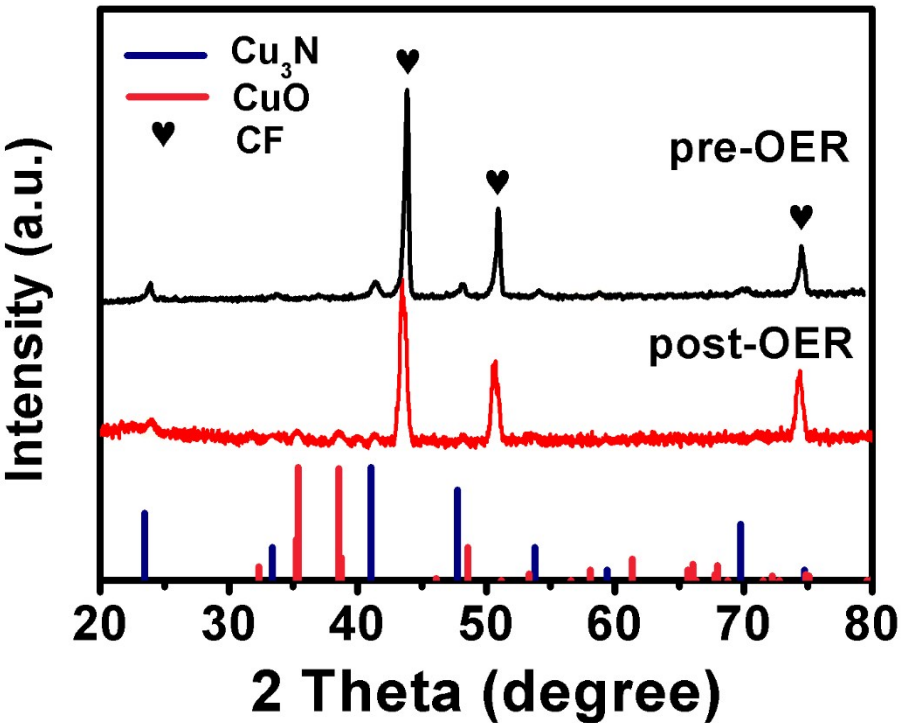

Fig. S5. XRD patterns for Cu_3N NA/CF before and after OER test.

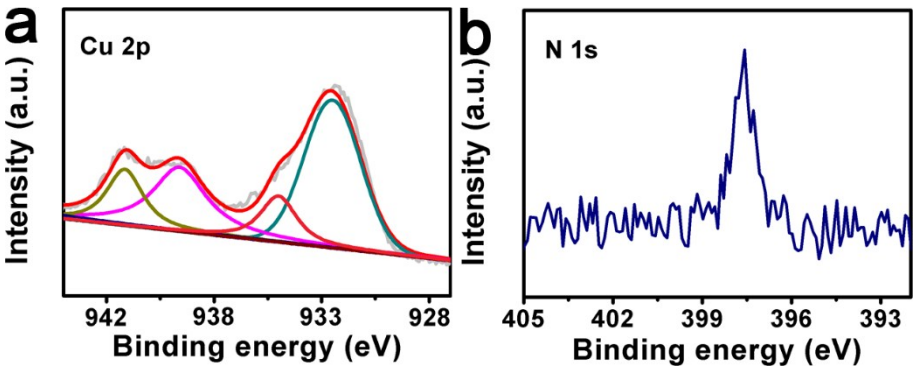

Fig. S6. XPS analysis in (a) Cu 2p and (b) N 1s regions for post-OER Cu_3N NA/CF.

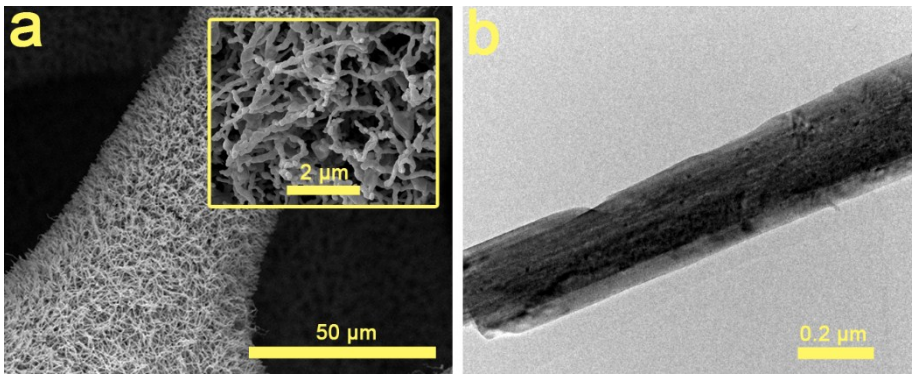

Fig. S7. (a) SEM image and (b) TEM image after OER test.

Table S1. Comparison of OER performance for Cu_3N NA/CF with other non-noble-metal electrocatalysts in 1.0 M KOH.

Catalyst	j (mA cm^{-2})	Overpotential (mV)	Ref.
Cu_3N NA/CF	20	298	This work
Cu–N–C NA/CF	20	314	4
CuO-TCNQ/CF	25	317	5
2D CuO nanosheet bundles	10	350	6
Cu_2O/C	10	330	7
$Ni_{59}Cu_{19}P_9$	10	318.7	8
$Cu(OH)_2$@CoNiCH NTs/CF	30	288	9
NC@CoN/Cu_3N/CF	10	257	10
Cu_2O−Cu foams	10	350	11
Co_3O_4@C-MWCNTs	10	320	12
$CoMoO_4$ nanorod	10	343	13

References

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