Dandelion-like Co_3O_4 mesoporous nanostructures supported by Cu foam for efficient oxygen evolution and lithium storage

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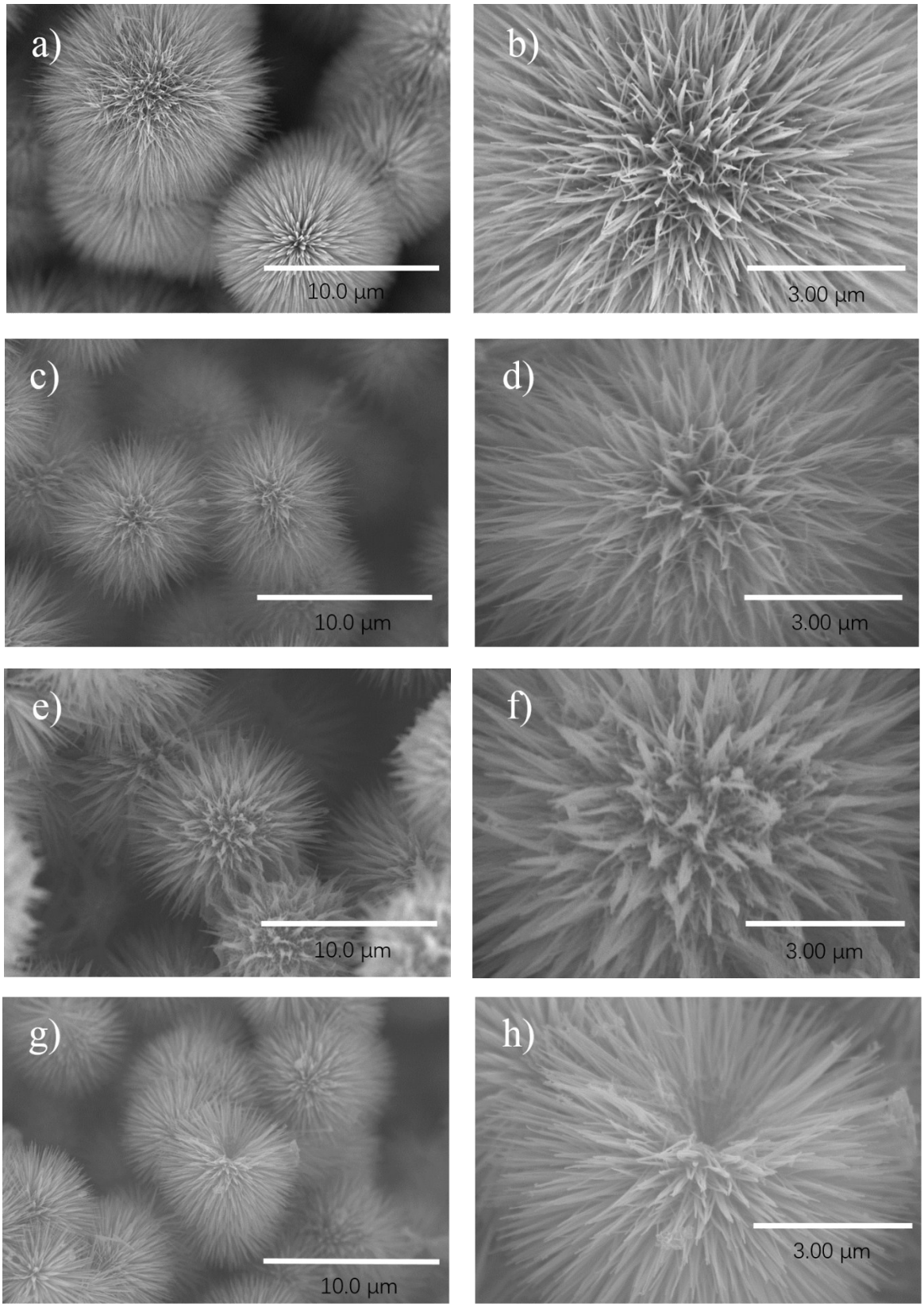
Experimental Section

***Preparation of Co_3O_4@Cu foam*:** The Co_3O_4@Cu foam was prepared by a combination of hydrothermal synthesis and annealing. Briefly, $Co(NO_3)_2 \cdot 6H_2O$ (1 mmol), NH_4F (2.7 mmol) and $CO(NH_2)_2$ (7.5 mmol) were dissolved in deionized water (30 ml) and stirred for 30 min. Then, the fully mixed solution and Cu foam (φ = 12 mm) were transferred to a Teflon-lined stainless steel autoclave (50 ml), and heated at 110 °C for 12 h. After the autoclave was cooled naturally to ambient temperature, the precipitate was washed by absolute alcohol and deionized water, and vacuum-dried at 60 °C overnight. Finally, the precipitate was annealed at different temperatures (200, 300, 400 and 500 °C) for different times (1, 2, 3 and 4 h). For comparison, the Co_3O_4 powder was prepared by annealing at 300 °C for 2 h in the absence of Cu foam.

***Electrochemical testing*:** The OER properties were measured in 1M KOH aqueous solution by using a three-electrode mode on an electrochemical workstation (CHI 660D, CH Instruments). The Pt net and SCE were used as counter and reference electrodes, respectively. All potentials were converted to the reversible hydrogen electrode (RHE) based on the equation E(*vs.* RHE) = E(*vs.* SCE) + 0.244 + 0.059×PH. The OER activities were investigated by linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} and the LSV data were made with an 80% ohmic drop (iR) correction tested by impedance spectroscopy. Electrochemical impedance spectroscopy (EIS) was performed by applying an AC voltage of 5 mV from 100 kHz to 0.01 Hz.

CR-2025 coin-type cells were assembled to evaluate the lithium storage performance of the Co_3O_4@Cu foam inside an argon-filled glove box. The microporous polypropylene membrane, lithium foil, and 1 M solution of $LiPF_6$ in ethylene carbonate and dimethyl carbonate (volume ratio = 1:1) were used as the separator, counter and reference electrode, and electrolyte, respectively. The assembled cells were allowed to soak overnight, and the electrochemical tests were performed on a LAND battery testing unit. Cyclic voltammetry (CV) was performed using a CHI 660E electrochemical workstation between 0.01–3.00 V (*vs.* Li^+/Li) at a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was performed by applying an AC voltage of 5 mV from 100 kHz to 0.01 Hz.

Supplementary Figures and Tables



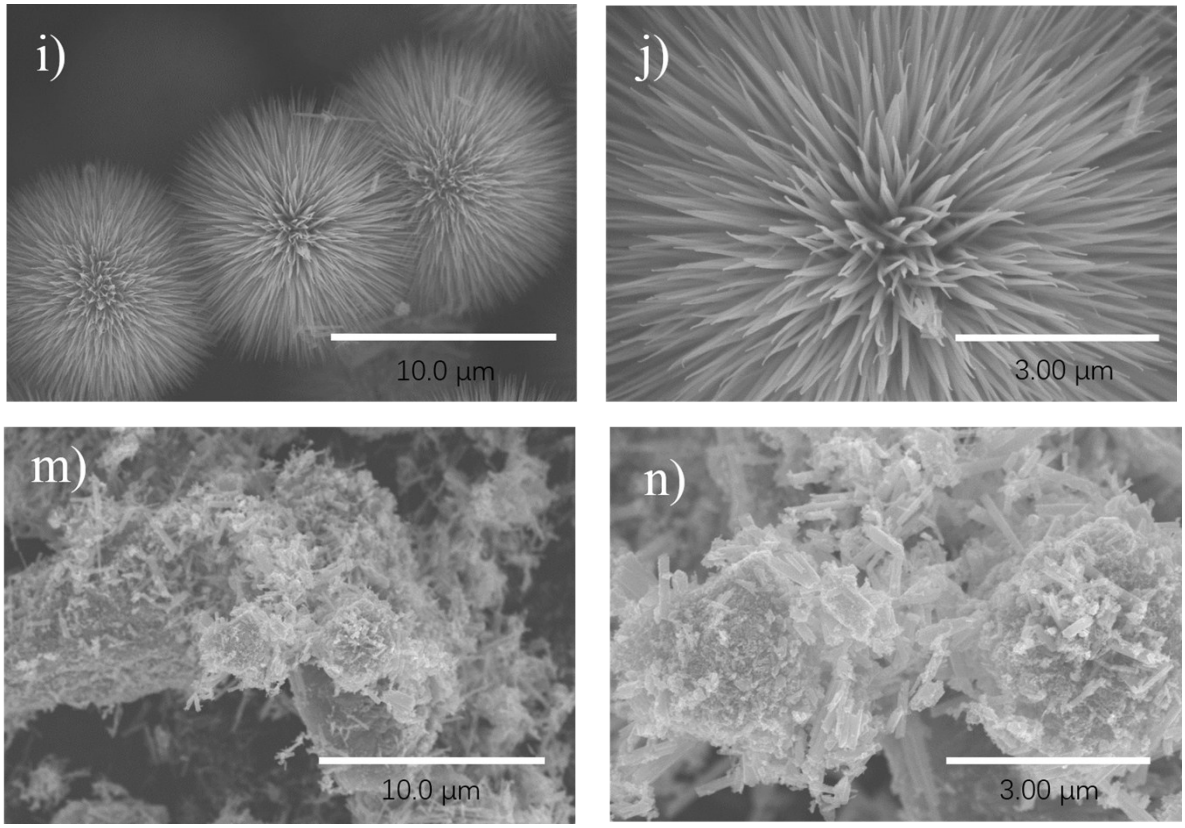


Fig. S1 – Low- and high-magnification SEM images of (a, b) Co_3O_4@Cu foam-300℃-2h, (c, d) Co_3O_4@Cu foam-400℃-2h, (e, f) Co_3O_4@Cu foam-500℃-2h, (g, h) Co_3O_4@Cu foam-300℃-1h, (i, j) Co_3O_4@Cu foam-300℃-4h, and (m, n) Co_3O_4 powder-300℃-2h.

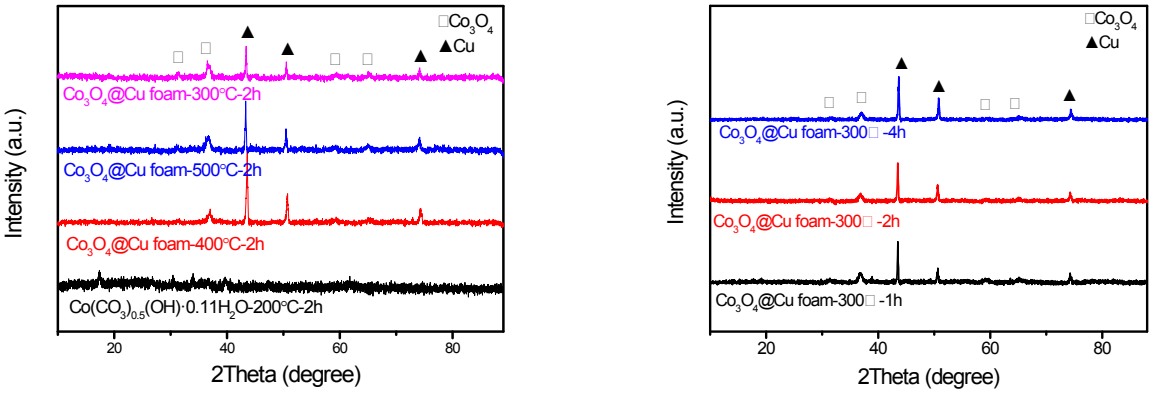


Fig. S2 – XRD patterns of Co_3O_4@Cu foam annealed at different temperatures for different times.

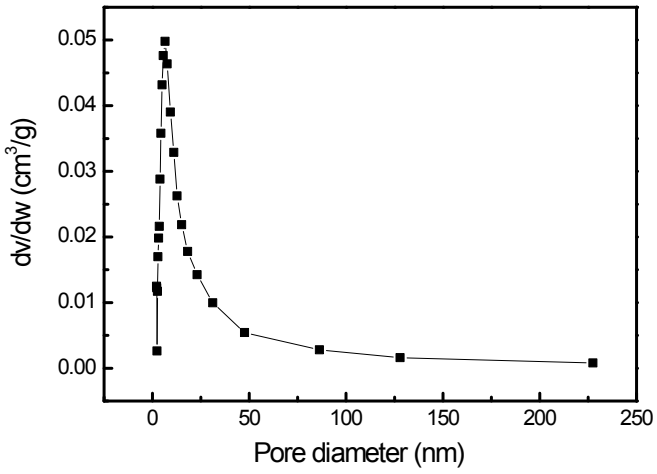


Fig. S3 – BJH pore size distribution of Co_3O_4@Cu foam annealed at 300 °C for 2 h.

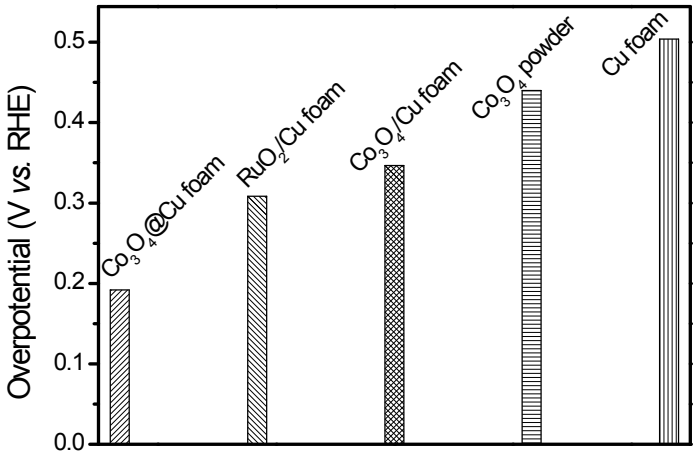


Fig. S4 – Overpotential of Co_3O_4@Cu foam, RuO_2/Cu foam, Co_3O_4/Cu foam, Co_3O_4 powder and Cu foam at 10 mA cm^{-2}.

Table S1 – The OER performances of our Co_3O_4@Cu foam and previously reported, various Co_3O_4-based nanocomposites.

Electrocatalyst	Overpotential (mV) at 10 mA cm^{-2}	Tafel slope ($mV\ dec^{-1}$)	Testing environment	Reference
Co_3O_4@Cu foam	192	42.8	1.0 M KOH	this work
$ZnCo_2O_4$	390	46	1.0 M KOH	1
Co_3O_4/rGO	346	47	1.0 M KOH	2
G-Co_3O_4	313	56	1.0 M KOH	3
Co_3O_4C-NA	290	70	1.0 M KOH	4
Co_3O_4@C-MWCNTs	320	62	1.0 M KOH	5
N-doped Co_3O_4 nanosheets	310	59	1.0 M KOH	6
FeCo-ONS	308	36.8	1.0 M KOH	7
Co_3O_4@Ni foam	230	65	1.0 M KOH	8
Co_3O_4@Ni_3S_2/Ni foam	260	121.7	1.0 M KOH	9
Co_3O_4-C-NA/Ni foam	310	90	1.0 M KOH	10
Co_3O_4/$CoMoO_4$/Ni foam	244	52	1.0 M KOH	11

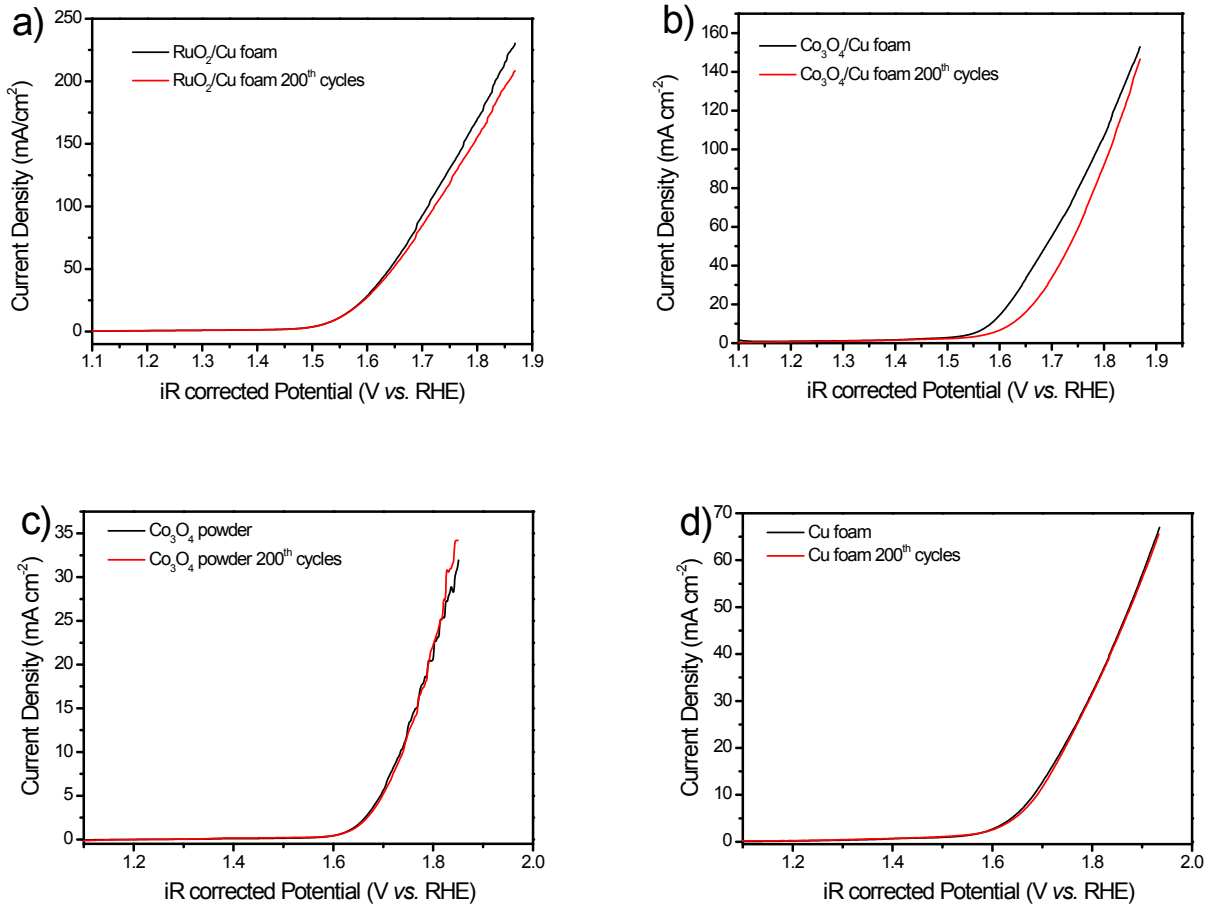


Fig. S5 – LSVs of RuO_2/Cu foam, Co_3O_4/Cu foam, Co_3O_4 powder and Cu foam before and after 200 scans (scan rate = 5.0 mV s^{-1}).

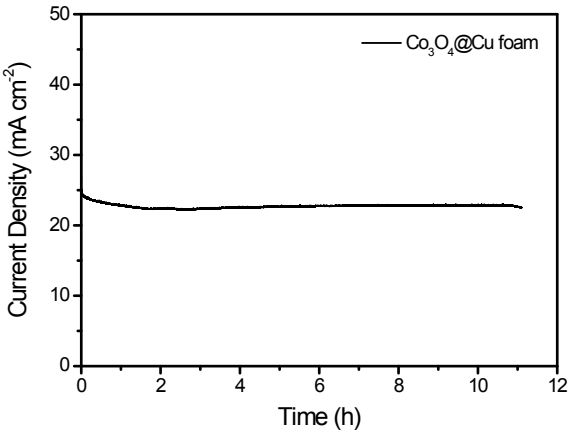


Fig. S6 – Amperometric i-t curve to record long-term durability at the potential of 1.57 V *vs.* RHE for 11 h.

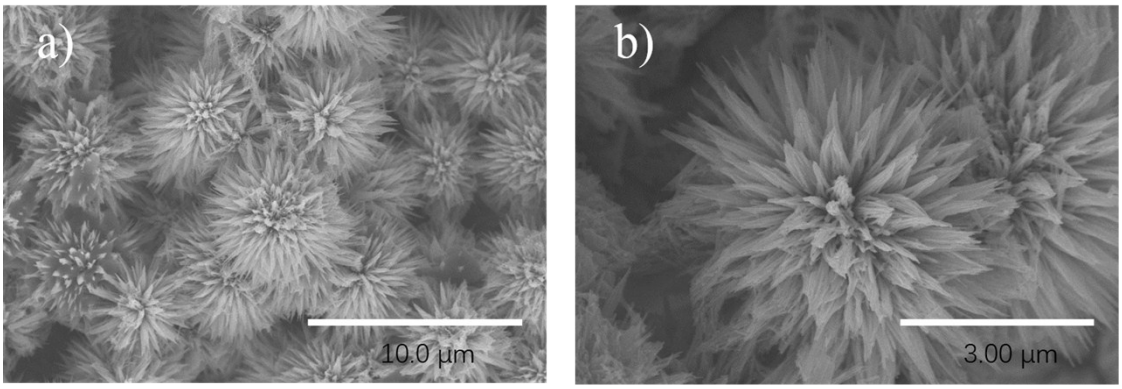


Fig. S7 – (a) Low- and (b) high-magnification SEM images of Co_3O_4@Cu foam after OER tests.

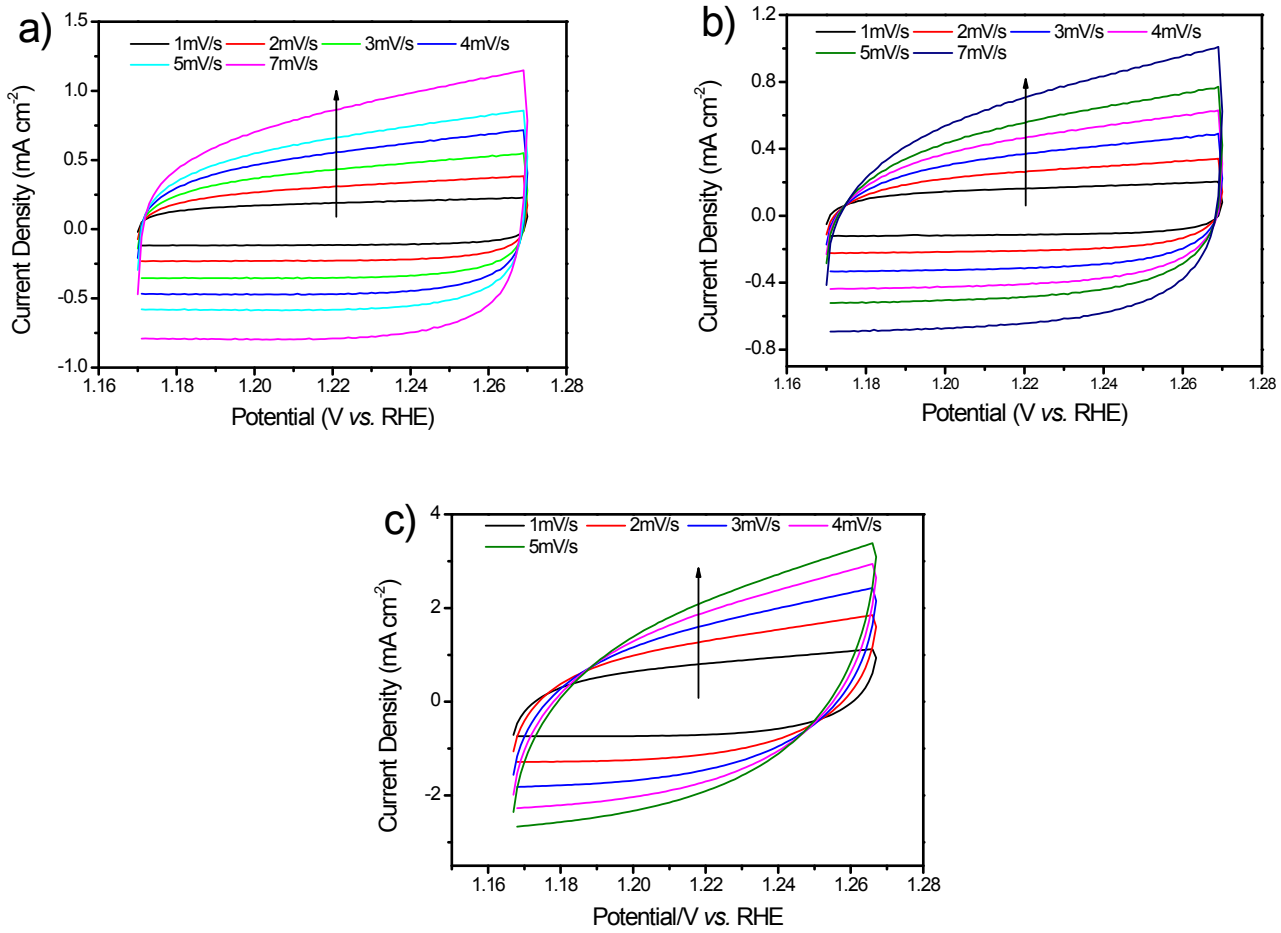


Fig. S8 – EDLC curves of samples with different scan rates. (a) RuO_2/Cu foam, (b) Co_3O_4/Cu foam, and (c) Co_3O_4@Cu foam.

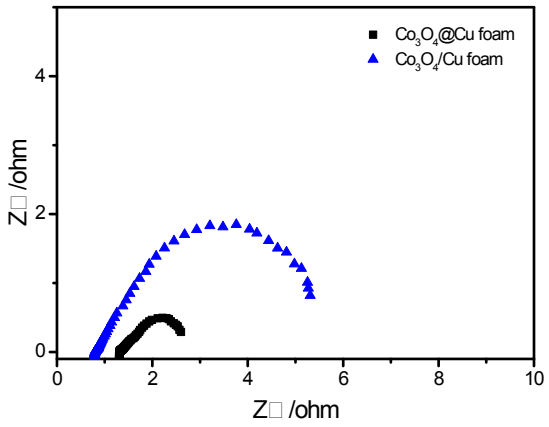


Fig. S9 – Nyquist plots of Co_3O_4@Cu foam and Co_3O_4/Cu foam in 1.0 M KOH.

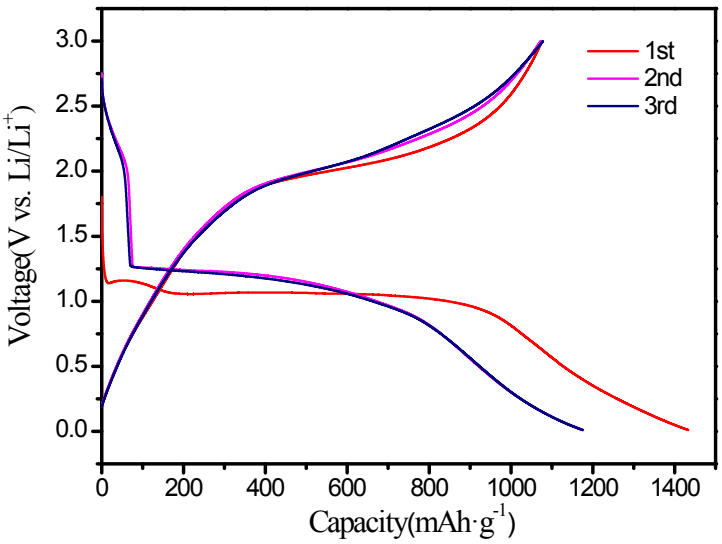


Fig. S10 – Charging–discharging curves of the Co_3O_4@Cu foam electrode at 0.5C.

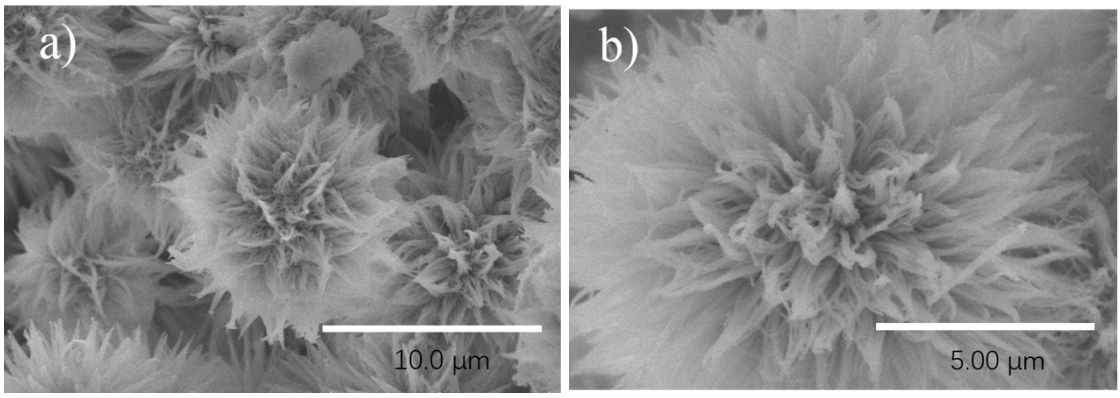


Fig. S11 – (a) Low- and (b) high-magnification SEM images of Co_3O_4@Cu foam after 100 cycles at a current density of 2C.

Table S2 – The cycle and rate performances of our Co_3O_4@Cu foam and previously reported, other Co_3O_4-based composite anodes.

Samples	Specific capacity (mA h g^{-1}) (cycling numbers) (current density)	High rate capacity (mA h g^{-1})	Reference
Co_3O_4@Cu foam	882 (100) (2C)	626 (5C)	this work
Co_3O_4/C	490.5 (50) (0.5C)	676 (2C)	12
Co_3O_4 nanosheets/graphene	851.5 (2000) (2.25C)	509.3 (5.62C)	13
C-doped Co_3O_4 HNFs	1121 (100) (0.22C)	607 (3.4C)	14
N, P-codoped C/ Co_3O_4	927 (100) (0.11C)	454 (1.1C)	15
MWCNTs/ Co_3O_4	813 (100) (0.11C)	514 (1.1C)	16
Co_3O_4/N-PC	1730 (100) (0.11C)	560 (11C)	17
Co_9S_8/C-T	709 (150) (0.22C)	362 (5.6C)	18
Co_3O_4@CNT	862 (60) (0.11C)	408 (5.6C)	19

Supporting References

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