Electronic Supplementary Material (ESI) for ChemComm.

This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information (ESI)

3D Free-standing hierarchical $CuCo_2O_4$ nanowire cathodes for rechargeable lithium-oxygen batteries

Wang Sun,[a] Yan Wang,[a] Haitao Wu,[a] Zhenhua Wang,[a, b] David Rooney, [a, c] Kening Sun [a, b, *]

[a] *Beijing Key Laboratory for Chemical Power Source and Green Catalysis, School of Chemistry and Chemical Engineering, BIT-QUB Joint Center on Novel Energy and Materials Research, Beijing Institute of Technology, Beijing, 100081, People's Republic of China;*

[b] *Collaborative Innovation Center of Electric Vehicles in Beijing, No.5 Zhongguancun South Avenue, Haidian District, Beijing, 100081, People's Republic of China;*

[c] *School of Chemistry and Chemical Engineering, Queen's University, Belfast, Northern Ireland BT9 5AG, United Kingdom;*

[*] *Email：bitkeningsun@163.com.*

Experimental

Materials synthesis

$CuCo_2O_4$@Ni foam (CCO-Ni) was prepared *via* a facile hydrothermal method. In a typical procedure Ni foam was treated in 0.1 M HCl to eliminate the surface oxide layer, and then washed with acetone and ethanol for 30 minutes each. 2 mmol $CoCl_2 \cdot 6H_2O$, 1 mmol $CuCl_2 \cdot 6H_2O$ and 3 mmol ammonium sulfate were dissolved in 50 ml deionized water. After being magnetically stirred for 10 minutes, 40 mmol urea was added in the mixed solution and stirred for another 30 minutes. Then the resulting solution and a cleaned Ni foam were transferred into an 80 ml Teflon-lined stainless steel autoclave. The sealed autoclave was maintained at 120 ^oC for 6 h. After the autoclave was cooled down to ambient temperature, the obtained CCO-Ni and precipitation were flushed with DI water and ethanol, followed by drying at 50 ^oC for 12 h. Finally, the samples were annealed at 400 ^oC in air atmosphere for 3 h.

Materials characterizations

The crystal structure of CCO-Ni and CCO precipitation were characterized by X-ray diffraction (XRD) on a PANalytical X'Pert PRO with Cu Kα radiation. The morphology of CCO-Ni was examined by scanning electron microscopy (SEM, QUANTA FEG 250). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were obtained using a JEOL JEM-2100F. X-ray photoelectron spectroscopy (XPS) was employed by Physical Electronics 5400 ESCA. Brunauer-Emmett-Teller (BET) surface area was performed on a Quantachrome Nova 1200e Surface Area Analyzer. Cyclic voltammetry (CV) was carried out between 2.0 and 4.5 V by a CHI660E electrochemical station.

Electrochemical measurements

Coin-cell-type Li-O_2 batteries (2025 size) were assembled in a glove box filled with Ar. Seven holes (Φ 1.5 mm) are evenly distributed on the cell pans for oxygen access. The CCO-Ni cathode was separated with Li foil by a glass fibre separator (18 mm diameter, Whatman), and the electrolyte was 1.0 M $LiClO_4$ in dimethyl sulfoxide (DMSO). The average mass loading of CCO for the cathodes was approximately 0.5 mg cm^{-2}. The batteries ran in cartridges filled with 1 atm of pure oxygen to avoid CO_2 and H_2O from air at 25 ^oC. Electrochemical tested by LAND-CT2001A.

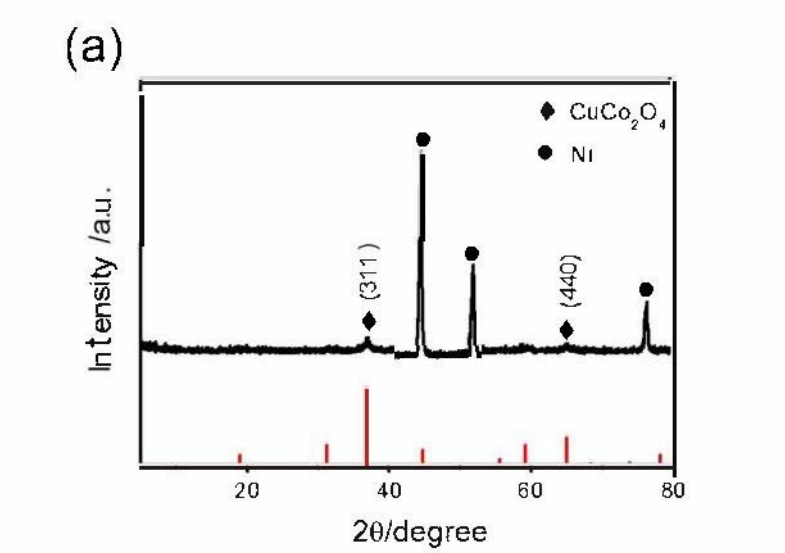

Fig. S1 XRD pattern of CCO-Ni.

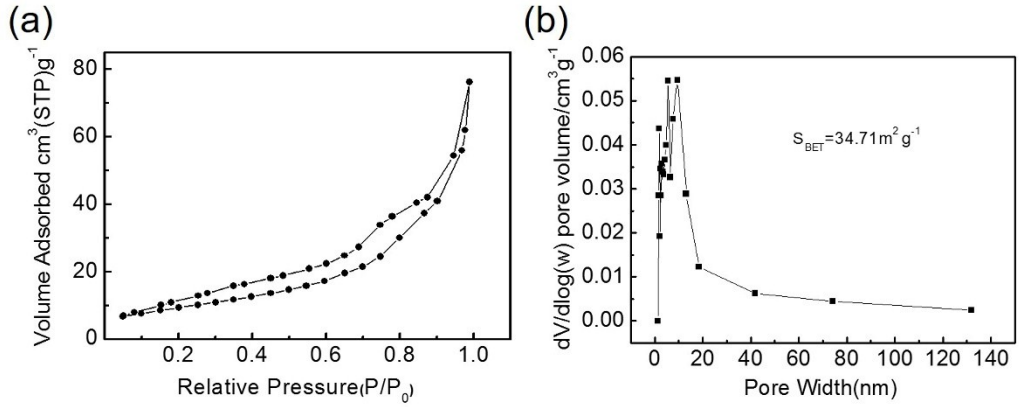

Fig. S2 (a) Nitrogen adsorption-desorption isotherms of CCO-Ni foam and (b) pore size distribution curves of CCO-Ni.

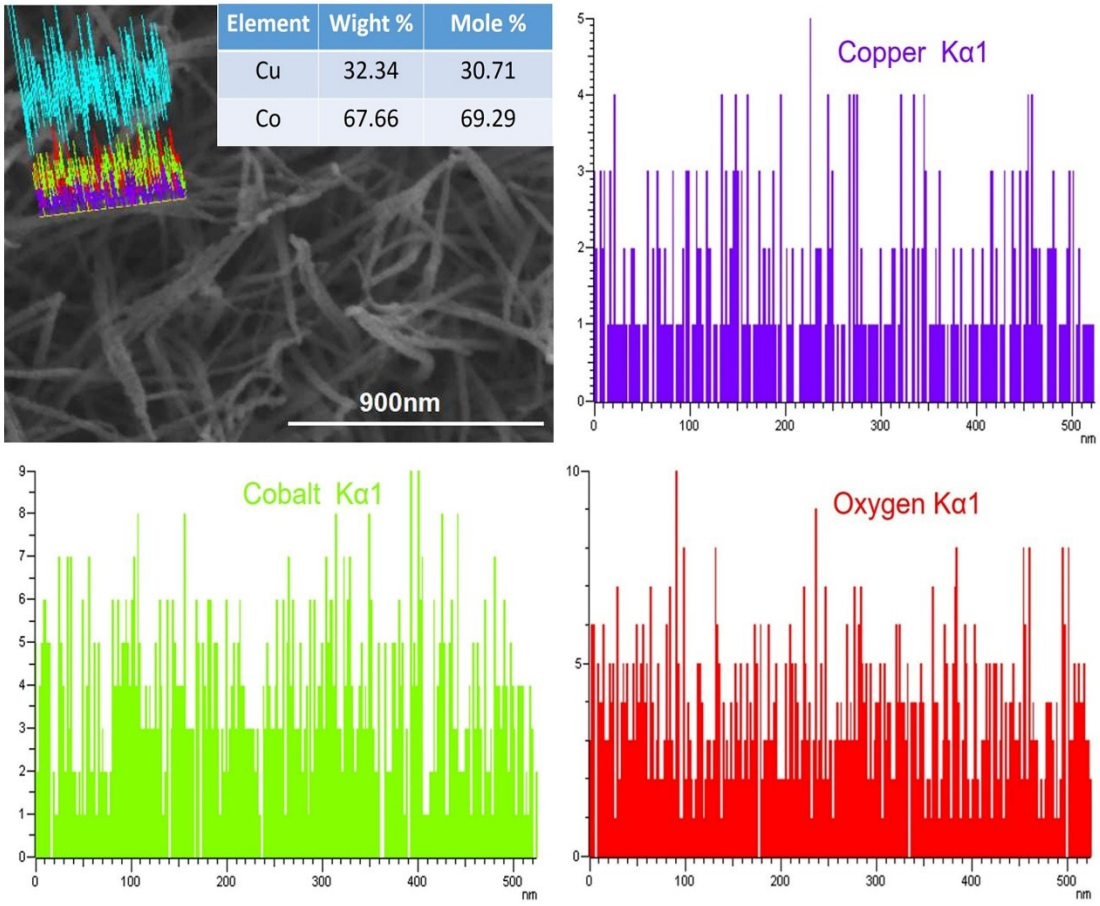

Fig. S3 EDS mapping images of the $CuCo_2O_4$ nanowires on Ni foam.

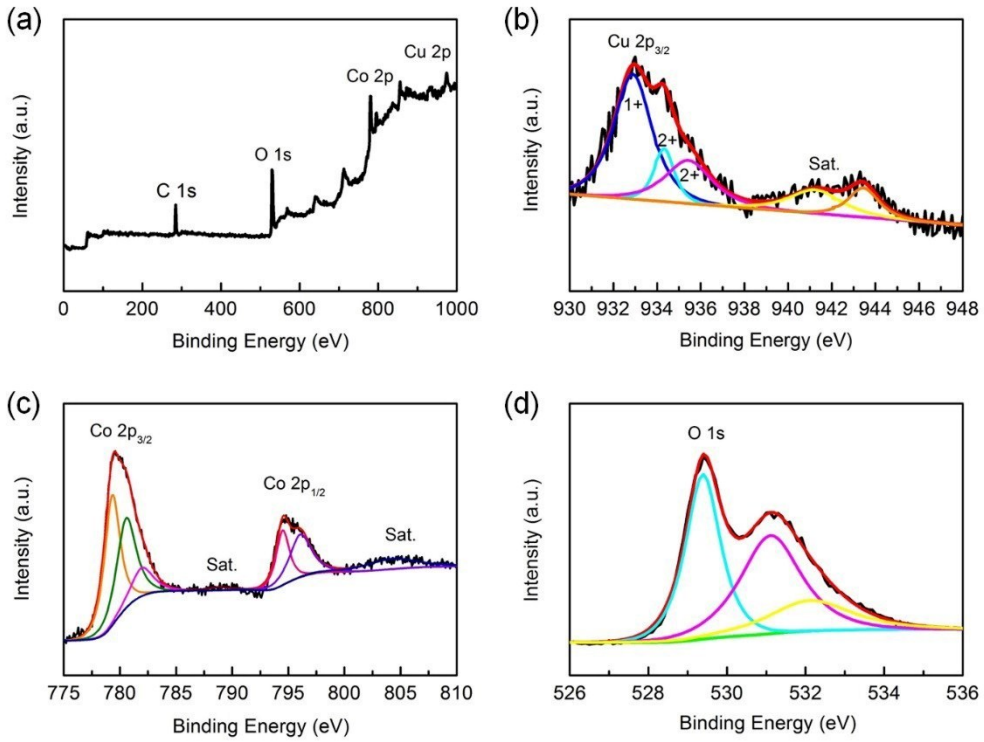

Fig. S4 XPS spectrums of $CuCo_2O_4$: (a) full spectrum, (b) Cu 2p spectrum, (c) Co 2p spectrum and (d) O 1s spectrum.

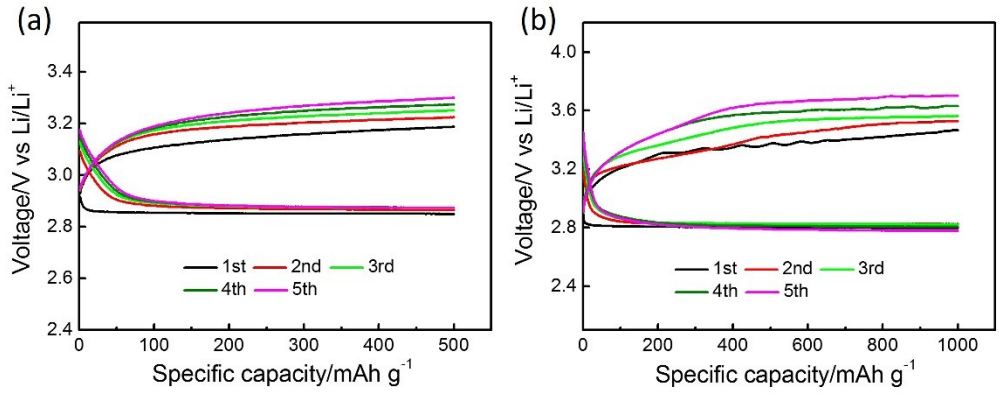

Fig.S5 Discharge-charge profiles of the initial five cycles of the Li-O_2 batteries with CCO-Ni cathodes at a current density of 0.1 mA cm^{-2} with a cut-off capacity of (a) 500 mAh g^{-1} and (b) 1000 mAh g^{-1}.

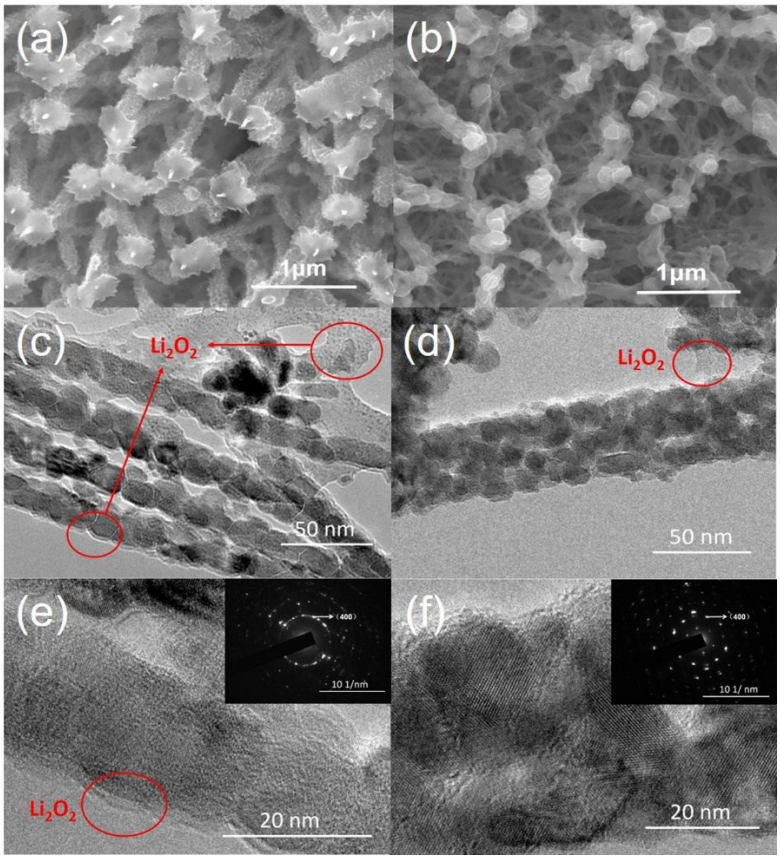

Fig. S6 SEM images of the electrode with CCO-Ni (a) after the first discharge and (b) after first charge; (c) TEM image of the electrode with CCO-Ni after the first discharge at 0.1mA cm^{-2}, and the corresponding (e) HRTEM image and SAED pattern; (d) TEM image of the electrode with CCO-Ni after recharge at 0.1mA cm^{-2}, and the corresponding (f) HRTEM image and SAED pattern.

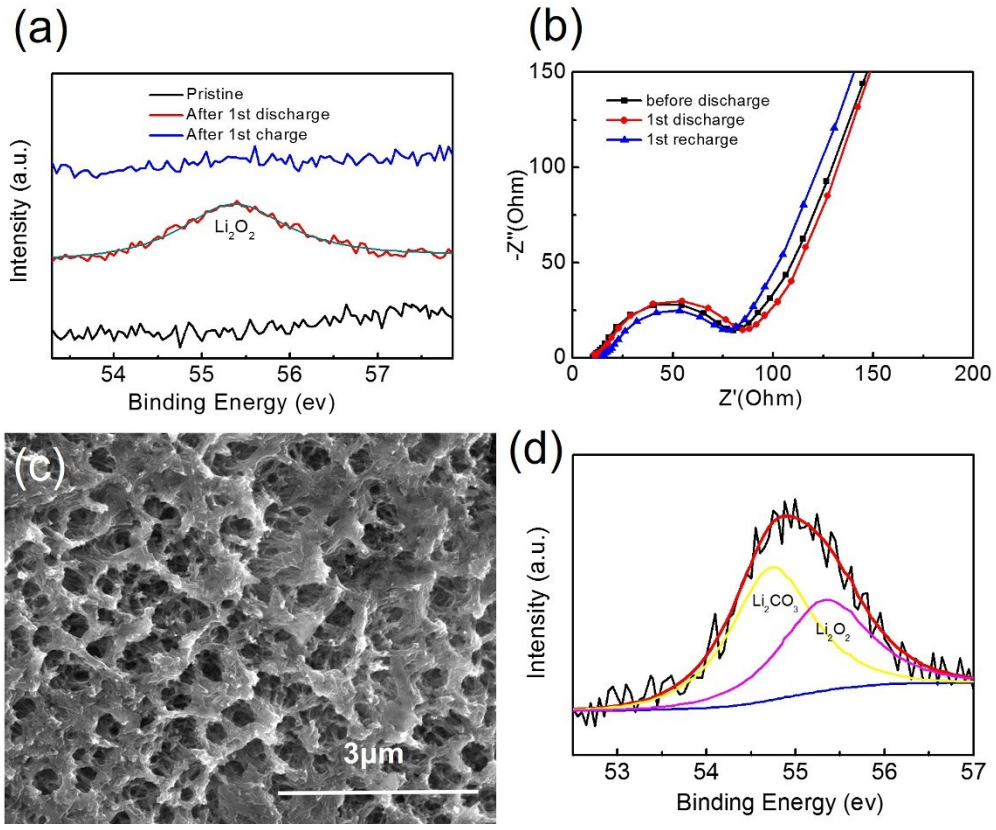

Fig. S7 XPS spectrum of Li 1s and (b) Nyquist plots of batteries with pristine electrode, after first discharge and after recharge; (c) SEM image of the electrode with CCO-Ni after 70 cycles; (d) the corresponding Li 1s XPS spectrum of the electrode with CCO-Ni after 70 cycles.

Table S1 Summary of electrochemical performance of Li-O_2 batteries with $CuCo_2O_4$ based catalysts

Material	Morphology	Specific capacity	Overpotential	Cycle performance	Electrolyte	Ref.
$CuCo_2O_4$	Nanoparticle	50 mA g^{-1} 7962 mAh g^{-1}	0.95	1000 mAh g^{-1} 100 mA g^{-1} 50 cycles	1 M TEGDME/ LiTFSI	17
$CuCo_2O_4$	Mesoporous nanoparticle	100 mA g^{-1} 5288 mAh g^{-1}	1.77	1000 mAh g^{-1} 0.057 mA cm^{-2} 70 cycles	0.5 M LiTFSI/ TEGDME	18
$CuCo_2O_4$	Microspheres	100 mA g^{-1} 7456 mAh g^{-1}	0.76	500 mAh g^{-1} 100 mA g^{-1} 25 cycles	1 M $LiCF_3SO_3$/ TEGDME	19
$CuCo_2O_4$	Microflowers		0.90	1000 mAh g^{-1} 100 mA g^{-1} 120 cycles	1 M LITFSI/ TEGDME	24
$CuCo_2O_4$	Nanowire	0.1 mA cm^{-2} 13654 mAh g^{-1}	0.54	1000 mAh g^{-1} 0.1 mA cm^{-2} 76 cycles	1 M $LiClO_4$/ DMSO	This work