Supplementary Information

Ultrasmall Co$_3$O$_4$ nanoparticles as long-lived high-rate lithium-ion battery anode

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1. Experimental

1.1 Synthesis of the precursor Co-PBA nanoparticles

In a typical procedure, 3 mmol K$_3$Co(CN)$_6$, 5.6 g PVP (K40) and 6 mmol CoCl$_2$·6H$_2$O were dissolved into a mixed solution of 25 mL ethanol and 75 mL deionized water. The obtained pink solution was kept away from light for 24 h after stirred for 2 h. Then it was centrifuged and washed for several times with deionized water and ethanol and finally dried overnight at 100 °C under vacuum.

1.2 Synthesis of the ultrasmall S-Co$_3$O$_4$ nanoparticles

The collected precursor Co-PBAs were crystallized at 360 °C for 1 h at a heating rate of 1 °C min^{-1} under an air atmoparticle.

By the way, the comparison sample C-Co_3O_4 (commercial Co_3O_4) was just purchased from the Internet (Sinopharm Chemical Reagent Co., Ltd., SP).

1.3 Materials characterization

The XRD patterns were recorded on a D8-Advance power diffractometer equipped with a Cu Kα radiation source ($\lambda = 1.54178$ Å). The morphology of these samples was characterized by a field emission scanning electron microscopy (15 kV, JEOL, JSM-6700F) and TEM (JEOL JEM2010). Thermogravimetry (TG) measurement was carried out on a NETZSCH TG 209F1 Libra instrument in air flux at a scan rate of 10 °C min^{-1}. Brunauer–Emmett–Teller (BET) surface areas were measured using Tristar II 3020 instrument by nitrogen adsorption at 77 K. Raman spectra were obtained from a LabRamHR using an argon ion laser with a wavelength of 785 nm. Co K-edge X-ray absorption fine structure (XAFS) was recorded at the 1W2B beamline of the Beijing Synchrotron Radiation Facility (BSRF, Beijing). X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were both analysed by the ATHENA software package. To further obtain the magnitudes of the EXAFS spectra in R-space (Å), the extracted EXAFS signal was Fourier-transformed in k-ranges of 2.4-12.5 Å^{-1} by using a Hanning window function after weighted by k^2. The lengths of actual bond are approximately 0.2-0.4 Å longer because the Fourier-transformed peaks were not phase corrected. The soft X-ray absorption spectroscopy

(s-XAS) of Co L-edge was collected at the BL12B-a (MCD) line station of the Hefei Synchrotron Radiation Facility (HALF). To get the desired electrodes, the coin cells, which were charged or discharged to the desired cut-off voltages, have been disassembled by an electric crimping machine (MTI Co.). Finally, electrodes were washed with dimethyl carbonate (DMC) and sealed by a 3 M sellotape in Ar atmoparticle after drying. The electrodes for XAFS and s-XAS were collected after fully charged or discharged for three or four cycles.

1.4 Electrochemical measurements

The battery tests were carried out in a half-cell configuration. Lithium disc was used as a counter electrode to assemble the CR2032-type coin cells, and all the processes were carried out in a glovebox filled with argon (MBraun, Germany). The working electrode consists of active materials, conductivity agent (Ketjenblack), and polymer binder (polyvinylidene fluoride, PVDF) with a weight ratio of 7:2:1. After mixed fully in N-methyl-2-pyrrolidinone, the obtained slurry was casted on Cu foil and dried at 110°C under vacuum overnight. After drying, slice to obtain circular electrodes with a diameter of 16 mm. The mass loading of the active material was 0.5-1 mg cm^{-2}. The electrolyte was a solution of 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 in weight). Whatman Glass Microfibre Filter (Grade GF/D) were used as separator. The electrochemical performance of the cells was assessed on a Land CT2001A cell test system (Wuhan, China) in the range of 0.01-3 V (vs. Li$^+$/Li). Cyclic voltammetry (CV) was measured from 0.01 to 3 V (vs. Li$^+$/Li) at the scan rate of 0.2

mV s^{-1}. Electrochemical impedance spectroscopy (EIS) testing with an amplitude of 10

mV from 10^5 Hz to 0.01 Hz. EIS and CV were both obtained on a CHI660D (Chenhua,

Shanghai) electrochemical workstation.
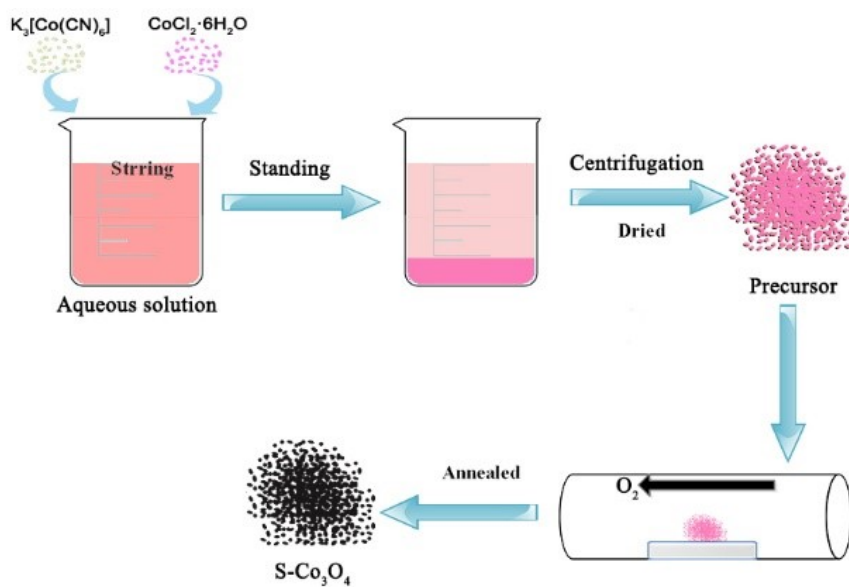
2. Rusults and discussion

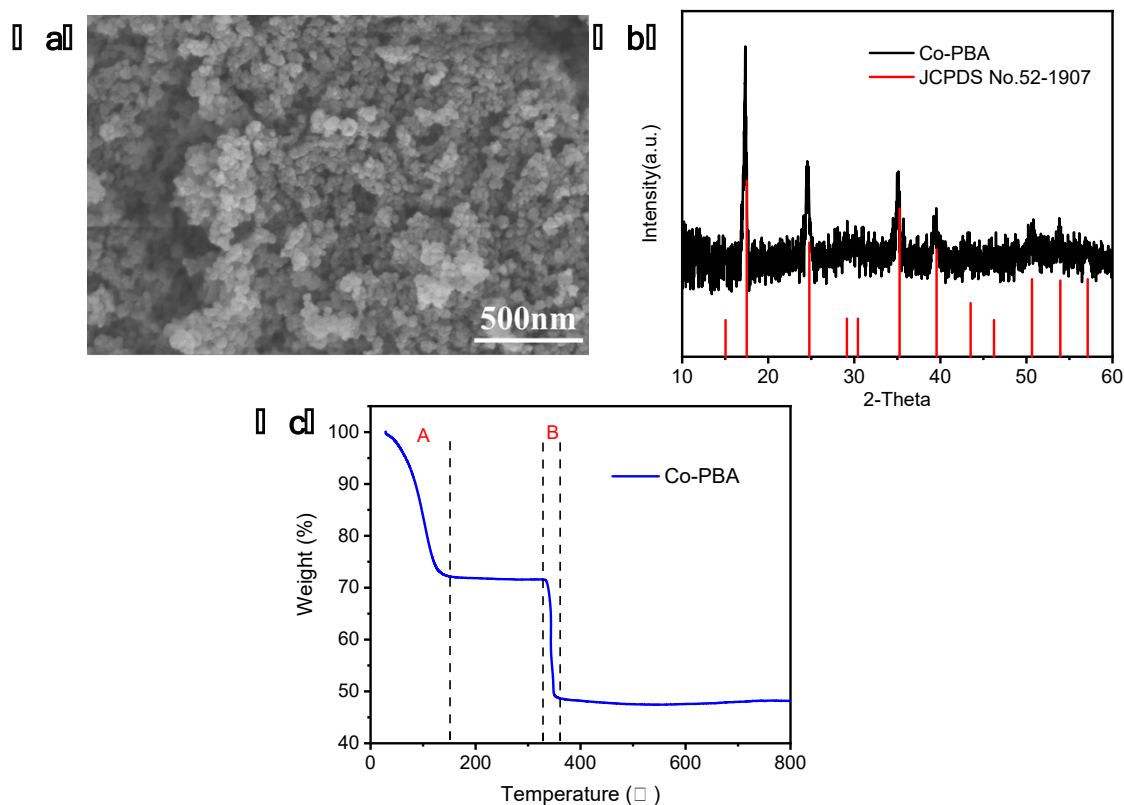**Figure S1.** Diagrammatic sketch of synthesis process for S-Co$_3$O$_4$ spinel sample.

Figure S2. (a) SEM image, (b) XRD pattern and (c) TG curves of the precursor Co-PBA nanoparticles.

As shown in Fig. S2b, Co-based Prussian blue analogues (Co-PBA) can be indexed as a typical face-centered cubic structure (JCPDS no. 52-1907) with no impurity phase. Thermogravimetric (TG) characteristic (Fig. S2c) was employed to determine the optimum calcination temperature of the precursor. With temperature rising, the first mass drop occurs below 160 ℃, corresponding to the loss of the adsorbed and interstitial water. The second drop occurs at 330-355 ℃, corresponding to the phase transition to oxide. At subsequent temperatures up to 800 ℃, the substance stabilizes

as Co_3O_4. Take hint from the TG data, phase-pure Co_3O_4 was successfully prepared by annealing the precursor at 360 ℃.
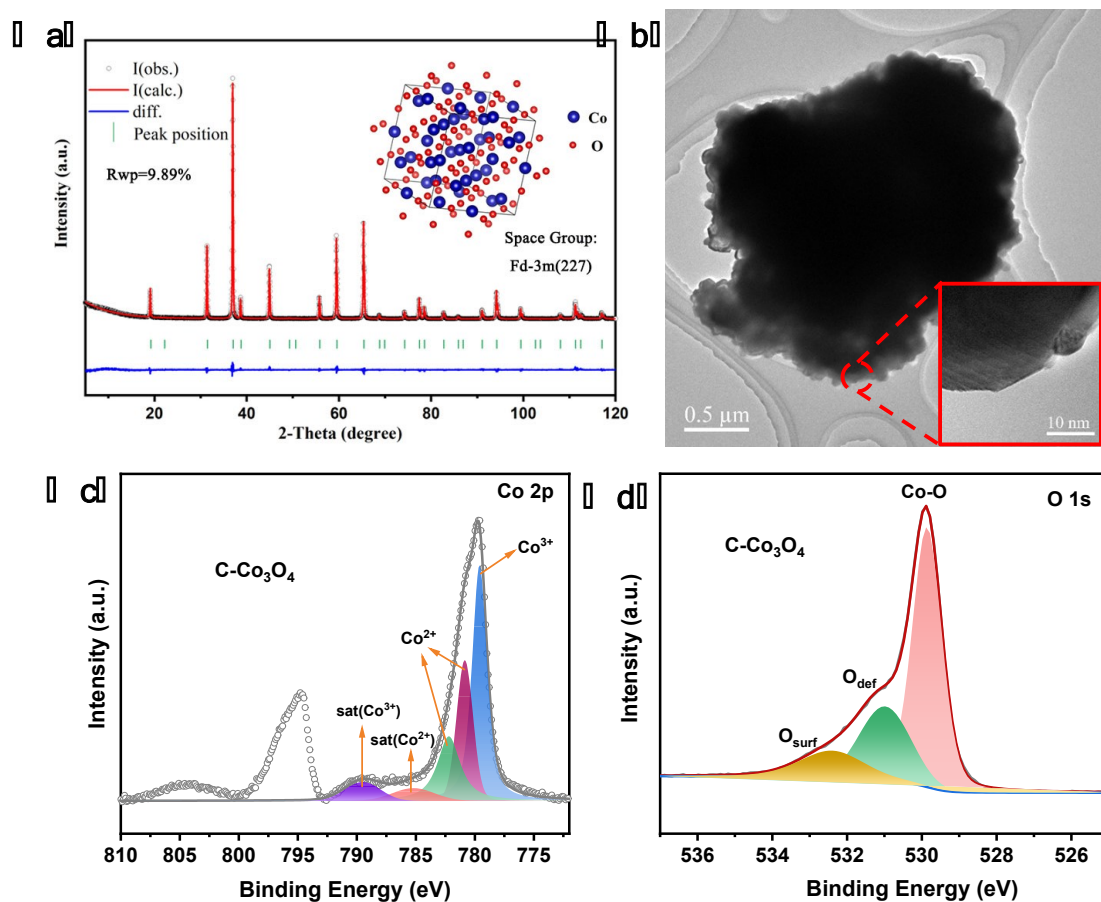

Figure S3. Structural and morphology characterization of the C-Co3O4. (a) Rietveld refinement of the PXRD data (a=b=c=8.066 Å); (b) TEM image and a magnified view; XPS analysis of (c) Co 2p and (b) O 1s.
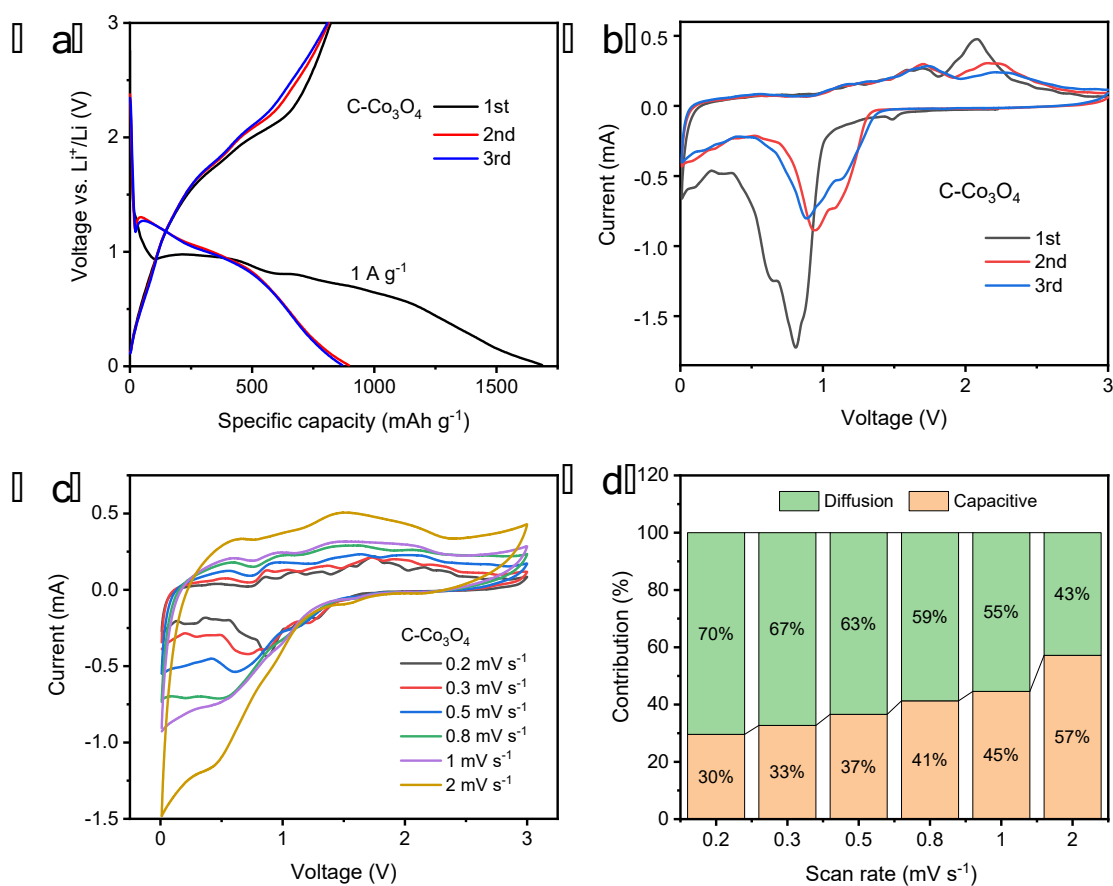
Figure S4. Electrochemical performance and kinetic analysis of C-Co$_3$O$_4$ forlithium storage behavior. (a) Charge/discharge curves at 1 A g^{-1}; (b) CV data at 0.2 mV s^{-1}; (c) CV curves obtained with various scan rates; (d) The calculated contribution ratio of the capacitive and diffusion-controlled capacities at different scan rates.

The electrochemical reactions are summarized as follow:

Discharge: $Co_3O_4 + 8Li^+ + 8e^- \rightarrow 4Li_2O + 3Co$

Charge: $4Li_2O + 3Co \rightarrow Co_3O_4 + 8Li^+ + 8e^-$
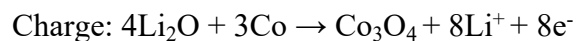
The theoretical capacity of Co$_3$O$_4$ is 890 mAh g^{-1}. The calculation is the following: C=nF/3.6M, where C is the theoretical specific capacity, n is the electron transfer

number (n=8), F is the Faraday constant ($F = 96485\ \text{C mol}^{-1}$), and M is the relative molecular mass ($M=240.8\ \text{g mol}^{-1}$).
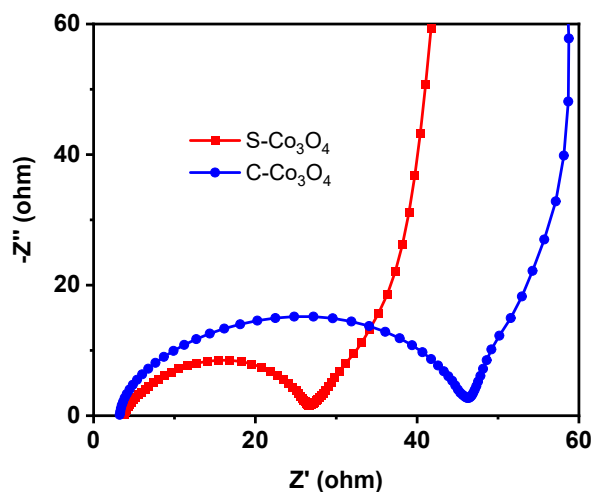

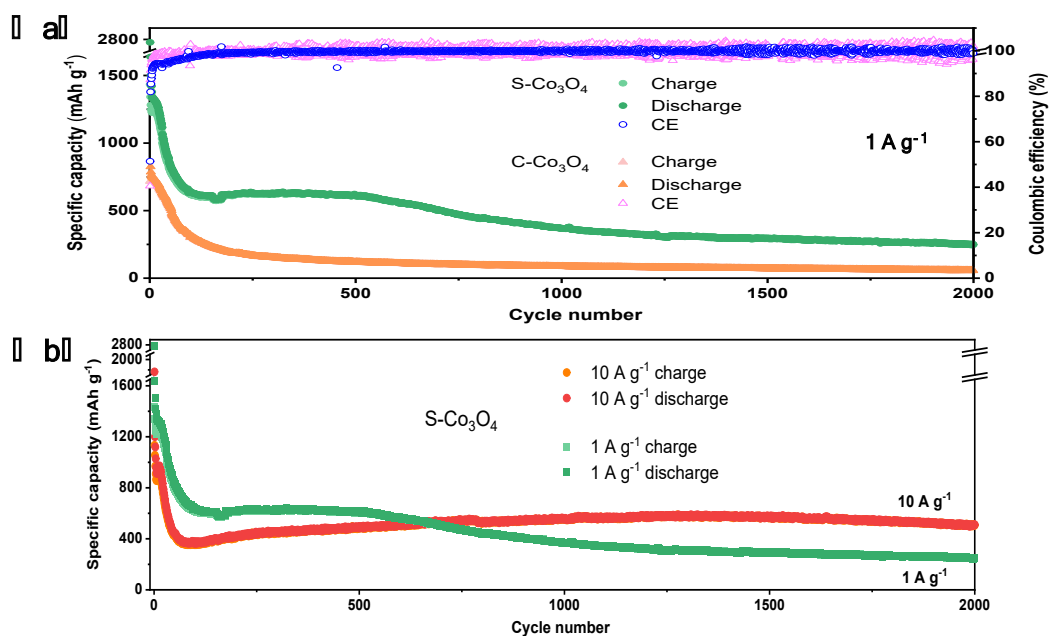**Figure S5.** The impedance spectra of S-Co$_3$O$_4$ anode and C-Co$_3$O$_4$ anode .

Figure S6. (a) Cycling performance at 1 A g^{-1} of both S-Co_3O_4 and C-Co_3O_4; (b)

Cycling performance of S-Co_3O_4 at 10 A g^{-1} and 1 A g^{-1}.

As for the performance at 1 A g^{-1} in Fig. S6a, for S-Co_3O_4 electrode, a splendid

electrochemical performance could also be found until the 510th cycle with over 610

mAh g^{-1} capacity. Then the capacity started to decline, and finally exhibited 249.7 mAh

g^{-1} at the 2000th cycle. The capacity of C-Co_3O_4 is evidently worse than that of S-Co_3O_4,

which is also because that the large micro size brought less active sites and more serious

structure collapse. Additionally, the steady capacity for S-Co_3O_4 electrode at 10 A g^{-1}

at the 2000th cycle (511.2 mAh g^{-1}) is amazingly superior than that at 1 A g^{-1} at the same

cycle (249.7 mAh g^{-1}, Fig. S6b), which may be the result of different distribution of

components in SEI at different current densities (Fig. S10), verify the superiority of the
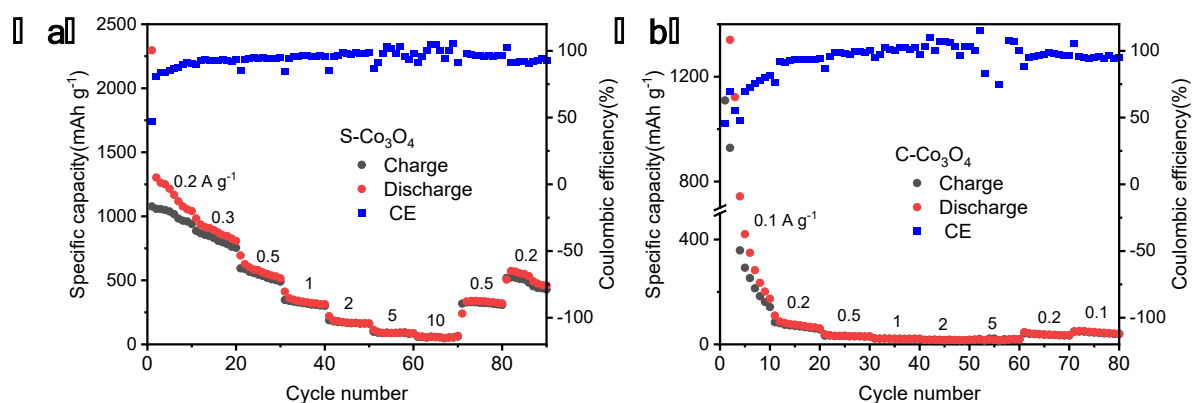
long-cycle high-rate application of S-Co_3O_4.

Figure S7. Rate performance of (a) S-Co_3O_4 and (b) C-Co_3O_4.

The rate performance of the S-Co_3O_4 electrode is measured at 0.2, 0.3, 0.5, 1, 2, 5, 10, 0.5 and 0.2 A g^{-1} every ten cycles (Fig. S7a†), and the reversible capacities are 1303.0, 936.4, 626.6, 360.1, 186.9, 98.7, 61.1, 334.7 and 572.4 mAh g^{-1}, respectively. As for the C-Co_3O_4 electrode, it presents a reversible capacity of 1121.9, 87.5, 35.1, 22.2, 16.1, 18.1, 42.3 and 51.1 mAh g^{-1} at the current of 0.1, 0.2, 0.5, 1, 2, 5, 0.2 and 0.1 A g^{-1}, respectively.
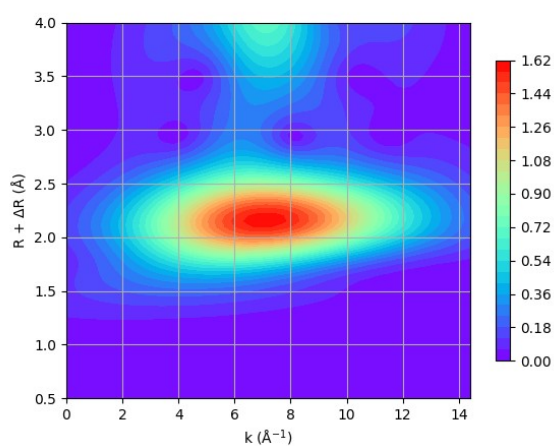

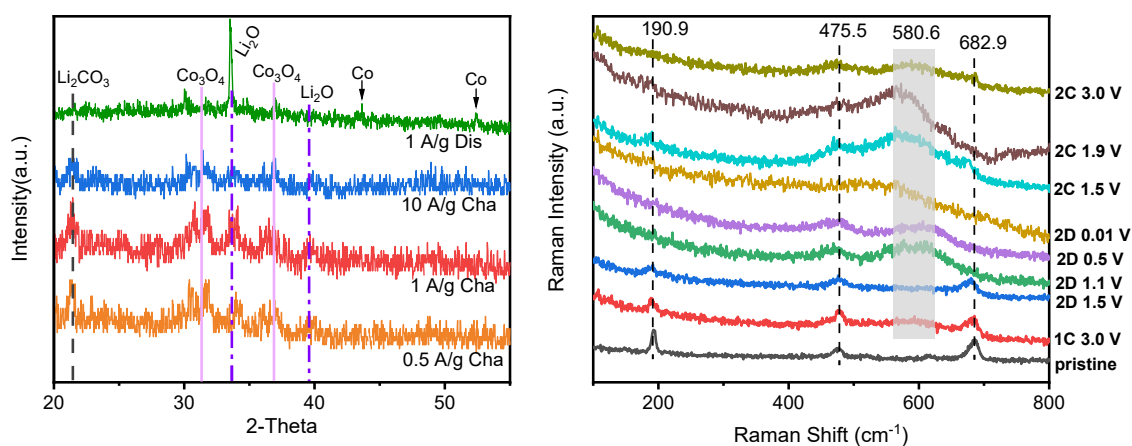**Figure S8.** WT contour plots of Co-foil.

Figure S9. (a) Ex situ XRD patterns of S-Co_3O_4 electrodes collected after fully discharged and fully charged after 10 cycles at different current densities; (b) Ex situ Raman spectra of S-Co_3O_4 electrodes collected during the first and the second diacharge/charge process.

For ex situ XRD, the fully charged electrodes at different current density are mainly Co_3O_4 accompanied by little residual Li_2O and Li_2CO_3 in SEI layer, while the fully discharged electrode is mainly Co metal and Li_2O. For ex situ Raman, 1C, 2D and 2C denote the first charge, the second discharge and the second charge, respectively. The peaks located at 190.9, 475.8 and 682.9 cm^{-1} are related to Co_3O_4, and the appearance of the broad peak at around 580.6 cm^{-1} is due to Li_2O and the homogeneous phase $Li_xCo_3O_4$.[1]
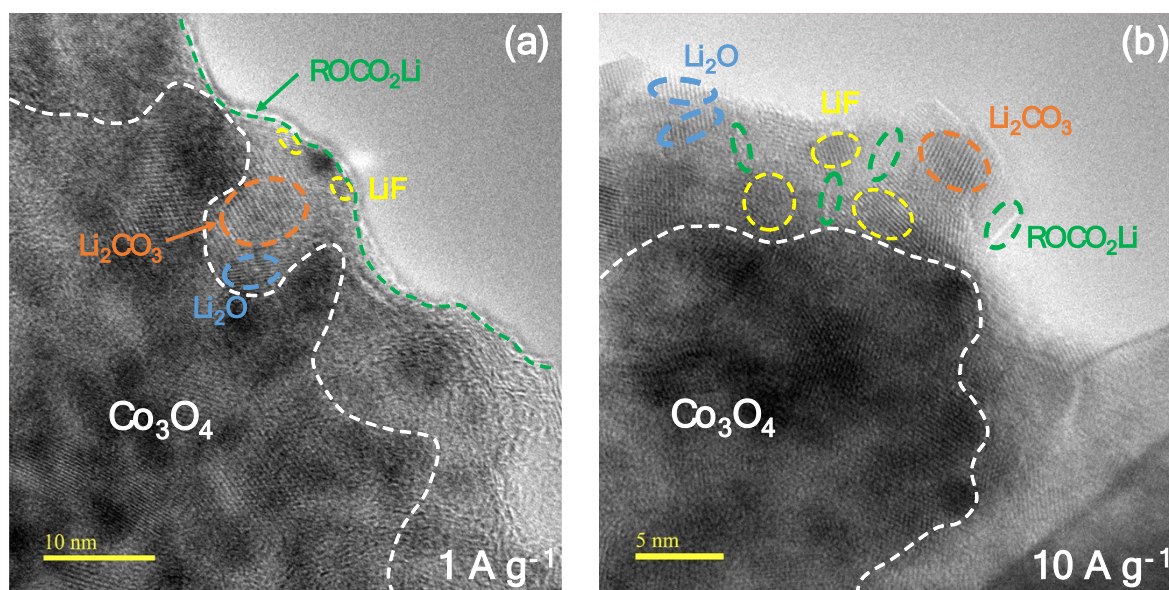

Figure S10. HRTEM images of SEI of fully oxidized S-Co_3O_4 after 10 cycles at (a) 1 A g^{-1} and (b) 10 A g^{-1}. The LiF (yellow dotted line) lattice spacing corresponding to (111) is ~0.23 nm, the Li_2CO_3 (orange dotted line) lattice spacing corresponding to (-

110) is ~0.42 nm, (-112) is ~0.26 nm, and the Li_2O (blue dotted line) lattice spacing corresponding to (111) is ~0.27 nm. The green dotted line represents the organic component $ROCO_2Li$ (OC = O) in the SEI.

The mosaic SEI was composed of randomly distributed organic and inorganic components at 10 A g^{-1}, which the organic component ($ROCO_2Li$) was an outer layer and the inorganic component was wrapped in an inner layer at 1 A g^{-1}. The layered configuration at 1 A g^{-1} led to the poor flexibility of the SEI and the unsatisfactory stability of the LIB for long cycle. On the contrary, the random distribution of $ROCO_2Li$ in the mosaic SEI at 10 A g^{-1} could enhance the flexibility of the SEI, accelerate the Li$^+$ transport and maintain good stability of the LIB.[2]
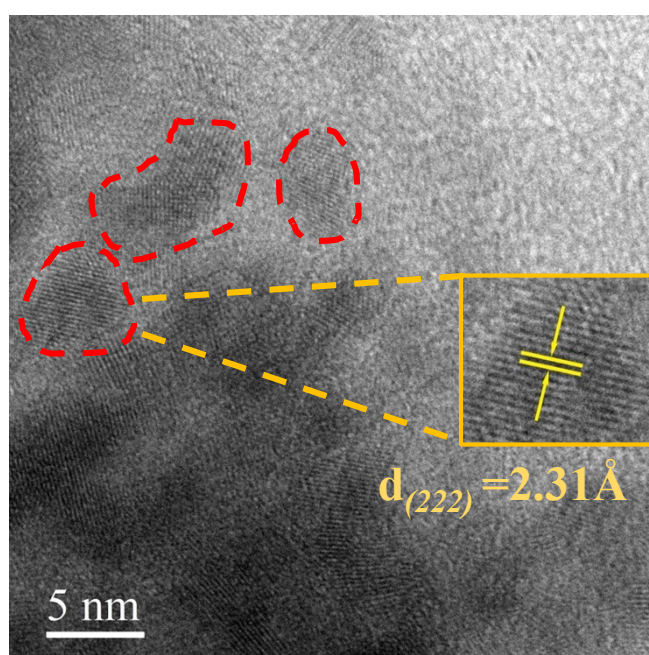

Figure S11. HRTEM image of the S-Co_3O_4 electrode after 2000 cycles at 10 A g^{-1}.
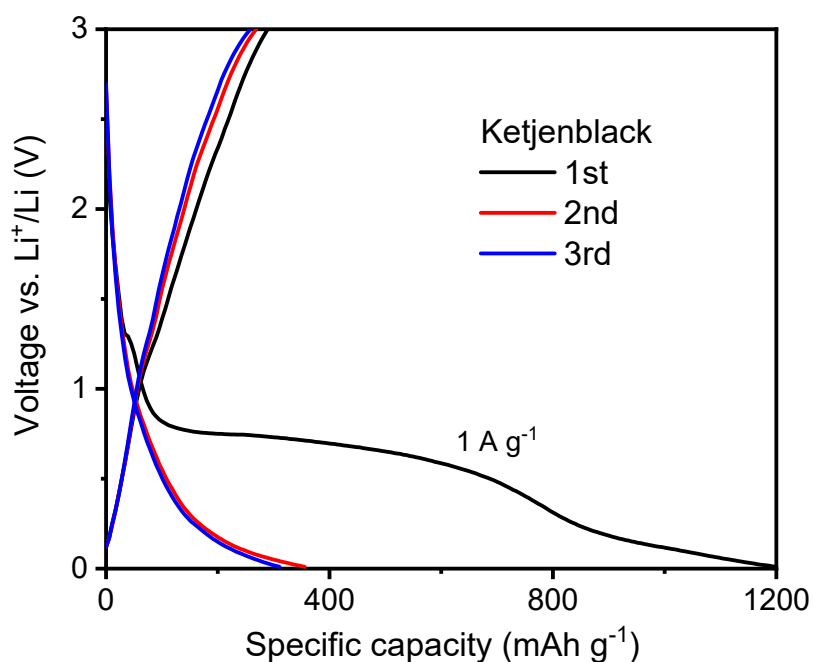
Figure S12. The initial three charge/discharge curves at a current density of 1 A g^{-1}

for Ketjenblack.

Ketjenblack and PVDF were mixed fully with a weight ratio of 9:1. Then made and

tested in the same way as Co_3O_4. The first discharge and charge specific capacities of

Ketjenblack are 1200.0 mAh g^{-1} and 289.6 mAh g^{-1}.

Table S1. Performances of recently reported LIBs (half-cell) based on Co_3O_4.

Co_3O_4	Voltage, V (*vs.* Li$^+$/Li)	Capacity, mAh g^{-1}	Cycling stability, [a] mAh g^{-1}	Refs.
RGO-Co_3O_4 PNR Co_3O_4 PNR	0.01-3	1118 @ 0.2 A g^{-1} 1049 @ 0.2 A g^{-1}	1118 @ 200th @ 0.5 A g^{-1} 526 @ 200th @ 0.5 A g^{-1}	3
Co3O4@NGFs	0.01-3	766.4 @ 0.1 A g^{-1}	408.4 @ 600th @ 2 A g^{-1}	4
H-Co3O4@IEH-Graphene	0.01-3	777 @ 0.2 A g^{-1}	1015 @ 250th @ 0.2 A g^{-1}	5

Co3O4 nanotubes	0.01-3	500 @ 0.05 A g^{-1}	500 @ 100th @ 0.48 A g^{-1}	6
Co3O4/graphene	0.01-3	800 @ 0.05 A g^{-1}	935 @ 30th @ 0.05 A g^{-1}	7
Needle-like Co3O4 nanotubes	0.01-3	918 @ 0.05 A g^{-1}	380 @ 80th @ 0.05 A g^{-1}	8
Co3O4NW arrays	0.01-3	700 @ 0.11 A g^{-1}	450 @ 20th @ 20 C 240 @ 20th @ 50 C	9
C-doped Co3O4 HNTs	0.01-3	950 @ 0.5 A g^{-1}	950 @ 300th @ 0.5 A g^{-1}	10
ZnO-Co3O4@CC	0.01-3	1785 @ 0.2 A g^{-1}	533.6 @ 400th @ 1 A g^{-1} 447.8 @ 400th @ 2 A g^{-1}	11
HNc-Co3O4	0.01-3	1053 @ 0.1 mA cm^{-1}	~600 @ 100th @ 0.1 mA cm^{-1}	2
Co3O4(1000)	0.01-3	~650 @ 1 A g^{-1}	1100 @ 150th @ 1 A g^{-1}	12
Co3O4	0.01-3	~1200 @ 1 A g^{-1}	927 @ 850th @ 1 A g^{-1}	13
S-Co3O4	0.01-3	**1686.7 @ 0.1 A g-1**	**511.2 @ 2000th @ 10 A g-1**	**This work**

[a] (Cycling stability is expressed as the energy storage capacity retention after several charging/discharging cycles at a specific rate).

Table S2. Performances of recently reported LIBs (half-cell) based on different types of anode materials.

Types	Materials	Voltage, V (vs. Li$^+$/Li)	Capacity, mAh g^{-1}	Cycling stability, [b] (capacity, rate, retention%)	Refs.
Oxides	Fe$_3$O$_4$-α-Fe$_2$O$_3$	0.005-3	1100 (0.1 A g^{-1})	40 (1067, 0.1 A g^{-1}, 97%)	14
	γ-Fe$_2$O$_3$ extracted from red mud	0.005-3	697 (0.15 A g^{-1})	60 (5433, 0.15 A g^{-1}, 78%)	15
	Fe$_3$O$_4$–HPGN	0.005-3	1002 (0.1 A g^{-1})	25 (900, 0.1 A g^{-1}, ~90%)	16

Category	Material	Voltage range (V)	Capacity (mAh g⁻¹)	Cycling stability	Ref.
	SnO_2-TRG	0.005-2.5	1021 (0.1 A g⁻¹)	100 (777, 0.5 A g⁻¹, 66%)	17
	SCM-TiO_2	1-3	220 (0.15 A g⁻¹)	250 (150, 0.15 A g⁻¹, 68%)	18
	$CuCo_2O_4$ nano wall	0.01-3	836 (1.25C)	120 (550, 0.375C, 61%)	19
	MOF-derived CuO	0.01-3	535 (0.1 A g⁻¹)	40 (481, 0.1 A g⁻¹, 90%)	20
Sulfides	Cu_3SnS_4	0.01-3	1082 (0.2 A g⁻¹)	950 (890, 0.5 A g⁻¹, 76%,)	21
	SnS_2-RGO-SnS_2 layer by layer	0.01-3	1404 (0.1 A g⁻¹)	200 (1357, 0.1 A g⁻¹, 97%) (909, 0.5 A g⁻¹, 90%)	22
Carbides	Fe_3SnC@CNF	0.01-3	573 (0.2 A g⁻¹)	1000 (500, 0.2 and 1 A g⁻¹, 96%)	23
	VC@C	0.01-3	640 (0.1 A g⁻¹)	1000 (440, 0.1 and 1 A g⁻¹, 82%)	24
	MXene	0.01-3	350 (0.1 A g⁻¹)	1000 (330, 0.1 A g⁻¹, 94%)	25
	PMo_{12}@PPy/$Ti_3C_2T_x$	0.01-3	395 (0.1 A g⁻¹)	300 (764, 0.1 A g⁻¹, 254%) 2000 (170, 3 A g⁻¹, ~340%)	26
Metal–organic framework (MOF)	Cu-BDC	0.01-2.5	194 (0.48 A g⁻¹)	50 (161, 0.48 A g⁻¹, 83%)	27
	Mn-BTC	0.01-2	694 (0.103 A g⁻¹)	100 (576, 0.103 A g⁻¹, 83%) (~400, 1 A g⁻¹, ~90%)	28
	Co-MOF (BDC)	0.01-3	1564 (0.1 A g⁻¹)	700 (601, 0.1 and 0.5 A g⁻¹, ~67%) 1000 (435, 0.1 and 1 A g⁻¹, 76%)	29
	dual ligand Fe-MOF (DMA cation)	0.01-3	600 (0.25 A g⁻¹)	100 (825, 0.25 A g⁻¹, 137%) 1100 (~460, 1 and 2 A g⁻¹, 99%)	30
Covalent-organic framework (COF)	Tp-Azo COF	0.01-3	623 (0.1 A g⁻¹)	3000 (306, 1 A g⁻¹, 100%)	31
	IISERP-CON	0.01-3	720 (0.1 A g⁻¹)	1000 (~580, 0.5 A g⁻¹, 98%)	32

	$CH_3NH_3PbBr_3$	0.01-2	332 (0.2 A g^{-1})	200 (121, 0.2 A g^{-1}, 36%)	33
	1D-benzidine lead iodide	0.01-2.5	646 (0.1 A g^{-1})	50 (585, 0.1 A g^{-1}, 91%)	34
Hybrid perovskite	iodo bismuthate				35
	I. ADB (1D)	0.01-2.5	520 (0.1 A g^{-1})	250 (~530, 0.1 A g^{-1}, ~62%)	
	II. IMB (0D)	0.01-2.5	450 (0.1 A g^{-1})	250 (~400, 0.1 A g^{-1}, ~77%)	
	III. ATB (1D)	0.01-2.5	230 (0.1 A g^{-1})	250 (~220, 0.1 A g^{-1}, ~44%)	
This work	**S-Co$_3$O$_4$**	**0.01-3**	**1686.7 @ 0.1 A g^{-1}**	**2000 (511.2, 10 A g^{-1}, 45%)**	

[b] Cycling stability is expressed as the energy storage capacity retention and corresponding retention percentage after several charging/discharging cycles at a specific rate.

E. g:

"200 (121, 0.2 A g^{-1}, 36%)" means that the cell can cycle to 200th at 0.2 A g^{-1}, with a 36% capacity retention of 121 mAh g^{-1}.

"1000 (435, 0.1 and 1 A g^{-1}, 76%)" means that the cell can cycle to 1000th at 1 A g^{-1} after activation at 0.1 A g^{-1} for several cycles, with a 76% capacity retention of 435 mAh g^{-1}.

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