Supplementary Information

Co₃O₄ Nanoneedle Array as a Multifunctional "Super-reservoir" Electrode for Long Cycle Life

Li-S Batteries

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Experimental Section

Acid treatment of carbon cloth: Carbon cloth (W0S1002, CeTech Co., Taichung, Taiwan) was ultrasonically cleaned with deionized (DI) water and ethanol for 15 min, respectively. Then it was put into 8 M HNO₃ solution and refluxed at 90 °C for 8 h to produce acid treated carbon cloth.^{S1}

Preparation of the Li₂S₈ electrolyte: The active material was introduced into the electrolyte in the form of Li_2S_8 . The Li_2S_8 electrolyte (0.2 M) was prepared by dissolving stoichiometric amounts of Li_2S (195 mg) and sulfur (945 mg), lithium bis(trifluoromethanesulfone) imide (LiTFSI, 1 M) and

LiNO₃ (1 wt %) in a mixture (21 mL) of 1,3-dioxolane/1,2-dimethoxy-ethane (DOL/DME) with a volume ratio of $1:1.^{S2}$

Disassembly of the batteries: The $CC@Co_3O_4$ electrodes in different cycling voltages were disassembled and washed with of DOL/DME for 3 times in a glove box. The extracts were combined. The washed electrodes were placed in a glove box for 3 days to dry.



Fig. S1 SEM images of the CC@Co-precursor.



Fig. S2 (a) The N_2 adsorption-desorption isotherm and (b) the pore size distribution of the $CC@Co_3O_4$.



Fig. S3 Galvanostatic charge-discharge profiles of the CC@Co₃O₄ reservoir at 0.5 C.



Fig. S4 Cycling performance of the CC reservoir at 0.5 C.



Fig. S5 Digital photographs of Li_2S_8 solution treated with (a) $CC@Co_3O_4$, (b) $CC@Co_3O_4$ -1 and (c) CC.



Fig. S6 UV-Vis spectra of the CC@Co₃O₄ extracts in different charge/discharge voltages of the first cycle at 0.5 C.



Fig. S7 Digital photos of the CC@Co₃O₄ extracts in different charge/discharge voltages of the first cycle at 0.5 C.



Fig. S8 SEM images of the (a) as-prepared CC@Co₃O₄-1. (b, c) CC@Co₃O₄-1 in fully discharged state of the first cycle at 0.5 C. (d) CC in fully charged state of the first cycle at 0.5 C.



Fig. S9 (a) XPS survey of the CC@Co₃O₄ and (b) XPS spectra of S 2p in fully discharged state of the first cycle at 0.5 C.



Fig. S10 EIS spectra and corresponding equivalent circuit of the CC and CC@Co₃O₄ after 300 cycles at 0.5 C.



Fig. S11 EIS spectra of the (a) CC and (b) CC@Co₃O₄ electrodes before cycling.



Fig. S12 Arrhenius plots for the reaction rate of (a) CC and (b) $CC@Co_3O_4$ as super reservoir for Li–S batteries.

The Arrhenius plots for CC and CC@Co₃O₄ give linear plots with negative slopes of -27.245 and -10.561, respectively. The activation energy is calculated by:

$$slope = -\frac{E_a}{R}$$
$$E_a = -slope \times R$$

where E_a (kJ mol⁻¹) represents the activation energy, R is the ideal gas law constant (8.314 J mol⁻¹ K⁻¹). Therefore, the reaction activation energies for CC and CC@Co₃O₄ are respectively 226.5 and 87.5 kJ mol⁻¹ S^{5-S8}, which indicates that the activation energy of the electrochemical transformation of active material could be greatly reduced due to the catalytic effect of Co₃O₄ for Li–S batteries."



Fig. S13 (a, c, e, g) SEM images of the CC@Co₃O₄ super reservoirs in fully discharged states of the 100^{th} , 200^{th} , 300^{th} and 500^{th} cycles and (b, d, f, h) in fully charged states of the 100^{th} , 200^{th} , 300^{th} and 500^{th} cycles.

Cathode	S loading (mg)	Rate (C)	Cycle	Capacity (mAh g ⁻¹)	Ref.
CC@Co ₃ O ₄	4.1	1	280	700	This work
ITO-carbon	4.0	1	200	1034	Ref. S2
N, S-G-Li ₂ S ₆	4.6	0.5	200	670	Ref. S3
Pt-Li ₂ S ₈	1.52	0.5	100	700	Ref. S4

Table S1 Sulfur loading and electrochemical performance of some reservoirs

Table S2 Peak voltages of the CC and CC@Co₃O₄

Samples	Peak 1 (V)	Peak 2 (V)	Peak 3 (V)
CC	2.37	1.92	2.53
CC@Co ₃ O ₄	2.36	1.96	2.48

Samples	Peak 1 (V)	Peak 2 (V)	Peak 3 (V)
CC	2.52	2.00	2.31
CC@Co ₃ O ₄	2.54	2.04	2.26

Table S3 Onset potentials of the CC and CC@Co₃O₄

Table S4 The fitting results of EIS spectra of the CC and CC@Co₃O₄ after 300 cycles

Samples	$R_{s}\left(\Omega ight)$	$R_{ct}\left(\Omega\right)$
CC	4.39	336
CC@Co ₃ O ₄	4.06	116

Table S5 The fitting results of EIS spectrum of the CC and the corresponding data related to the

 Arrhenius plot

T (K)	293	298	303	308	313
$R_{ct}\left(\Omega\right)$	146	127	116	92	78
$\ln\left(1/R_{ct}\right)$	6.8	7.9	8.6	10.9	12.8
1/T	3.41	3.36	3.30	3.25	3.19

Table S6 The fitting results of EIS spectrum of the $CC@Co_3O_4$ and the corresponding data related to the Arrhenius plot

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T (K)	293	298	303	308	313
$R_{ct}\left(\Omega ight)$	148	137	128	119	110
$\ln\left(1/R_{ct}\right)$	6.8	7.3	7.8	8.5	9.1
1/T	3.41	3.36	3.30	3.25	3.19

References

- S1 L. Shen, Q. Che, H. Li and X. Zhang, Adv. Funct. Mater., 2014, 24, 2630–2637.
- S2 H. Yao, G. Zheng, P. C. Hsu, D. Kong, J. J. Cha, W. Li, Z. W. Seh, M. T. McDowell, K. Yan, Z. Liang, V. K. Narasimhan and Y. Cui, *Nat. Commun.*, 2014, 5, 3943–3952.
- S3 G. Zhou, E. Paek, G. S. Hwang and A. Manthiram, Nat. Commun., 2015, 6, 7760–7771.
- S4 G. Babu, K. Ababtain, K. Y. S. Ng and L. M. R. Arava, Sci. Rep., 2015, 5, 8763-8770.
- S5 H. Lee, I. I. Nedrygailov, C. Lee, G. A. Somorjai, J. Y. Park, Angew. Chem. Int. Ed., 2015, 54, 2340–2344.
- S6 A. Hervier, J. R. Renzas, J. Y. Park and G. A. Somorjai, *Nano Lett.*, 2009, 11, 3930–3933.
- S7 N. Katada, S. Sota, N. Morishita, K. Okumura and M. Niwa, *Catal. Sci. Technol.*, 2015, 5, 1864–1869.
- S8 O. S. Mendoza-Hernandez, H. Ishikawa, Y. Nishikawa, Y. Maruyama, Y. Sone and M. Umeda, *Electrochim. Acta*, 2014, 131, 168–173.