

Supporting information

Hierarchical CoO microflower film with excellent electrochemical lithium/sodium storage performances

Ling Chang, Kai Wang, Liang-ai Huang, Zhishun He, Shasha Zhu, Miaomiao Chen, Haibo Shao,

Jianming Wang*

Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

*Corresponding author.

Tel.: +86-571-87951513; Fax: +86-571-87951895.

E-mail address: wjm@zju.edu.cn (J.M. Wang)

Supplementary Figures

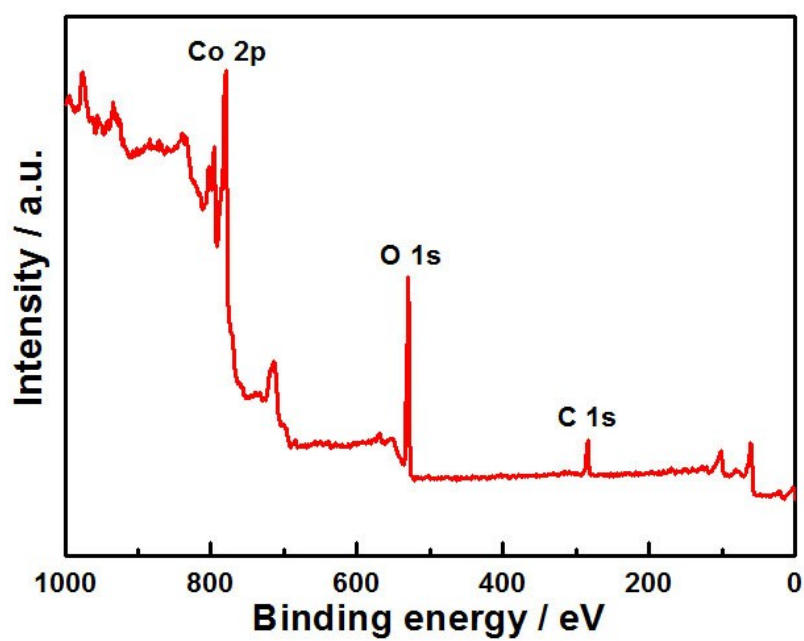


Figure S1 Wide-scan XPS spectrum for the CoO microflower film.

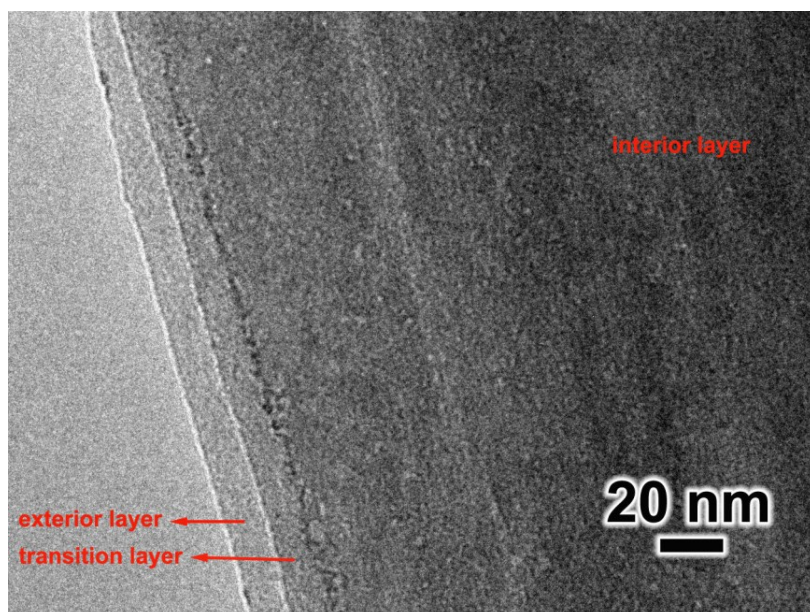


Figure S2 TEM image of Co(OH)F intermediate.

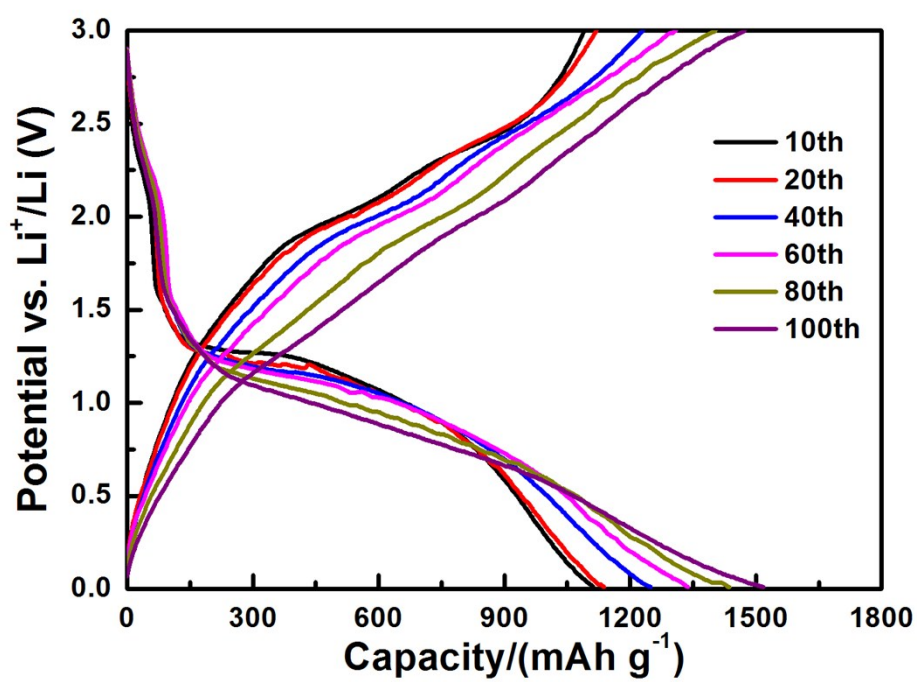


Figure S3 The galvanostatic discharge/charge voltage profiles of the CoO film electrode at typical cycles at 181.8 mA g⁻¹.

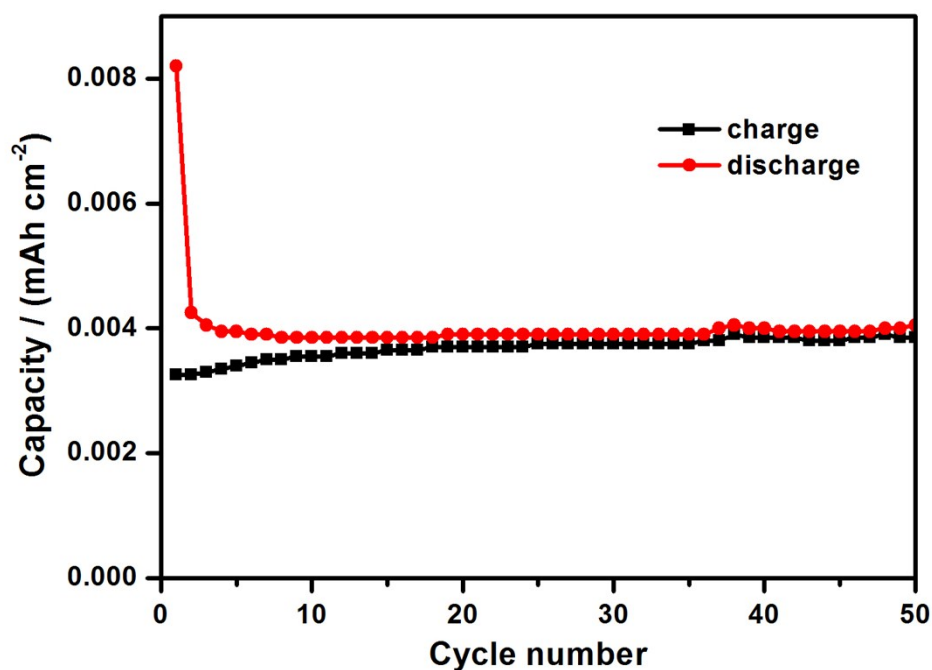


Figure S4 Cycling performance for sodium storage of the Cu substrate treated in the synthesis solution without $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ at a current density of $12.5 \mu\text{A cm}^{-2}$.

In order to clarify the effect of possible by-products, we made a control experiment, that is, Cu substrate was treated in the synthesis solution without $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ under the same experimental condition as that for synthesizing the $\text{Co}(\text{OH})\text{F}$ film. The subsequent treating procedure (including annealing) of the modified Cu substrate was also the same as that for preparing the CoO film. The sodium storage performance of the modified Cu substrate was investigated using CR 2025 coin cells assembled in an Ar-filled glove box. Fig. S4 showed the cycling performance of the modified Cu substrate at a current density of $12.5 \mu\text{A cm}^{-2}$. The modified Cu substrate only delivered a capacity of $0.0041 \text{ mAh cm}^{-2}$ after 50 cycles at a current density of $12.5 \mu\text{A cm}^{-2}$, while the CoO film electrode exhibited a capacity of $0.3056 \text{ mAh cm}^{-2}$ after 100 cycles at $100 \mu\text{A cm}^{-2}$. The result indicates that the influence of the Cu substrate on the specific capacity of the CoO microflower film electrode is negligible.

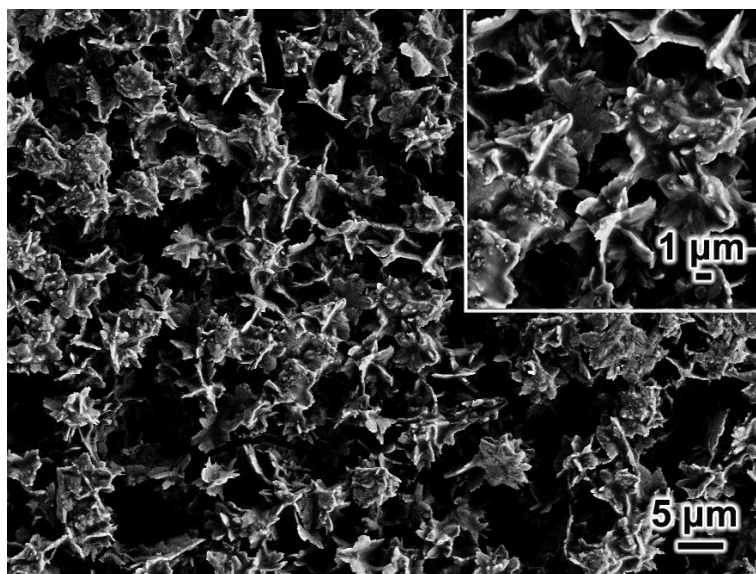


Figure S5 SEM images of CoO microflower film electrode after 100 cycles at 181.8 mA g^{-1} . The inset is the magnified SEM image.

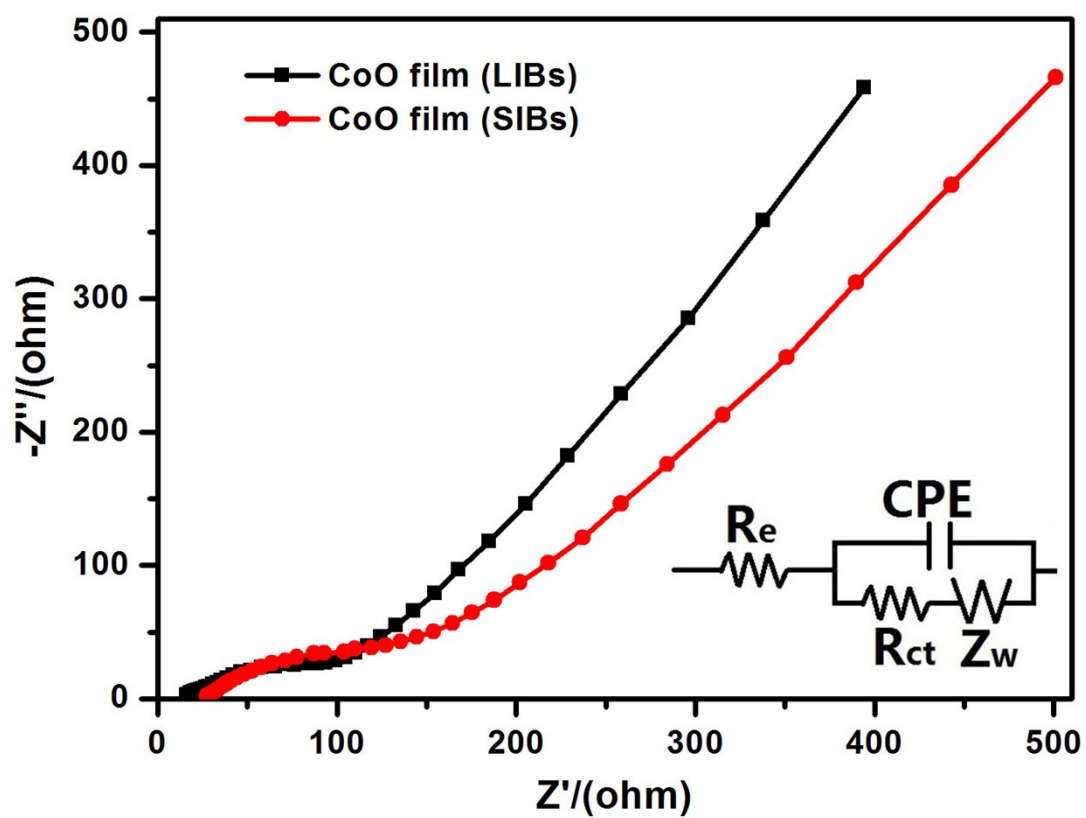


Figure S6 Nyquist plots of the CoO film electrode for LIBs at open circuit state after 100 cycles at 181.8 mA g⁻¹ and the CoO film electrode for SIBs at open circuit state after 100 cycles at 90.9 mA g⁻¹. The inset is the corresponding equivalent circuit.

Supplementary Table

Table S1 A rough lithium storage performance comparison of cobalt oxide based materials in this work and the recently reported references

Electrode materials	Reversible Capacity (mAh g ⁻¹)/cycle number	Current density (mA g ⁻¹)	Refs.
Co ₃ O ₄ /onion-like carbon	632 / 100	200	[1]
CoO nanosheets on graphene	640 / 150	100	[2]
Co ₃ O ₄ /rGO-350	673 / 100	180	[3]
CoO/rGO-350	732 / 100	150	[3]
CoO/carbon nanofiber	633 / 52	100	[4]
MWCNTs/Co ₃ O ₄	813 / 100	100	[5]
Co-CoO _x nanowire arrays	740 / 1000	20 000	[6]
rGO/CoO	994 / 100	100	[7]
Co ₃ O ₄ /Co/carbon	505 / 600	2000	[8]
CoO microflower film	1297.9 / 500	454.5	This work

Table S2 A rough sodium storage performance comparison of CoO microflower film material in this work and other anodes in the recently reported references

Electrode materials	Reversible Capacity (mAh g ⁻¹)/cycle number	Current density (mA g ⁻¹)	Refs.
Co ₃ O ₄ /MCNTs	293 / 15	34	[9]
bowl-like hollow Co ₃ O ₄	290 / 10	890	[10]
W-Fe ₂ O ₃	129 / 100	100	[11]
CuO nanowires	303 / 50	50	[12]
NiCo ₂ O ₄ @G	400 / 100	100	[13]
CoO microflower film	277.8 / 100	90.9	This work

Table S3 Impedance parameter values obtained by the fitting of the Nyquist plots in Fig. S6

Samples	R_e (Ω)	R_{ct} (Ω)	CPE ($\mu\text{F cm}^{-2}$)	n	Z_w ($\Omega \text{ cm}^{-2}$)
CoO film (LIBs)	13.12	119.6	725.41	0.4319	53.53
CoO film (SIBs)	25.80	145.0	335.57	0.5205	116.3

References

- [1] Y. Wang, F. Yan, S. W. Liu, A. Y. S. Tan, H. H. Song, X. W. Sun, H. Y. Yang, *J. Mater. Chem. A*, 2013, **1**, 5212-5216.

- [2] X. L. Huang, R. Z. Wang, D. Xu, Z. L. Wang, H. G. Wang, J. J. Xu, Z. Wu, Q. C. Liu, Y. Zhang, X. B. Zhang, *Adv. Funct. Mater.*, 2013, **23**, 4345-4353.
- [3] J. X. Zhu, Y. K. Sharma, Z. Y. Zeng, X. J. Zhang, M. Srinivasan, S. Mhaisalkar, H. Zhang, H. Hng, Q. Y. Yan, *J. Phys. Chem. C*, 2011, **115**, 8400-8406.
- [4] M. Zhang, E. Uchaker, S. Hu, Q. F. Zhang, T. H. Wang, G. Z. Cao, J. Y. Li, *Nanoscale*, 2013, **5**, 12342-12349.
- [5] G. Huang, F. F. Zhang, X. C. Du, Y. L. Qin, D. M. Yin, L. M. Wang, *ACS Nano*, 2015, **9**, 1592-1599.
- [6] L. Zhan, S. Q. Wang, L. X. Ding, Z. Li, H. H. Wang, *J. Mater. Chem. A*, 2015, **3**, 19711-19717.
- [7] X. N. Leng, X. D. Ding, J. J. Hu, S. F. Wei, Z. H. Jiang, J. S. Lian, G. Y. Wang, Q. Jiang, J. A. Liu, *Electrochim. Acta*, 2016, **190**, 276-284.
- [8] K. Q. Zhou, L. F. Lai, Y. C. Zhen, Z. S. Hong, J. H. Guo, Z. G. Huang, *Chem. Eng. J.*, 2017, **316**, 137-145.
- [9] Q. J. Deng, L. P. Wang, J. Z. Li, *J. Mater. Sci.*, 2015, **50**, 4142-4148.
- [10] J. W. Wen, D. W. Zhang, Y. Zang, X. Sun, B. Cheng, C. X. Ding, Y. Yu, C. H. Chen, *Electrochim. Acta*, 2014, **132**, 193-199.
- [11] Z. G. Wu, Y. J. Zhong, J. Liu, J. H. Wu, X. D. Guo, B. H. Zhong, Z. Y. Zhang, *J. Mater. Chem. A*, 2015, **3**, 10092-10099.
- [12] L. J. Wang, K. Zhang, Z. Hu, W. C. Duan, F. Y. Cheng, J. Chen, *Nano Res.*, 2014, **7**, 199-208.
- [13] Y. R. Wang, H. Huang, Q. S. Xie, Y. P. Wang, B. H. Qu, *J. Alloys Compd.*, 2017, **705**, 314-319.

