

Realizing enhanced cyclability of cactus-like NiCo₂O₄ nanocrystals anode enabled by molecular layer deposition

*Jia-Bin Fang, Qiang Ren, Chang Liu, Ji-An Chen, Di Wu, Ai-Dong Li**

National Laboratory of Solid State Microstructures, Department of Materials Science and Engineering, College of Engineering and Applied Sciences, Jiangsu Key Laboratory of Artificial Functional Materials, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

Electronic mail: adli@nju.edu.cn

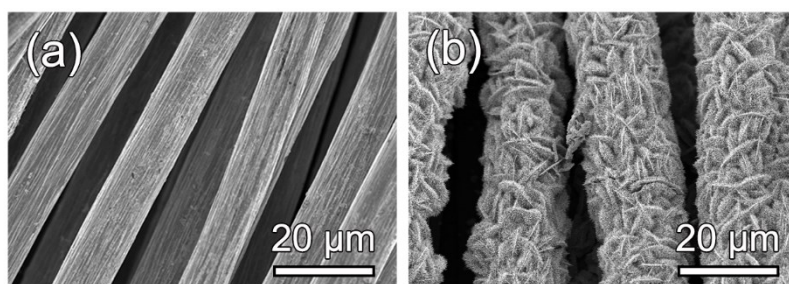


Figure S1. SEM images of bare CC (a) and cactus-like NiCo₂O₄ flakes on CC (b).

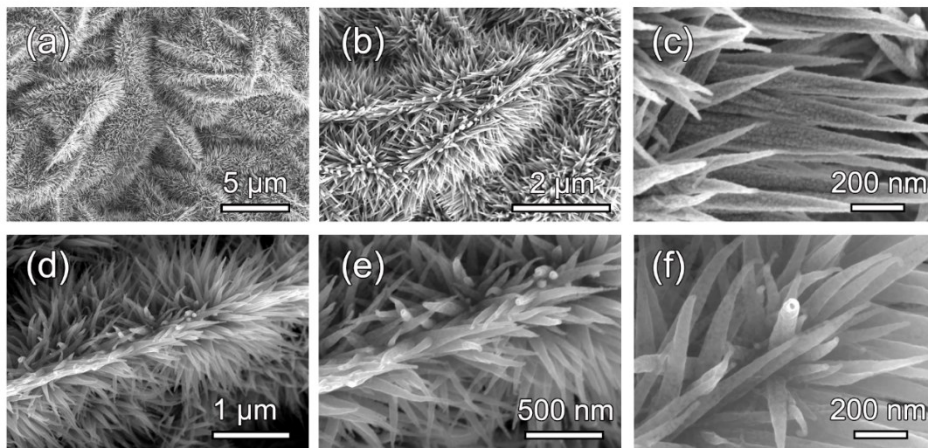


Figure S2. SEM images of (a-c) bare NiCo₂O₄ and (d-f) NiCo₂O₄@Al₂O₃/carbon with different magnifications.

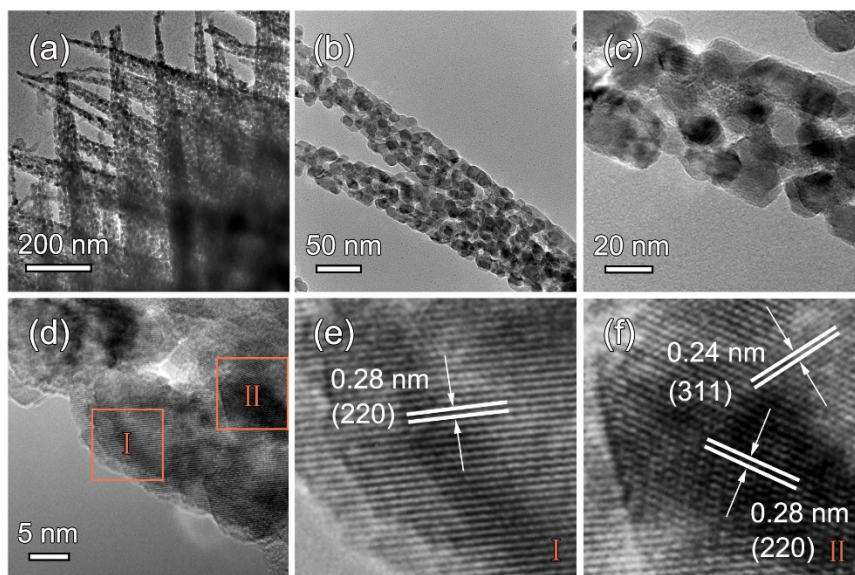


Figure S3. (a, b) Low-magnification TEM images, (c-f) high-magnification TEM images of bare NiCo₂O₄.

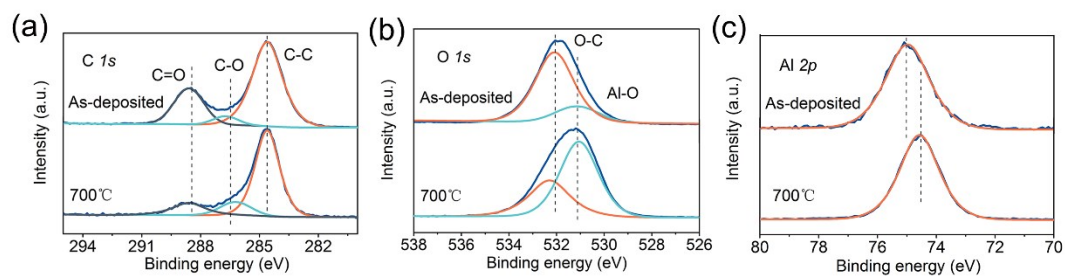


Figure S4. XPS spectra of as-deposited and annealed alucone films on Si: (a) C 1s, (b) O 1s and (c) Al 2p.

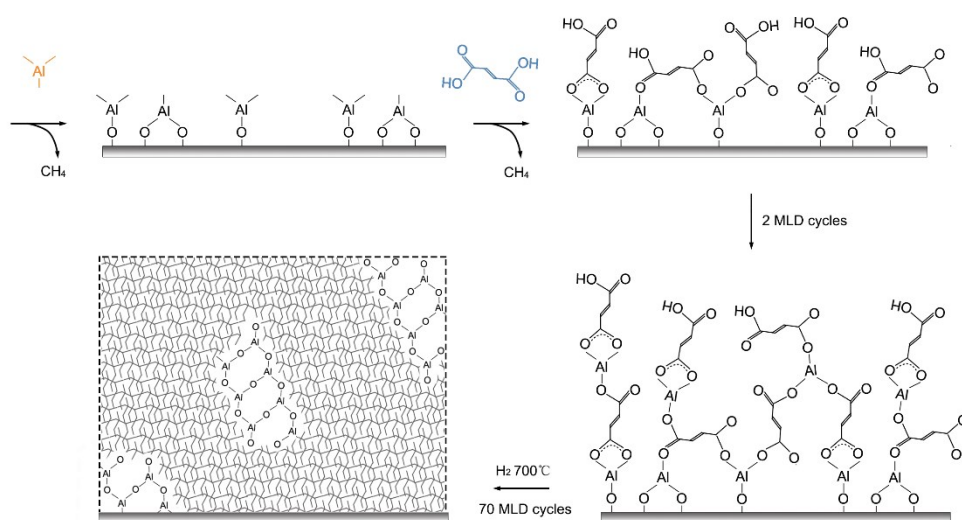


Figure S5. A schematic of the possible reaction mechanism and subsequent pyrolysis for the TMA-fumaric acid film.

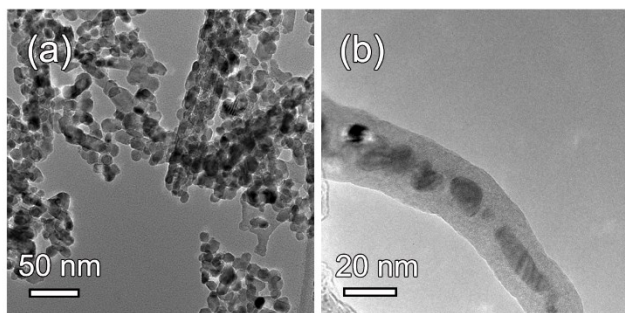


Figure S6. TEM images of (a) bare NiCo₂O₄ and (b) NiCo₂O₄@Al₂O₃/carbon ultrasonic dispersion for 10 min in alcohol.

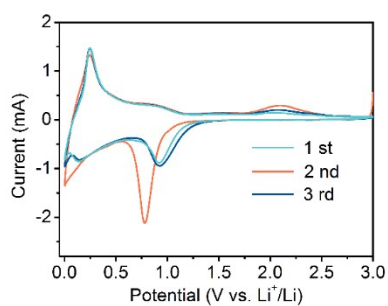


Figure S7. CV curves of bare NiCo₂O₄ for the first three cycles at the scan rate of 0.1 mV s⁻¹.

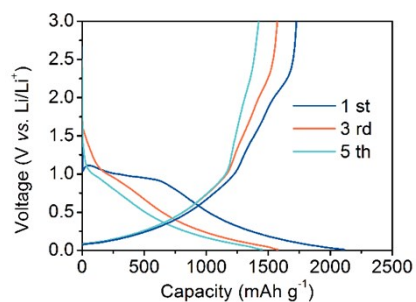


Figure S8. Charge/discharge curves for the 1st, 3rd and 5th cycles at 200 mA g⁻¹ of bare NiCo₂O₄ electrode.

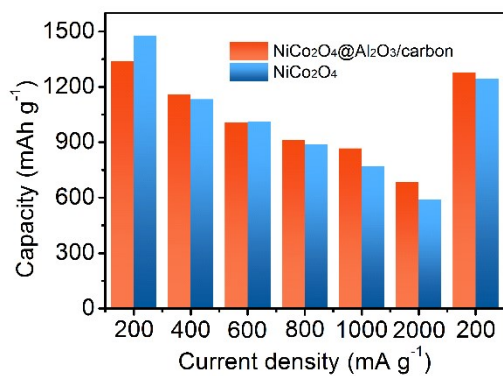


Figure S9. Column view of rate performance of NiCo₂O₄@Al₂O₃/carbon and bare NiCo₂O₄ electrodes.

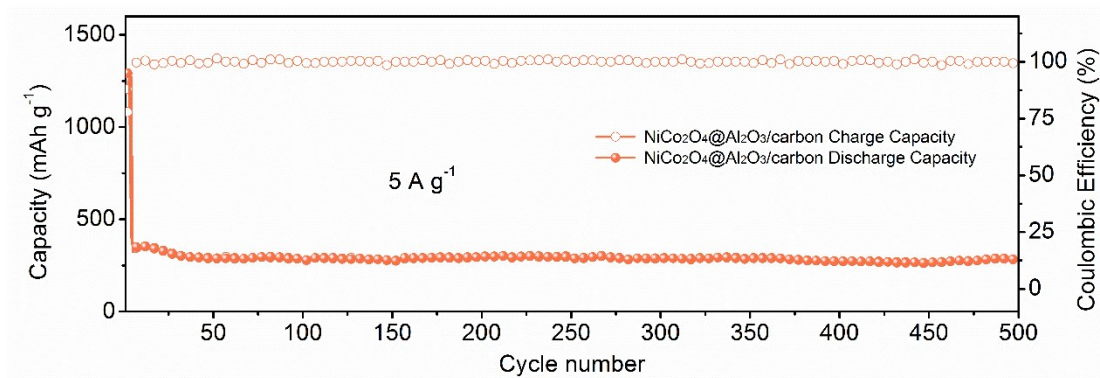


Figure S10. Cycling performance of NiCo₂O₄@Al₂O₃/carbon electrode at 5 A g⁻¹.

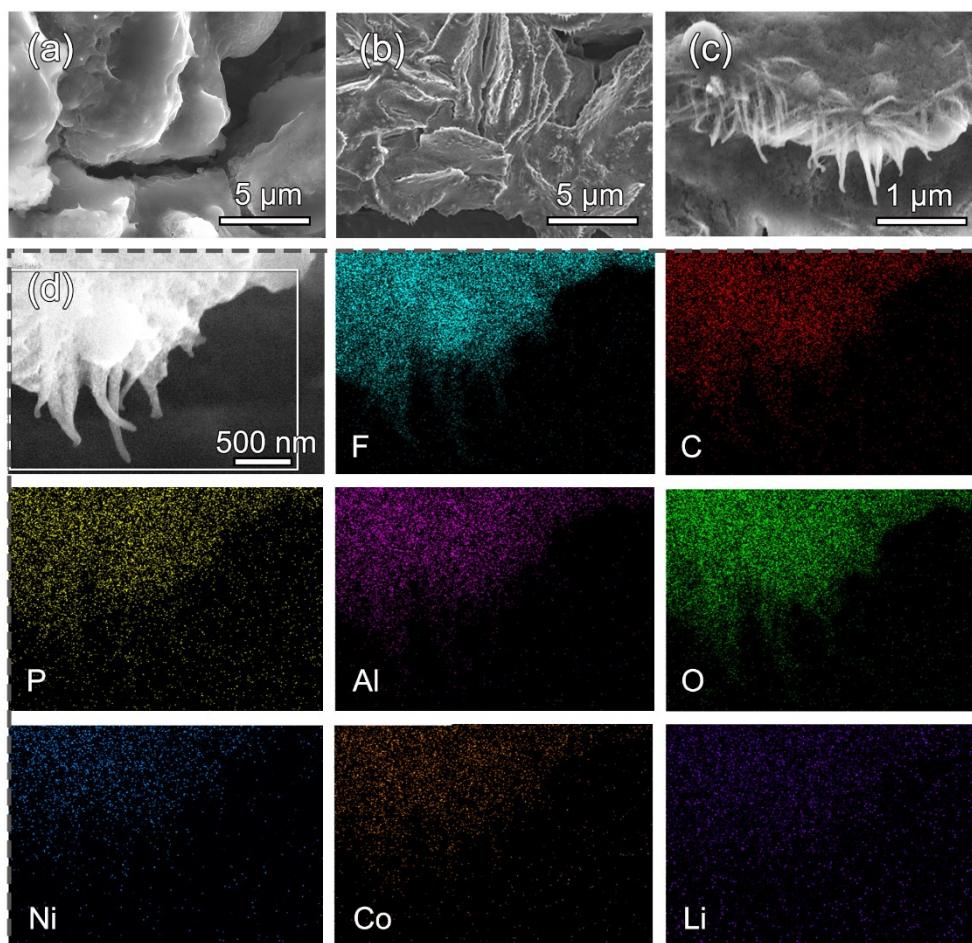


Figure S11. (a) SEM image for cycled NiCo_2O_4 anode after 200 cycles; (b, c) SEM images and (d) corresponding EDS mapping of elemental F, C, P, Al, O, Ni, Co, and Li for the cycled $\text{NiCo}_2\text{O}_4@Al_2O_3$ /carbon anode after 200 cycles.

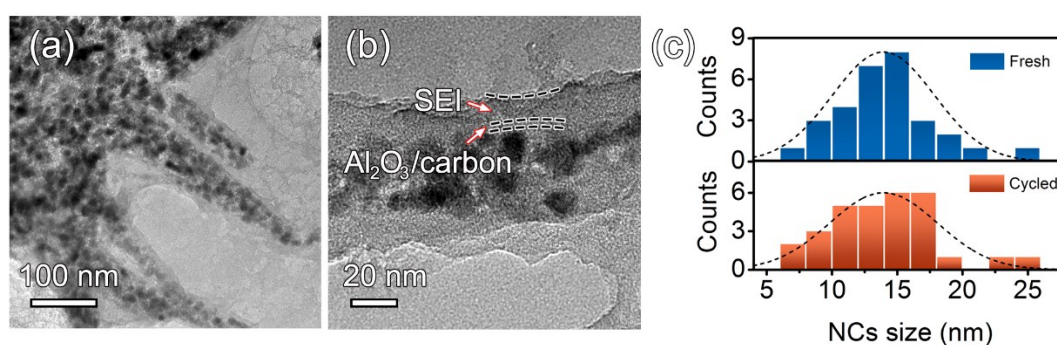


Figure S12. (a, b) TEM images of $\text{NiCo}_2\text{O}_4@Al_2O_3$ /carbon electrode after 200 charge/discharge cycles at 2 A g^{-1} . The thickness of SEI layer is $\sim 10 \text{ nm}$ indicated by the upper arrow; (c) Distribution of NiCo_2O_4 NCs size in $\text{NiCo}_2\text{O}_4@Al_2O_3$ /carbon before and after cycling.

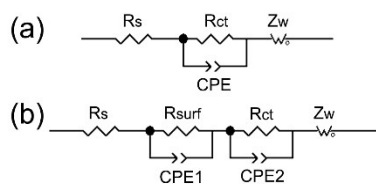


Figure S13. Equivalent electrical circuit diagram.

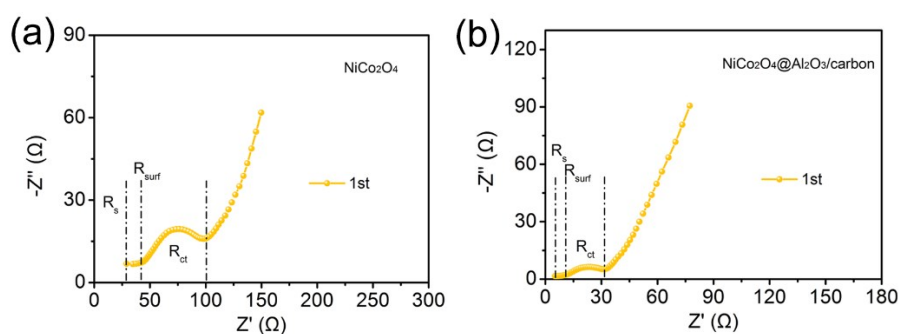


Figure S14. Electrochemical impedance spectra of (a) bare NiCo_2O_4 and (b) $\text{NiCo}_2\text{O}_4@/\text{Al}_2\text{O}_3/\text{carbon}$ after the first cycle.

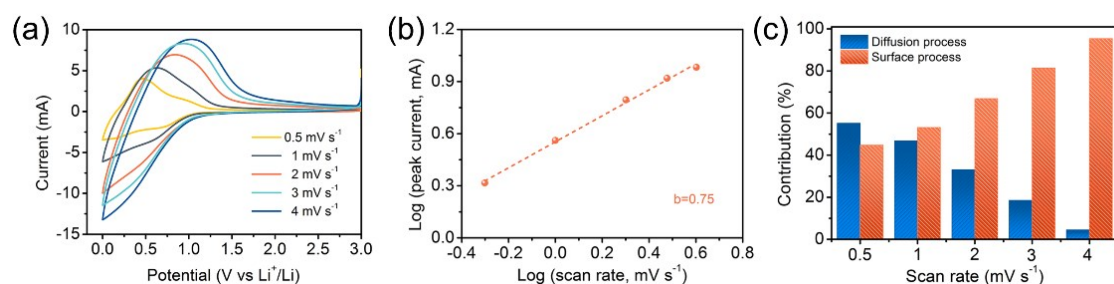


Figure S15. Kinetics analyses of electrochemical behavior: (a) CV profiles of $\text{NiCo}_2\text{O}_4@/\text{Al}_2\text{O}_3/\text{carbon}$ anode at various scan rates; (b) Relationship between the log (peak current) and log (scan rate); (c) Contribution ratios of capacitive and diffusion-controlled charge storage at different scan rates.

Table S1

Comparison of Li-ion storage performances between recent reported NiCo_2O_4 based

anodes and this work.

Anode material	Current density (A g ⁻¹)	Cycle number	Reversible capacity (mAh g ⁻¹)	Refs.
NiCo ₂ O ₄ @N-doped carbon submicrospheres	1	1000	371.4	[1]
NiCo ₂ O ₄ @ZIF-67/GO	0.5	80	1025	[2]
	2	80	740	
NiCo ₂ O ₄ @Ni-B composites	0.5	500	865	[3]
NiCo ₂ O ₄ -holey graphene	0.178	450	931.2	[4]
Fe ₂ O ₃ /NiCo ₂ O ₄ composite	0.178	200	1528	[5]
NiCo ₂ O ₄ @MnO ₂ composites	1	100	841.9	[6]
	0.1	70	1571.9	
Ni-NiCo ₂ O ₄ @ZnCo ₂ O ₄	1	600	1097.5	[7]
	0.1	70	1571.9	
NiCo ₂ O ₄ /CNT	1	200	1673	[8]
NiCo ₂ O ₄ @TiO ₂	2	800	749.74	[9]
PPC/NiCo ₂ O ₄	2	1100	363	[10]
	0.2	150	1574	
NiCo ₂ O ₄ @Al ₂ O ₃ /carbon	2	200	931.2	This work
	5	500	280	

References

1. D. K. Denis, Z. Wang, X. Sun, F. U. Zaman, J. Zhang, L. Hou, J. Li and C. Yuan, *ACS applied materials & interfaces*, 2019, **11**, 32052-32061.
2. Y. Kuang, C. Chen, K. Li, B. Hao, J. Ma, Y. Liao, H. Mao and F. Huo, *Nanoscale*, 2019, **11**, 15166-15172.
3. M. Li, Q. Zhou, C. Ren, N. Shen, Q. Chen, J. Zhao, C. Guo, L. Zhang and J. Li, *Nanoscale*, 2019, **11**, 22550-22558.
4. D. Yuan, Y. Dou, L. Xu, L. Yu, N. Cheng, Q. Xia, L. Hencz, J. Ma, S. X. Dou and S. Zhang, *Journal of Materials Chemistry A*, 2020, **8**, 13443-13451.
5. J. Liu, Y. Ding, T. Han, J. Long, X. Pei, Y. Luo, W. Bao, X. Lin and H. Zhang, *Chemical communications*, 2020, **56**, 2618-2621.
6. Z. Zhang, Y. Huang, J. Yan, C. Li, X. Chen and Y. Zhu, *Applied Surface Science*, 2019, **473**, 266-274.
7. H. Xin, D. Li, L. Shi, M. Ji, Y. Lin, J. Yu, B. Yang, C. Li and C. Zhu, *Chemical Engineering*

- Journal*, 2018, **341**, 601-609.
8. S.-K. Park, S. H. Yang and Y. C. Kang, *Chemical Engineering Journal*, 2018, **349**, 214-222.
 9. P. Liu, Q. Ru, Z. Wang, B. Wang, Q. Guo, P. Zhang, X. Hou, S. Su and F. C.-C. Ling, *Chemical Engineering Journal*, 2018, **350**, 902-910.
 10. C. Zhang, Z. Xie, W. Yang, Y. Liang, D. Meng, X. He, P. Liang and Z. Zhang, *Journal Of Power Sources*, 2020, **451**.