Boosting electrochemical properties of CoCo₂O₄ porous nanowire arrays by microwave-assisted synthesis for battery-supercapacitor hybrid devices

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Fig.S2 Specific capacity measured of CoCo₂O₄ and Co₃O₄ electrodes at different scan rates.

The specific capacity (C g⁻¹) of the prepared cobalt oxide (Co₃O₄ and CoCo₂O₄) in

three-electrode system were measured by cyclic voltammetry (CV) using the following equation (S1).

$$Cs (C g^{-1}) = \frac{\int_{V_1}^{V_2} I_{(V)} dV}{2mv}$$
(S1)

where *I* is the current; m is the mass; v is the potential scan rate and $\Delta V (V_2-V_1)$ is the potential window.



Fig.S3 *I-V* test curves of Co₃O₄ and CoCo₂O₄ electrode.

Single Electrode					Battery-supercapacitor hybrid device				
Structure of C0 ₃ O ₄ based material	Method of synthesis	Specific capacitance	Retention	Assembly	Specific capacitance	Energy density (Wh/kg)	Power density (W/kg)	Retention	Reference
Co ₃ O ₄	Soak-adsorption	314 C g ⁻¹ /785 F g ⁻¹ (0.5A g ⁻¹)	93% (5000 cycles @ 5A g ⁻¹)	Co ₃ O ₄ //AC	/	13	257	85.9% (10000 cycles @ 5A g ⁻¹)	1
Co ₃ O ₄ /rGO-C	Template nano- casting technique	354.6 C g ⁻ ¹ /709.1 F g ⁻¹ (1A g ⁻¹)	91.2% (6000 cycles @ 50mV s ⁻¹)	Co ₃ O ₄ /rGO- C//rGO	154.2 F g ⁻¹ (1A g ⁻¹)	48.2	750.5	88.7% (5000 cycles @ 50mV s ⁻¹)	2
C/ Co ₃ O ₄	Calcination	169.2 C g ⁻ ¹ /423 F g ⁻¹ (1A g ⁻¹)	83% (2000 cycles @ 3A g ⁻¹)	C/Co ₃ O ₄ //AC	60.76 F g ⁻¹ (1A g ⁻¹)	21.1	790	/	3
Co ₃ O ₄ /NiCo ₂ O ₄	Hydrothermal	134.2 C g ⁻ ¹ /335.5 F g ⁻¹ (0.5A g ⁻¹)	73.6% (5000 cycles @ 10A g ⁻¹)	Co ₃ O ₄ //AC	15 F g ⁻¹ (0.5A g ⁻¹)	5.2	26.5 W/kg	87.6% (3000 cycles @ 1A g ⁻¹)	4
Co ₃ O ₄ /MnO ₂	Annealing	292 F g ⁻¹ (4A g ⁻¹)	87.4% (5000 cycles @ 10A g ⁻¹)	Co ₃ O ₄ /MnO ₂ // AC	57.7 F g ⁻¹ (2A g ⁻¹)	46.2	/	84.5% (5000 cycles @ 10 A g ⁻¹)	5

Tab.S1 Battery-supercapacitor hybrid device performances of Co₃O₄-based electrode materials prepared by different methods reported in the literature.

CoCo ₂ O ₄	Microwave assisted hydrothermal	743.8 C g ⁻¹ (1A g ⁻¹)	89.7% (5000 cycles @ 15A g ⁻¹)	CoCo ₂ O ₄ //m- CNT	80.2 F g ⁻¹ (124.3 C g ⁻¹) (1A g ⁻¹)	26.8	775.4	82.3% (5000 cycles @ 3A g ⁻¹)	This work
Co ₃ O ₄ @MnO ₂	Hydrothermal	336 C g ⁻¹ /560 F g ⁻¹ (0.2A g ⁻¹)	95% (5000 cycles @ 5A g ⁻¹)	Co ₃ O ₄ @MnO 2 ^{//} activated GO	49.8 F g ⁻¹ (1A g ⁻¹)	17.7	158	81.1% (10000 cycles @ 3A g ⁻¹)	10
Co ₃ O ₄	Electrochemical deposition	403 C g ⁻¹ /806 F g ⁻¹	90.8% (5000 cycles @ 15A g ⁻¹)	Co ₃ O ₄ //AC	81 F g ⁻¹ (1A g ⁻¹)	25.3	752	86.5% (4000 cycles @ 5A g ⁻¹)	9
NiCo ₂ O ₄ / MWCNT/RGO	Hydrothermal	400.5 C g ⁻ ¹ //890 F g ⁻¹ (1A g ⁻¹)	91% (4000 cycles @ 5A g ⁻¹)	NiCo ₂ O ₄ / MWCNT/RG O//AC	94.2 F g ⁻¹ (1A g ⁻¹)	34.5	750	90.2% (5000 cycles @ 10A g ⁻¹)	8
NiMn LDH@Co ₃ O ₄	Hydrothermal	243.2 C g ⁻ ¹ /607.9 F g ⁻¹ (0.5A g ⁻¹)	97% (1000 cycles @ 5A g ⁻¹)	NiMn LDH@Co ₃ O ₄ // activated graphene	97.3 F g ⁻¹ (0.5 A g ⁻¹)	26.49	350	73 % (5000 cycles @3 A g ⁻¹)	7
Co ₃ O ₄	Hydrothermal	598.5 C g ⁻¹ (1A g ⁻¹)	93.7% (8000 cycles @ 10A g ⁻¹)	Co ₃ O ₄ //AC	99.0 F g ⁻¹ (1A g ⁻¹)	22.5	800	91.8% (10000 cycles @ 10 A g ⁻¹)	6

	Value					
Parameter	Hydrothermal synthesis C03O4	Microwave synthesis CoCo ₂ O ₄				
$R_{s}(\Omega)$	0.257	0.362				
$C_d(F)$	1.137	1.085				
$R_{ct}(\Omega)$	1.119	0.712				
$W_2(\Omega.s^{-0.5})$	1.710	0.979				

Tab.S2 Summary the values of different components in the fitting of EIS data.



Fig.S4 CV curves at different scan rates (a), and GCD curves at different current densities (b) of

the m-CNT electrode.



Fig.S5 (a) Comparative CV curves of m-CNT and $CoCo_2O_4$ electrodes in a three-electrode system at 10 mV s⁻¹. (b) CV curves of the BSH device measured at different potential windows at 50 mV

s⁻¹.



Fig.S6 Specific capacitance measured of CoCo₂O₄//m-CNT BSH at different current densities.

Parameter	Value	Deviation
$\mathrm{R}_{1}\left(\Omega ight)$	0.591	0.126
$C_1(F)$	0.456	0.403
$C_{2}(F)$	0.041	0.097
$\mathrm{R}_{2}(\Omega)$	1.764	0.355
$W_2(\Omega.s^{-0.5})$	1.518	0.862

Tab.S3 Summary the values of different components in the fitting of EIS data.

References

- 1. Y. Zhao, Y. Liu, J. Du, X. Zhang, J. Zhou, X. Li, C. Wu, Z. Zhu, E. Xie and X. Pan, *Applied Surface Science*, 2019, **487**, 442-451.
- C. Liu, A. Gao, F. Yi, D. Shu, H. Yi, X. Zhou, J. Hao, C. He and Z. Zhu, *Electrochimica Acta*, 2019, 326, 134965.
- 3. S. Li, K. Yang, P. Ye, K. Ma, Z. Zhang and Q. Huang, Applied Surface Science, 2020, 503, 144090.
- 4. Y. Liu, H. Zhang, Y. Yu, C. Zhu and X. Ma, *Journal of Alloys and Compounds*, 2020, **818**, 153357.
- 5. G. Liu, C. Kang, J. Fang, L. Fu, H. Zhou and Q. Liu, *Journal of Power Sources*, 2019, **431**, 48-54.
- 6. J. Zhu, B. Huang, C. Zhao, H. Xu, S. Wang, Y. Chen, L. Xie and L. Chen, *Electrochimica Acta*, 2019, **313**, 194-204.
- 7. H. Peng, C. Jing, J. Chen, D. Jiang, X. Liu, B. Dong, F. Dong, S. Li and Y. Zhang, *Crystengcomm*, 2019, **21**, 470-477.
- 8. T. Kavinkumar, K. Vinodgopal and B. Neppolian, *Applied Surface Science*, 2020, **513**, 145781.
- 9. X. Luo, M. Zhong, P. He, J. Shao, Q. Wang, K. Li and W. Zhao, *Journal of Alloys and Compounds*, 2020, **826**, 154241.
- 10. M. Huang, Y. Zhang, F. Li, L. Zhang, Z. Wen and Q. Liu, *Journal of Power Sources*, 2014, **252**, 98-106.