

Supporting Information

A new synthesis strategy for nitrogen-doped carbon nanofibers with cobalt oxide nanoparticles as anodic electrode materials for lithium ion batteries

Feng-Ming Liu,^a Ming-Yang Zhao,^a Shuo Wang,^a Ming Chen,^{*a} Xing Qian,^b Zhong-Yong Yuan^c, Yan Sun,^d Chun-Sheng Li^d and Rong Wan^{*a}

^a College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China *E-mail: chenming19830618@126.com, wanrong1992@163.com

^b College of Chemical Engineering, Fuzhou University, Fuzhou 350116, China.

^c School of Materials Science and Engineering, Nankai University, Tianjin 300071, China

^d School of Chemistry and Life Sciences, Suzhou University of Science and Technology

Experimental Section

Preparation of Samples.

The in situ synthesis of Co@NCNR and Co@NCNT arrays: 2 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 5 g melamine or 3 g triazole were added to 5 ml aqueous solution under tempestuously stirring to form a brown or purple colored slurry. Then, the colloidal compounds were milled continually to form a paste, following the evaporation of water. The obtained paste was dried at 80 °C for 24 h and manually ground into powder. The powder was transferred to a semiclosed quartz boat and heated at 350 °C for 1 h at a heating rate of 2 °C min^{-1} in a tubular furnace under N_2 flow, and the

temperature was increased to 700 °C at 2 °C min⁻¹ and kept at 700 °C for 3 h, followed by cooling to room temperature naturally.

The in situ synthesis of Co₃O₄@NCNR and Co₃O₄@NCNT arrays: The obtained Co@NCNR and Co@NCNT powder was calcined in a muffle furnace in air at 410 °C for 1 h with a heating rate of 5 °C min⁻¹, and the final product was obtained.

The synthesis of Co₃O₄@CB: 6 g CoCl₂·6H₂O and 5 g carbon black was dispersed in 5 ml deionized water and ground by mortar and pestle to form a slurry. Then the slurry was dried at 80 °C in oven overnight. The obtained powder was transferred to a quartz boat and covered by a quartz cap. Then heat treated at 410 °C for 1 h in air to form Co₃O₄@CB.

Material Characterization

The crystalline structure of the products was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab9 powder diffractometer equipped with Cu K_α radiation ($\lambda = 1.541 \text{ \AA}$). Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 analyser in air with a heating rate of 10 K min⁻¹. The morphology of the products was observed by field emission scanning electron microscopy (FE-SEM) on a ZEISS SUPRA 55 microscope and transmission electron microscopy (TEM) on a Tecnai G2 F20 microscope. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with a monochromatic Al K_α X-ray source (1486.6 eV). Raman spectra were collected on a Renishaw-1000 spectrometer by exciting a 514.5 nm Ar ion laser. N₂ adsorption-desorption isotherms were recorded at 77 K on a Quantachrome NOVA 2000e sorption analyzer.

Electrochemical Characterization

Co₃O₄@NCNR, Co₃O₄@NCNT or Co₃O₄@CB and polyvinylidene fluoride (PVDF) binder in a weight ratio of 9 : 1 were mixed in N-methylpyrrolidone (NMP)

and stirred for 24 h to make a slurry. The slurry was then spread on a Cu foil (13 mm in diameter, 0.3 mm in thickness) with a surface density of 1.0 mg cm⁻² and dried at 120 °C for 24 h to fabricate the working electrodes in vacuum. Lithium foil was used as both the reference electrode and the counter electrode (13 mm in diameter, 0.5 mm in thickness). 1.0 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was employed as the electrolyte. Celgard 2300 membrane (25 μm-thick polyethylene) was adopted as a separator. The assembly of CR2032-type coin cells was conducted in a high-purity Ar filled glovebox. Galvanostatic cycling was performed between 0.01 and 3 V vs Li⁺/Li at various C rates on a Land Battery Tester (Wuhan, China), where 1 C corresponds to 1000 mA g⁻¹. Cyclic voltammetry (CV) was conducted between 0.01 and 3 V at 0.1 mV s⁻¹ using a CHI660E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was performed on the same electrochemical system over the frequency range from 100 kHz to 100 mHz with a perturbation voltage of 5 mV. All of the electrochemical measurements were performed at 25 °C in an ambient atmosphere.

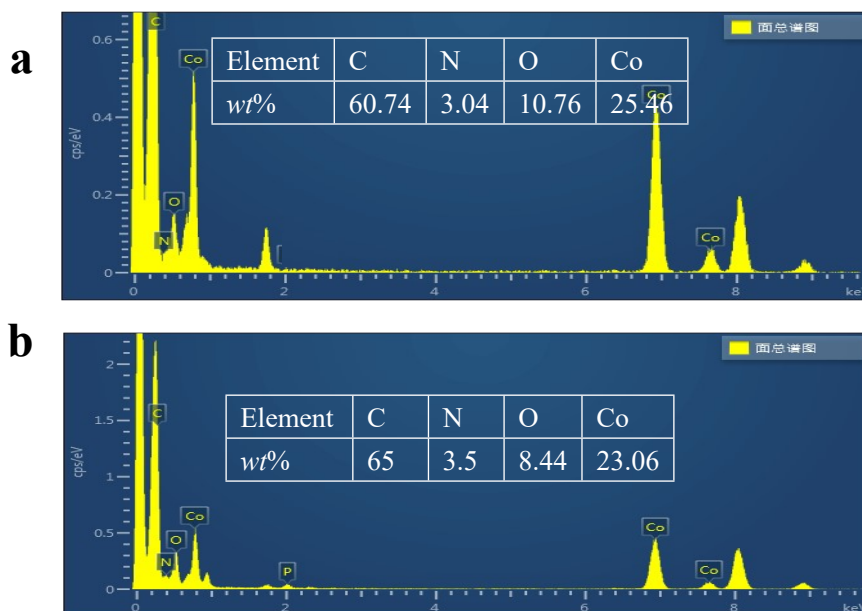


Fig. S1 EDS analysis for (a) Co₃O₄@NCNR and (b) Co₃O₄@NCNT, respectively.

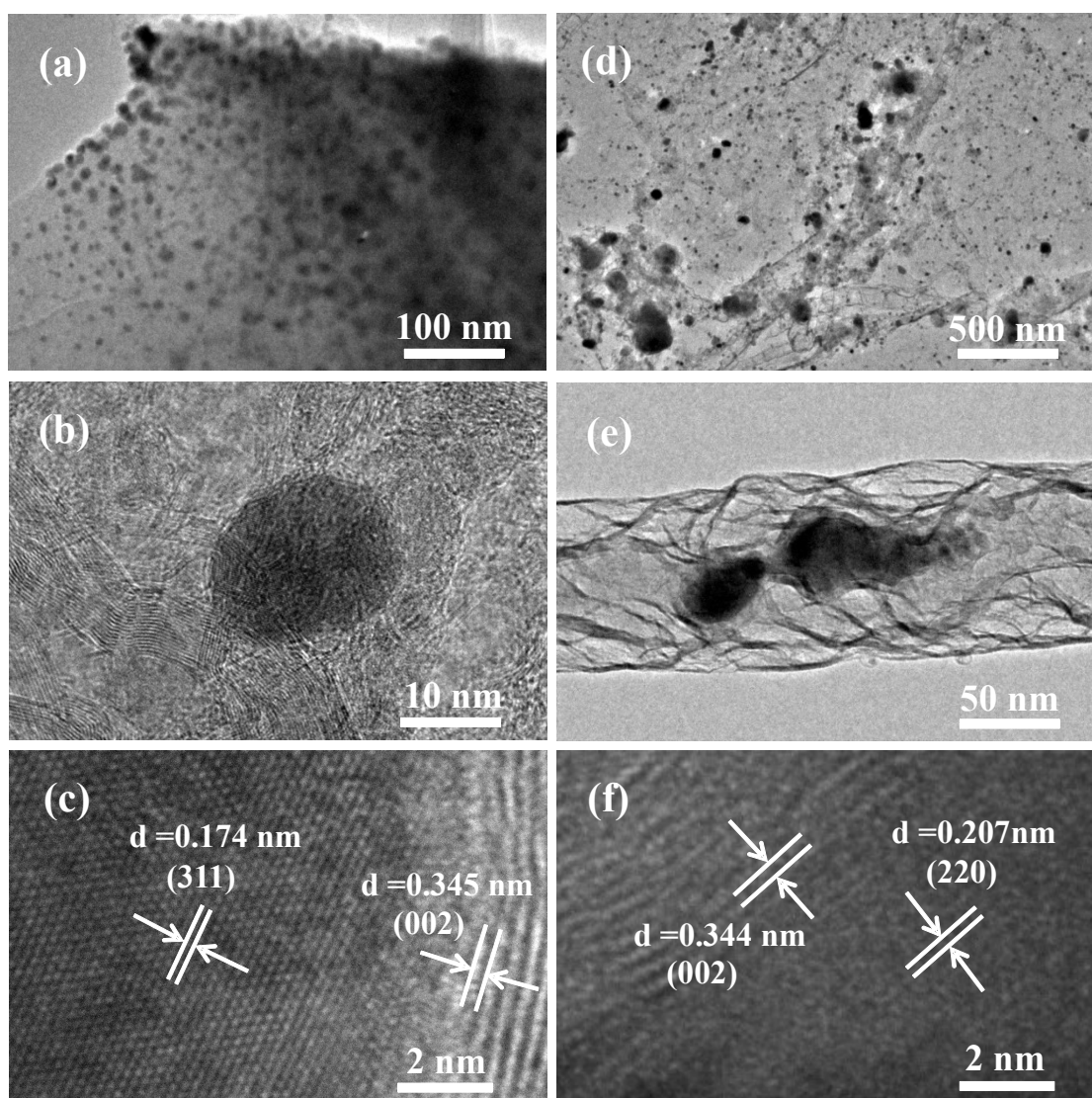


Fig. S2 TEM images of (a-c) Co_3O_4 @NCNR and (d-f) Co_3O_4 @NCNT, respectively.

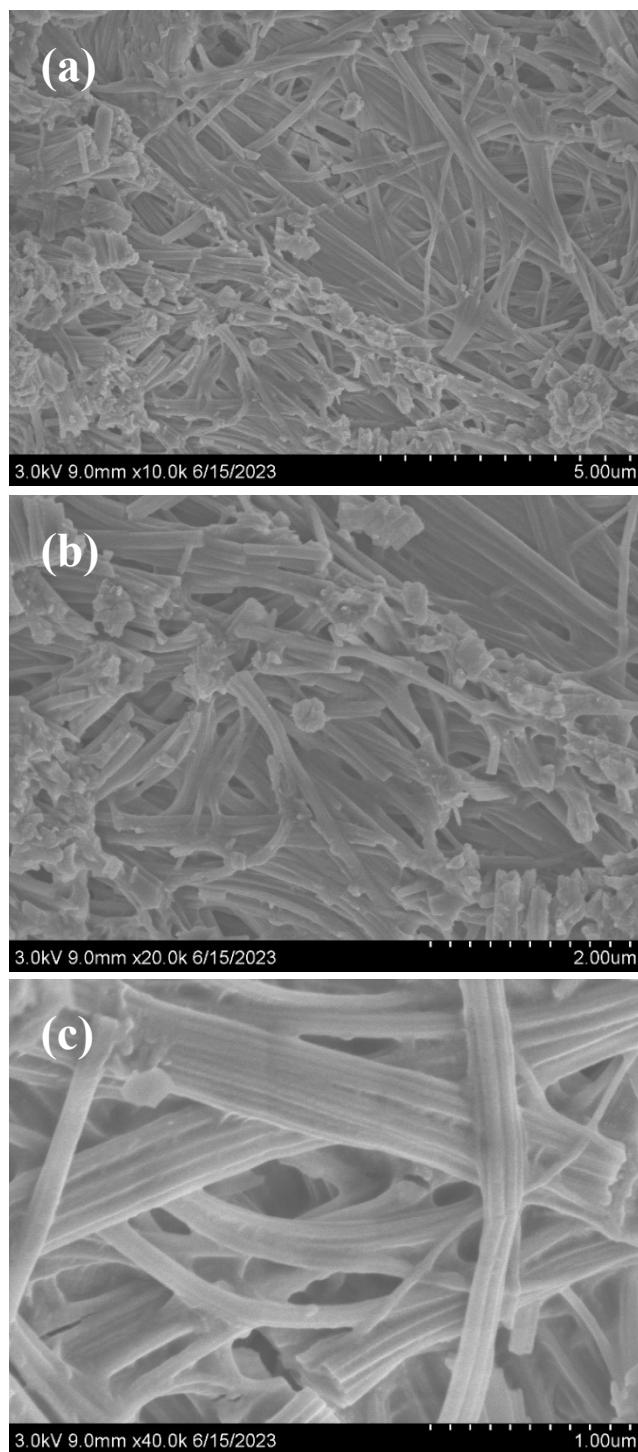


Fig. S3 SEM images of $\text{Co}_3\text{O}_4@\text{NCNR}$ precursor of one-dimensional Co(II)-triazole framework composed nanobelts.

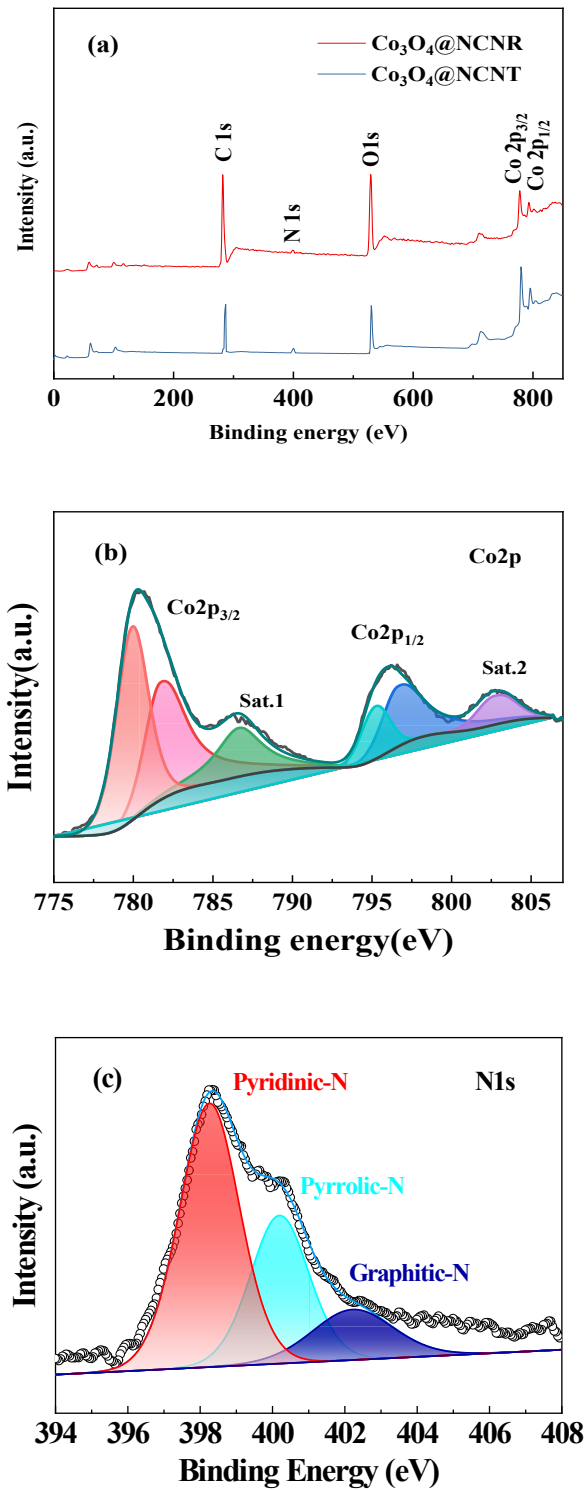


Fig. S4 (a) XPS survey spectra of $\text{Co}_3\text{O}_4@\text{NCNR}$ and $\text{Co}_3\text{O}_4@\text{NCNT}$ hybrids, High-resolution XPS of $\text{Co } 2p$ (b) and $\text{N } 1s$ (c) for $\text{Co}_3\text{O}_4@\text{NCNT}$.

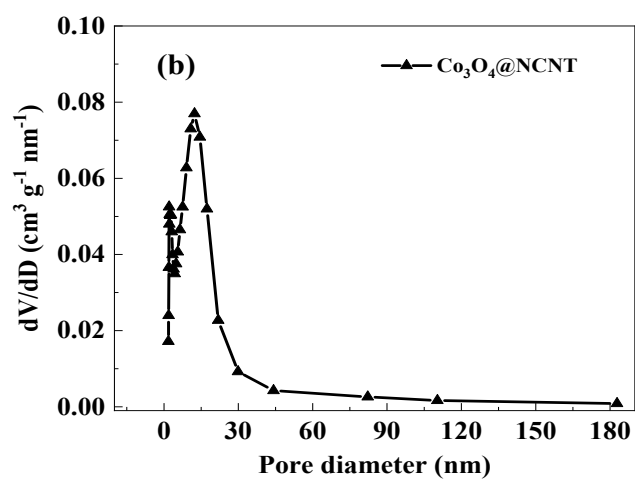
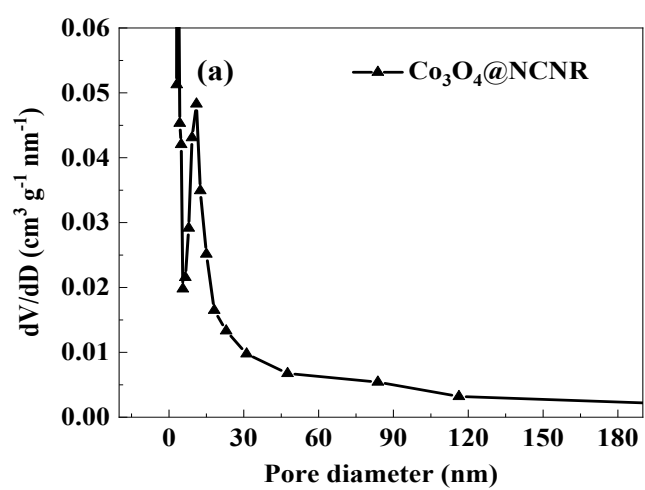


Fig. S5 The pore size distribution of (a) $\text{Co}_3\text{O}_4@\text{NCNR}$ and (b) $\text{Co}_3\text{O}_4@\text{CB}$ hybrid.

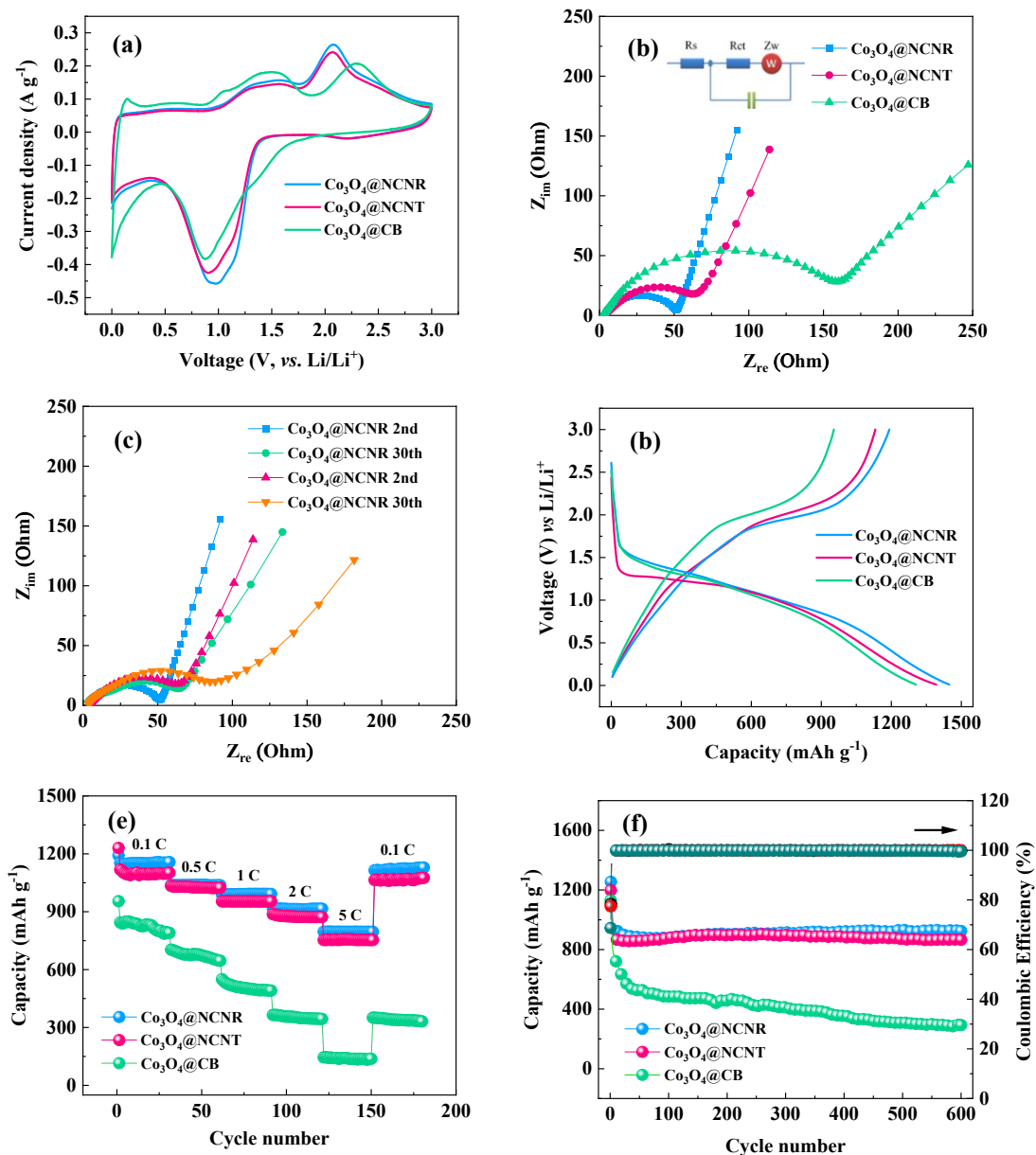


Fig. S6 $\text{Co}_3\text{O}_4@ \text{NCNR}$, $\text{Co}_3\text{O}_4@ \text{NCNT} || \text{Li}$ half-cells: (a) CV at 0.1 mV s⁻¹, (b) EIS and equivalent circuit model (inset), (c) voltage window of 0.01-3 V, (d) rate capability from 100 mA g⁻¹ to 5 A g⁻¹, and (e) long-term cycling performance at 1 A g⁻¹, the capacity based on the mass of Co_3O_4 .

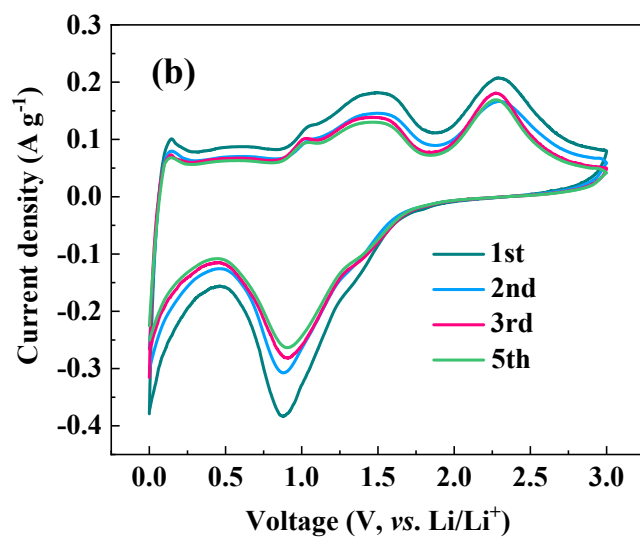
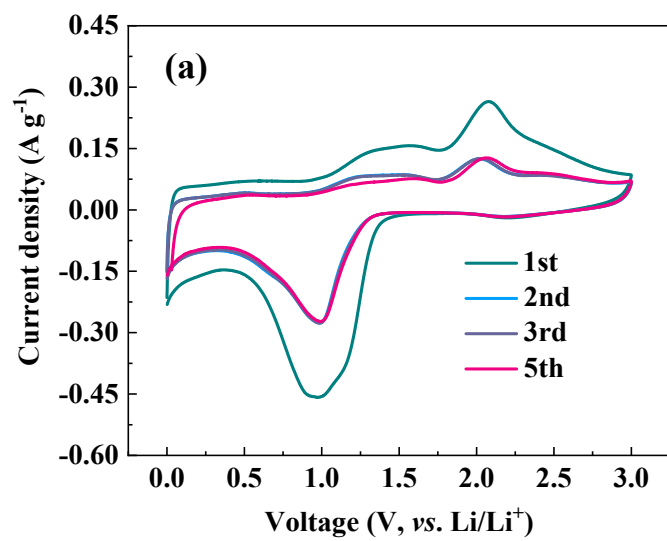


Fig. S7 CV curves of (a) $\text{Co}_3\text{O}_4@\text{NCNR}$ and (b) $\text{Co}_3\text{O}_4@\text{CB}$ hybrid electrodes at the 1st, 2nd, 3rd and 5th cycle.

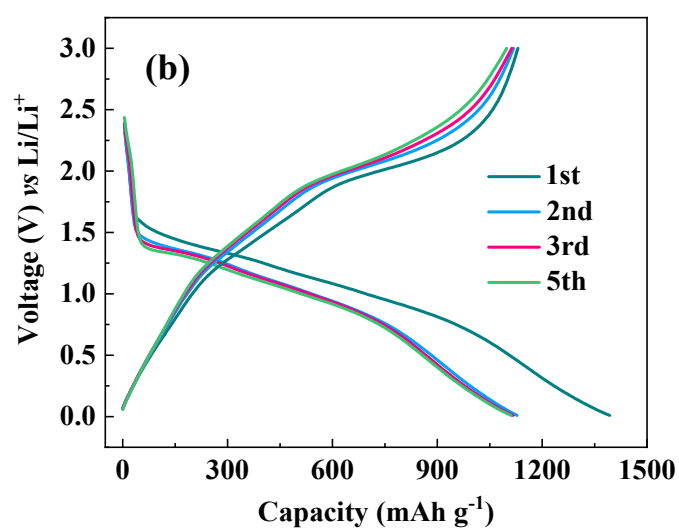
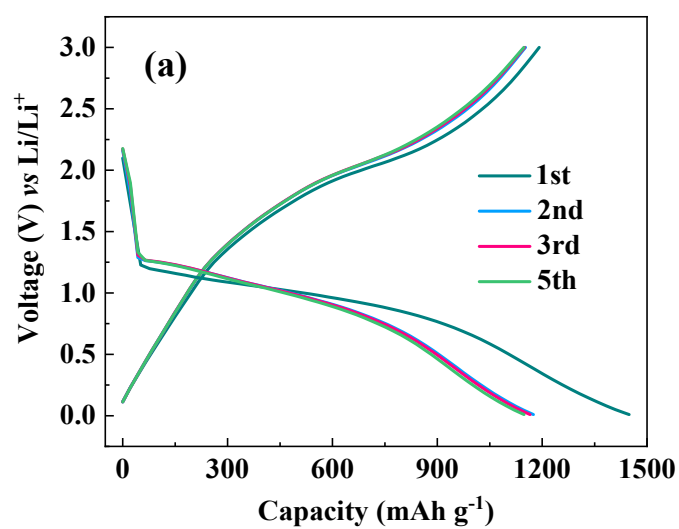


Fig. S8 Discharge/charge voltage window of (a) $\text{Co}_3\text{O}_4@\text{NCNR}$ and (b) $\text{Co}_3\text{O}_4@\text{NCNT}$ hybrid electrodes at the 1st, 2nd, 3rd and 5th cycle between 0.01-3 V.

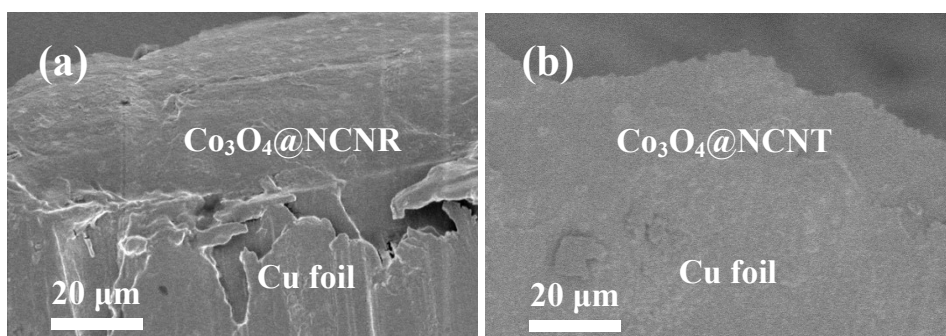


Fig. S9 The cross-sectional SEM images of (a) Co₃O₄@NCNR and (b) Co₃O₄@NCNT electrode after 600 cycles.

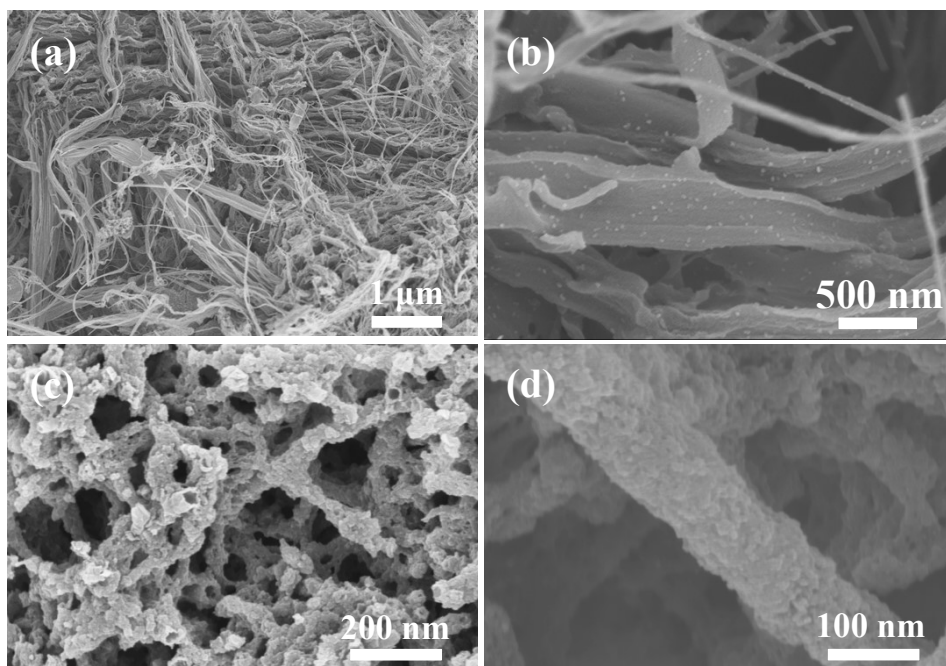


Fig. S10 Top-view SEM images of (a, b) Co₃O₄@NCNR and (c, d) Co₃O₄@NCNT electrode after 600 cycles.

Table S1. Comparison of the electrochemical performances of various Co₃O₄-based anode materials for LIBs.

Electrode materials	Current density [A g ⁻¹]	Initial discharge/charge capacities [mA h g ⁻¹]	Discharge capacity [mA h g ⁻¹] and (cycle number)	Rate capability [mA h g ⁻¹]	Ref.
Co ₃ O ₄ @C polyhedrons	1.0	1463/1118 (0.1 A g ⁻¹)	840 (150)	596 (5.0 A g ⁻¹)	[S1]
Co ₃ O ₄ /carbon (Co ₃ O ₄ /C)	0.089	1458/945 (0.089A g ⁻¹)	877 (200)	669 (2.0 A g ⁻¹)	[S2]
Double carbon coated cross-linked Co ₃ O ₄ (Co ₃ O ₄ NP@NC@CNTs)	1.0	1570/1020	1017(500)	537 (8.0 A g ⁻¹)	[S3]
Co@Co ₃ O ₄ /CNTs nanocomposite	2.0	1115/750	529 (600)	529 (2.0 A g ⁻¹)	[S4]
Co ₃ O ₄ nanoparticles embedded carbonaceous fibre (Co ₃ O ₄ /CF)	0.089	1246/733 (0.089 A g ⁻¹)	730 (100)	240 (4.45A g ⁻¹)	[S5]
three-dimensional Co ₃ O ₄ /C nanocomposites	2.0	1143/862 (0.1 A g ⁻¹)	561 (500)	593 (2.0 A g ⁻¹)	[S6]
Co ₃ O ₄ nanoparticles into nitrogen-doped graphitic carbon nanofibers (Co ₃ O ₄ @NGFs)	2.0	1060.2/500.8 (2.0 A g ⁻¹)	408.4 (600)	484.4 (2.0 A g ⁻¹)	[S7]
the in-situ fabricated 3D flower-like hybrid with Co ₃ O ₄ nanoparticles (Co ₃ O ₄ /NC)	0.5	1265.4/989.1 (0.1 A g ⁻¹)	671.1 (500)	498.8 (4.0 A g ⁻¹)	[S8]
N-doped carbon	1.0	1567/768	905 (350)	271	[S9]

coated hollow Co ₃ O ₄ nanocrystals H-N-C@Co ₃ O ₄ /CNT				(12.5 A g ⁻¹)	
Co ₃ O ₄ /Co@N-doped carbon nanotubes (T-Co ₃ O ₄ /Co@NC)	0.5	693/563.5	689.2 (400)	655.4 (0.2 A g ⁻¹)	[S10]
Nitrogen-doped carbon nanobelts decorated with Co ₃ O ₄ nanoparticles (Co ₃ O ₄ @NCNR)	1.0	1389.2/1050.7 (0.1 A g ⁻¹)	944.7(600)	768 (5.0 A g ⁻¹)	This work

References

- [S1] Y. L. Tan, C. X. Yang, W. W. Qian, X. Sui, C. Teng, Q. Li, Z. Lu, Carbon coated porous Co₃O₄ polyhedrons as anode materials for highly reversible lithium-ion storage, *J. Alloys Compd.*, 2021, **855**, 157387.
- [S2] G. R. Wang, F. L. Zhu, J. Xia, L. Wang, Y. S. Meng, Y. Zhang, Preparation of Co₃O₄/carbon derived from ionic liquid and its application in lithium-ion batteries, *Electrochim. Acta*, 2017, **257**, 138-145.
- [S3] Y. Wang, S. J. Fan, S. X. Wu, C. Wang, Z. G. Huang and L. Zhang, In situ synthesis and unprecedented electrochemical performance of double carbon coated cross-linked Co₃O₄, *ACS Appl. Mater. Interfaces*, 2018, **10**, 42372-42379.
- [S4] Y. T. Zhao, W. J. Dong, M. S. Riaz, H. X. Ge, X. Wang, Z. C. Liu and F. Q. Huang, "Electron-sharing" mechanism promotes Co@Co₃O₄/CNTs composite as the high-capacity anode material of lithium-ion battery, *ACS Appl. Mater. Interfaces*, 2018, **10**, 43641-43649.
- [S5] J. Sun, D. Li, Y. Xia, X. Zhu, L. Zong, Q. Ji, Y. A. Jia and D. Yang, Co₃O₄ nanoparticle embedded carbonaceous fibres: a nanoconfinement effect on enhanced lithium-ion storage, *Chem. Commun.*, 2015, **51**, 16267-16270.
- [S6] F. Wang, Y. X. Long, J. G. Zong, M. Zhao, S. Yang and X. Song, Three-dimensional nanocomposites with Co₃O₄ nanosheets parallelly embedded in carbon network walls for enhanced lithium-ion storage, *Dalton Trans.*, 2019, **48**, 8375-8383.
- [S7] Y. Chen, T. Wu, W. Chen, W. Zhang, L. Zhang, Z. Zhu, M. Shao, B. Zheng, S. Li, W. Zhang, W. Pei, J. Wu and F. Huo, Co₃O₄ nanoparticles embedded in nitrogen-doped graphitic carbon fibers as free-standing electrode for promotion of lithium ion storage with capacitive contribution, *Chem. Commun.*, 2020, **56**, 5767-5770.
- [S8] J. Li, D. Yan, S. Hou, T. Lu, Y. Yao, L. Pan, Metal-organic frameworks converted flower-like hybrid with Co₃O₄ nanoparticles decorated on nitrogen-doped carbon sheets for boosted lithium storage, performance, *Chem. Eng. J.*, 2018, **354**, 172-181.

- [S9] S. J. Huang, L. W. Yang, G. B. Xu, T. Y. Wei, J. Tian, X. Liu, H. P. Li, Z. Y. Xiang, J. X. Cao, X. L. Wei, Hollow Co_3O_4 @N-doped carbon nanocrystals anchored on carbon nanotubes for freestanding anode with superior Li/Na storage performance, *Chem. Eng. J.*, 2021, **415**, 128861.
- [S10] Z. Chen, S. Wang, Z. Zhang, W. Zhou, D. Chen, Facile synthesis of $\text{Co}_3\text{O}_4/\text{Co}$ @N-doped carbon nanotubes as anode with improved cycling stability for Li-ion batteries, *Electrochim. Acta*, 2018, **292**, 575-585.