

Interconnected hierarchical NiCo_2O_4 microspheres as high performance electrode material for supercapacitor

Ming Cheng,^a Hongsheng Fan,^a Yuanjun Song,^b Yimin Cui,^a and Rongming Wang^{*b}

^a Department of Physics, Beihang University, Beijing 100191, P. R. China

^b Beijing Key Laboratory for Magneto-Photoelectrical Composite and Interface Science, School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, P. R. China

E-mail: rmwang@ustb.edu.cn

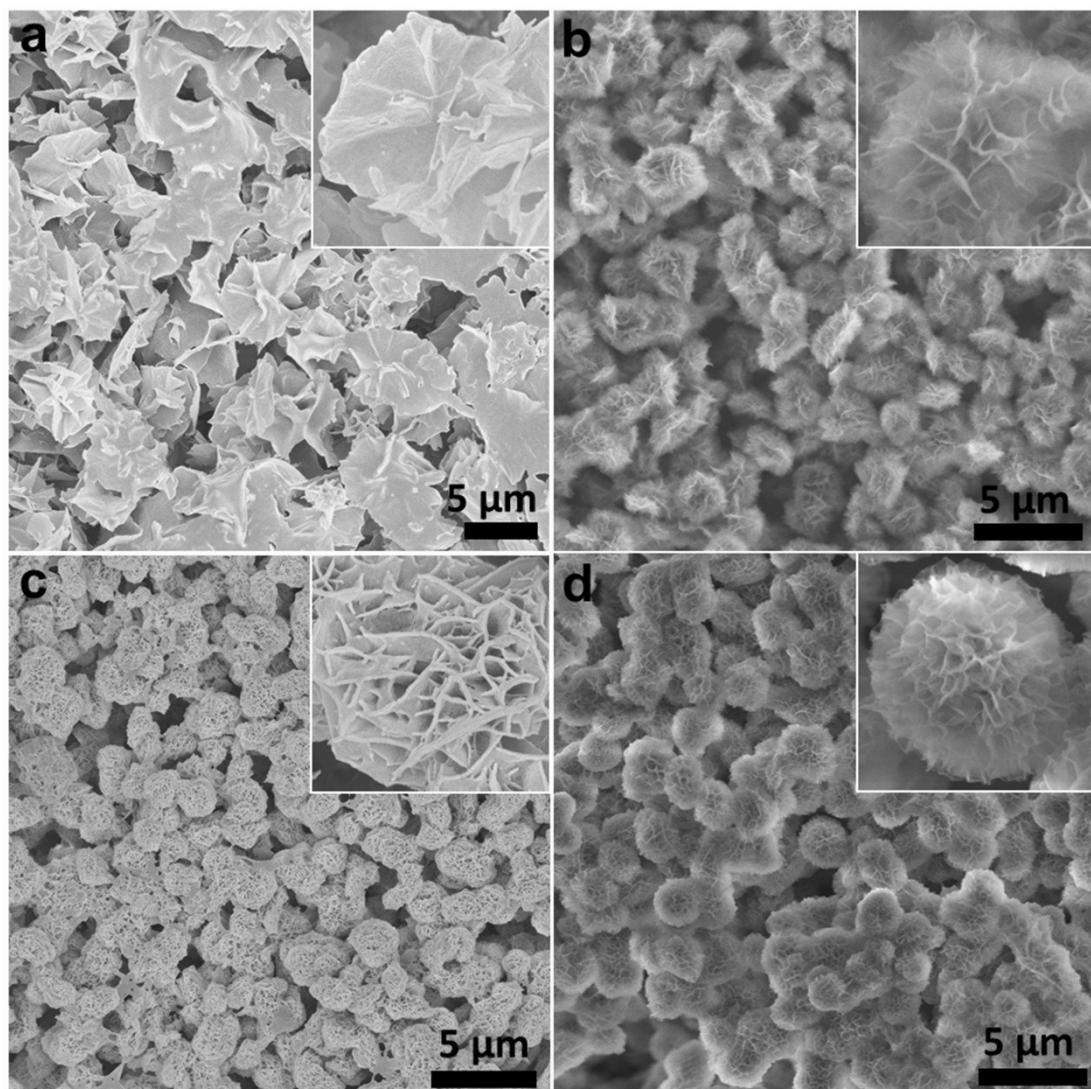


Fig. S1 Typical SEM images of the nickel-cobalt glycolate precursor synthesized with 1 mL deionized water and different amount of IPA and EG: (a) 40 mL IPA and 20 mL EG, (b) 35 mL IPA and 25 mL EG, (c) 30 mL IPA and 20 mL EG, (d) 25 mL IPA and 35 mL EG.

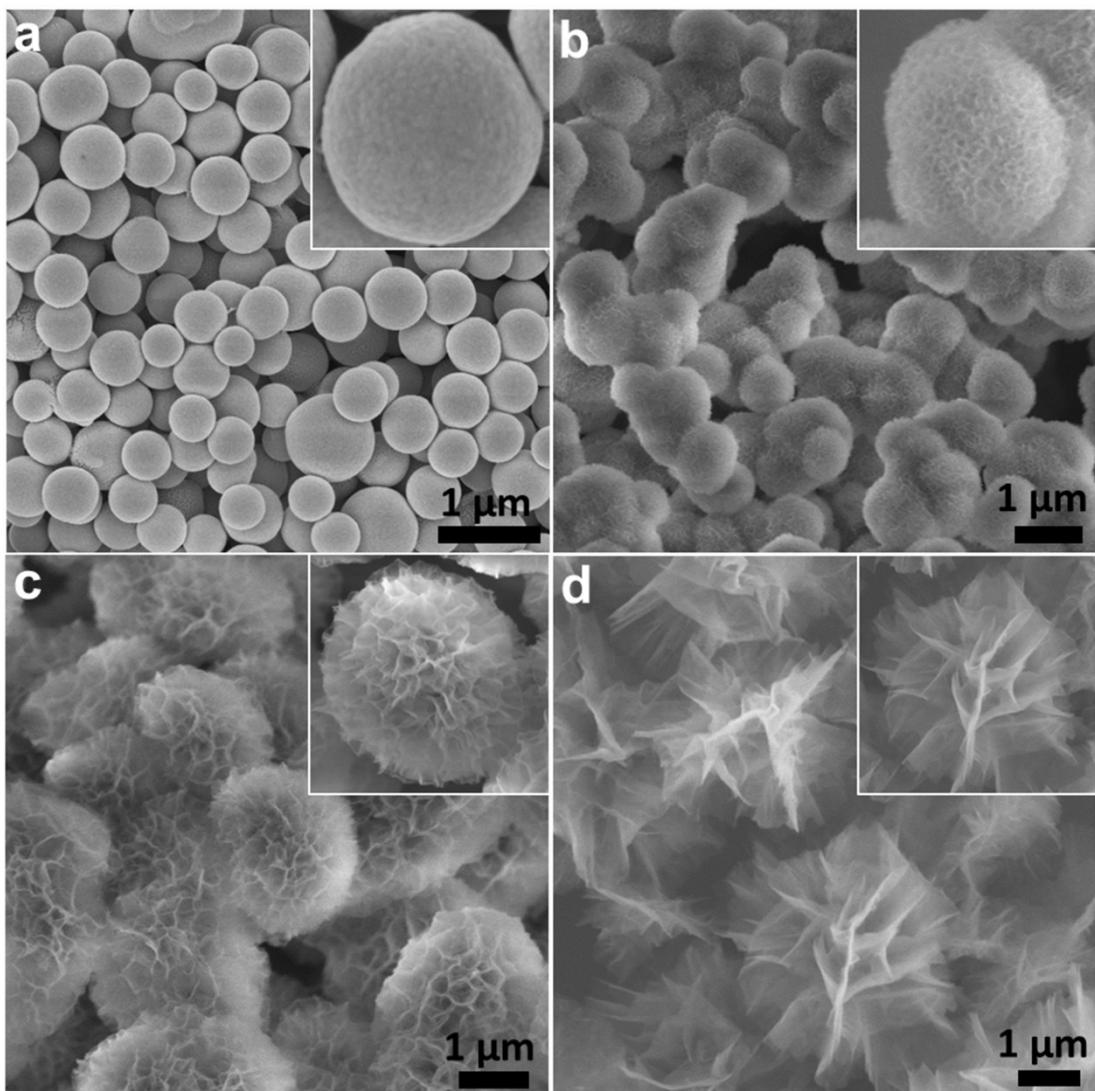


Fig. S2 Typical SEM images of the nickel-cobalt glycolate precursor synthesized with 25 mL IPA and 35 mL EG and different amount of deionized water: (a) 0 mL , (b) 0.5 mL, (c) 1 mL, (d) 1.5 mL.

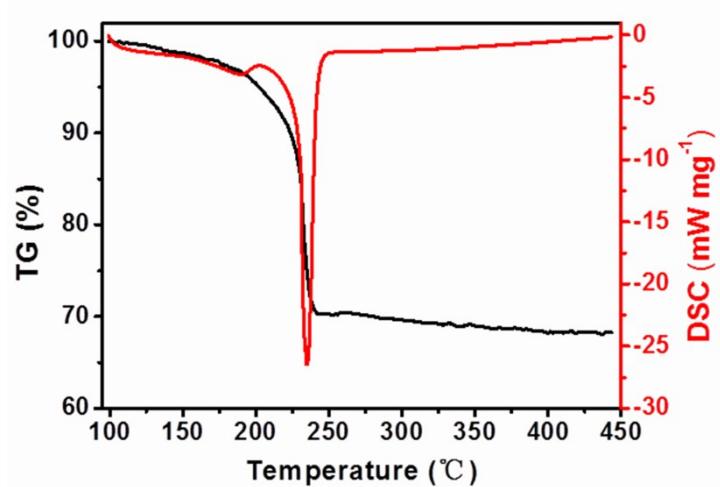


Fig. S3 TGA curves of the NiCo_2O_4 precursor.

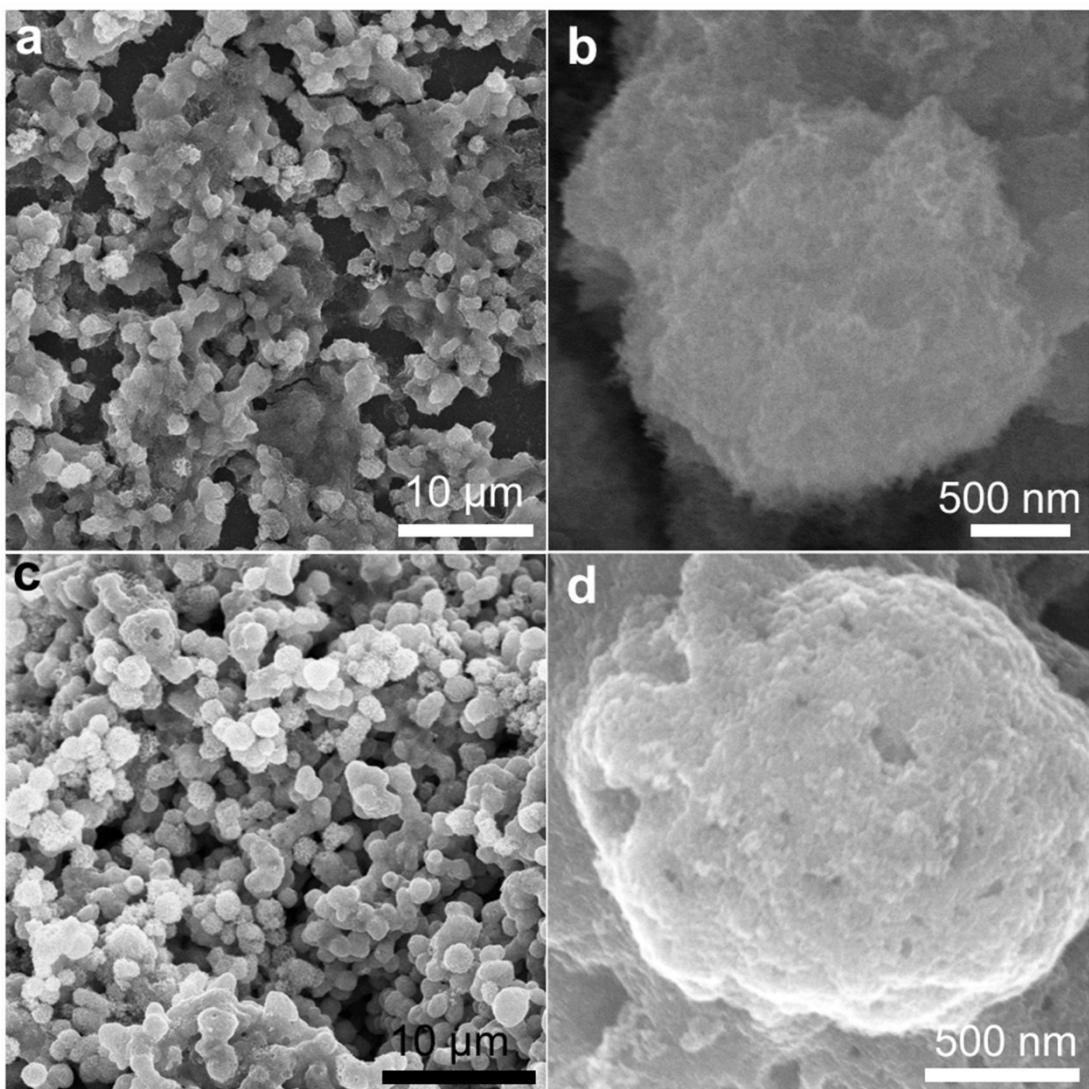


Fig. S4 SEM images of the obtained NiCo_2O_4 products after calcined at in air at 250 °C (a,b) and 300 °C (c,d).

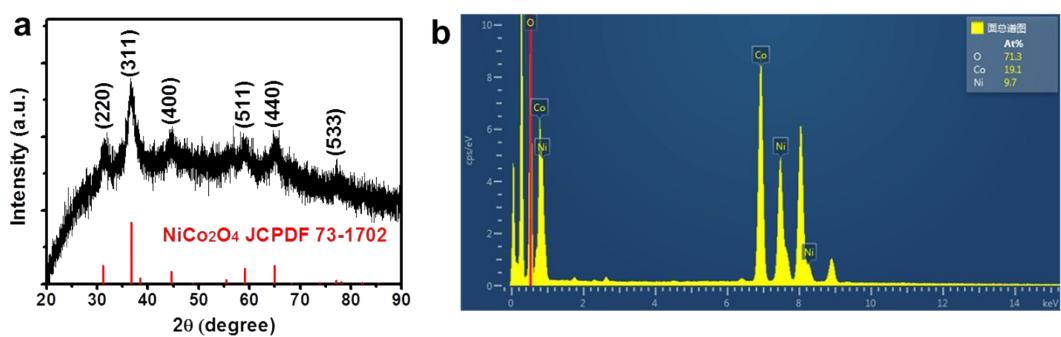


Fig. S5 XRD pattern (a) and EDS spectrum (b) of the IH- NiCo_2O_4 sample.

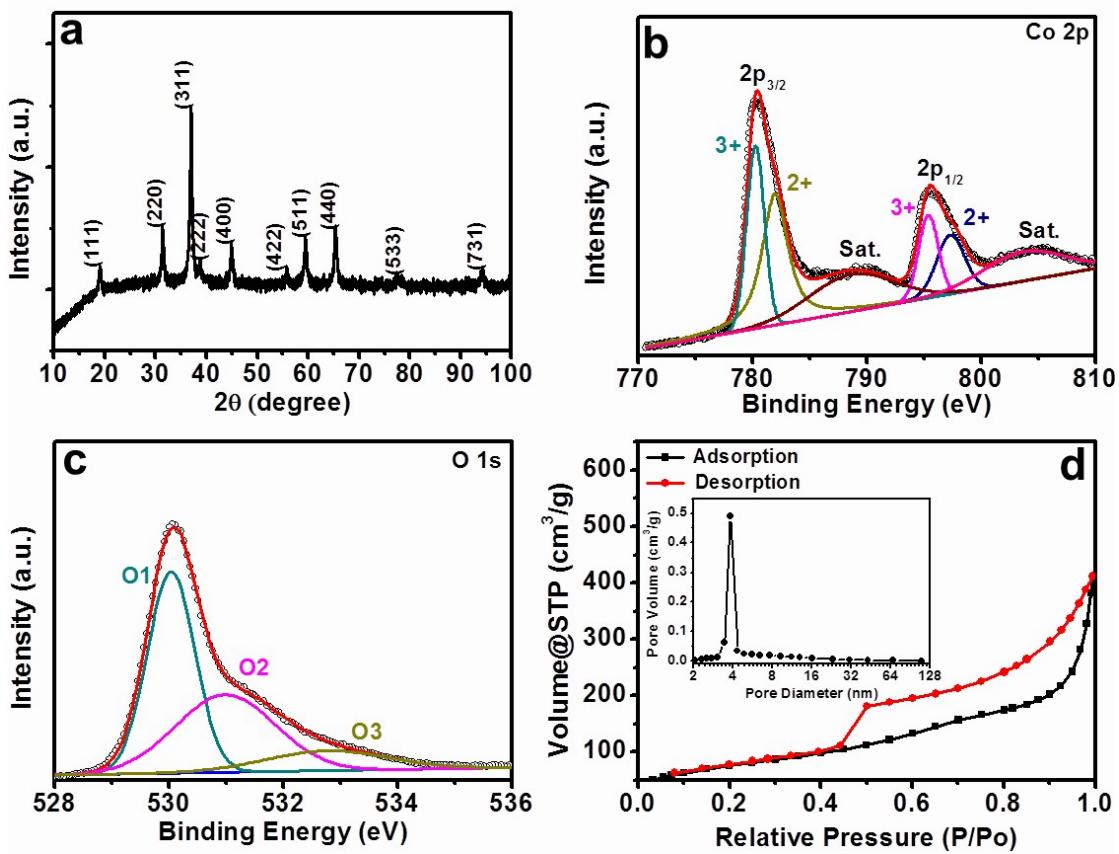


Fig. S6 (a) XRD pattern of the IH-Co₃O₄ sample. High resolution XPS spectra for the Co 2p (b) and O 1s (c) of the IH-Co₃O₄ sample. (d) Typical N₂ adsorption and desorption isotherms and the pore-size-distribution curves (inset) of the IH-Co₃O₄.

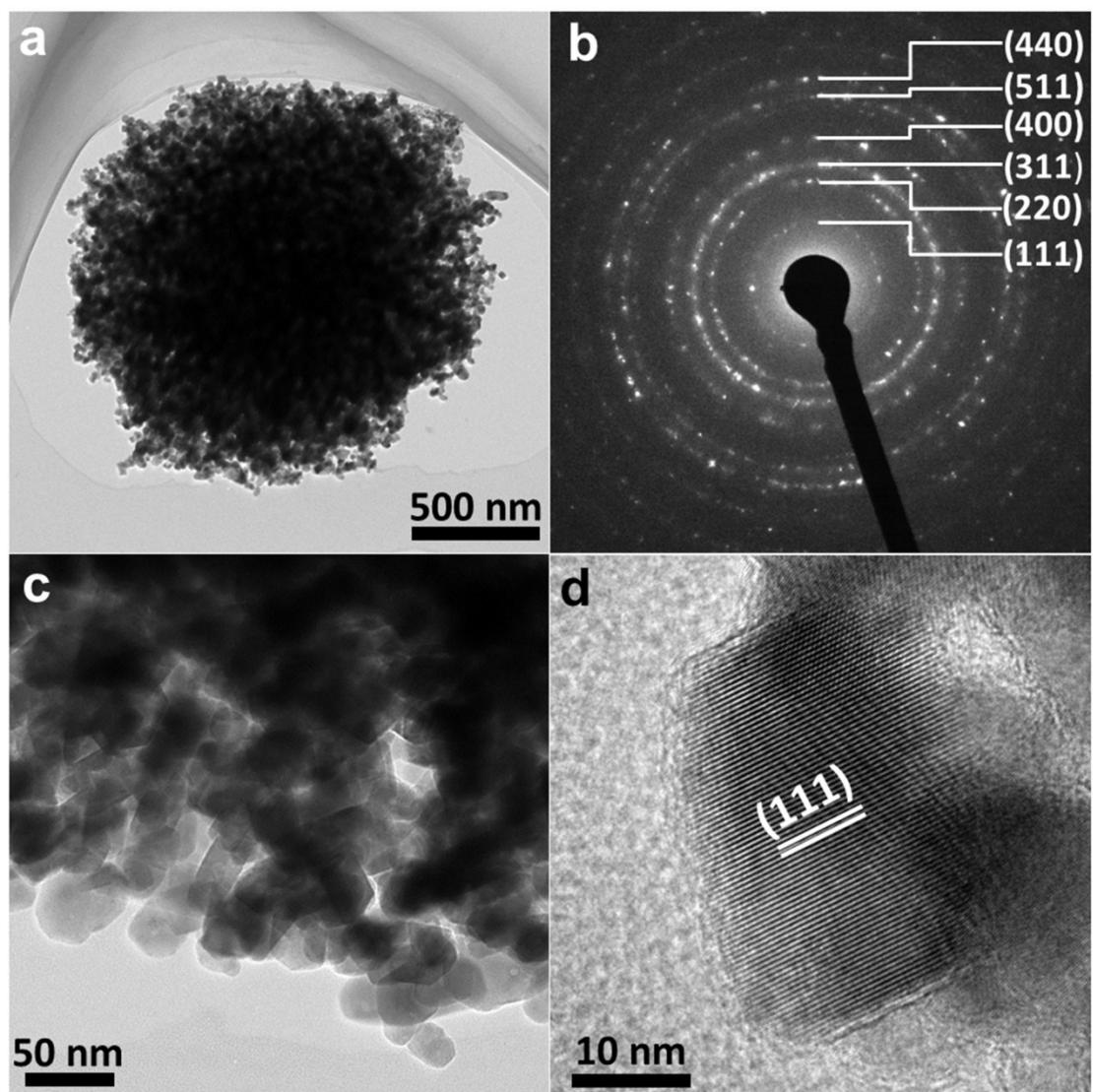


Fig. S7 TEM image (a) and corresponding SAED pattern (b) of an individual IH-Co₃O₄ microsphere. (c) TEM image of the local characteristic region of the IH-Co₃O₄ microsphere. (d) HRTEM lattice image of the IH-Co₃O₄ microsphere.

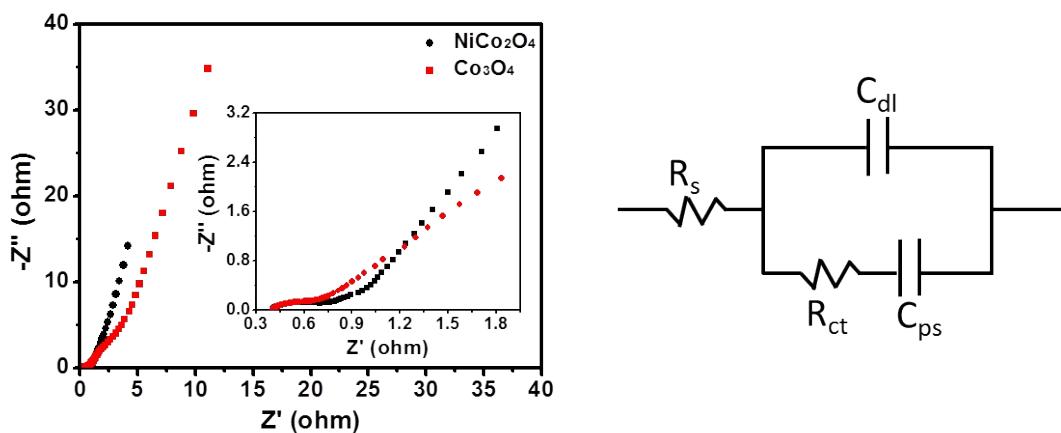


Fig. S8 EIS plots of the IH- NiCo_2O_4 and IH- Co_3O_4 and the equivalent circuit model for the EIS spectra.

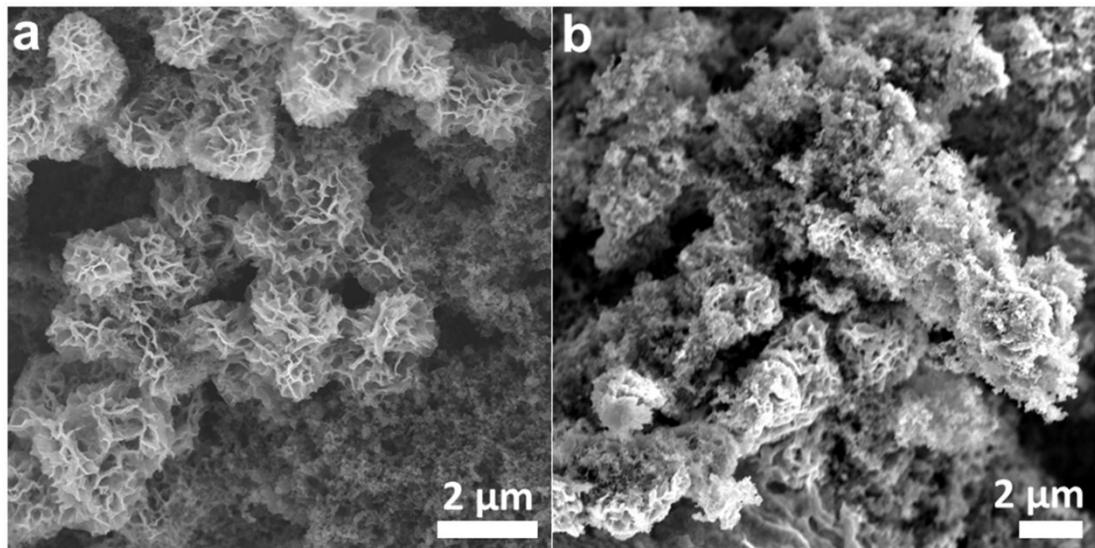


Fig. S9 SEM images of the IH- NiCo_2O_4 electrode before (a) and after (b) 7000 cycles at a high current density of 10 g A^{-1} .

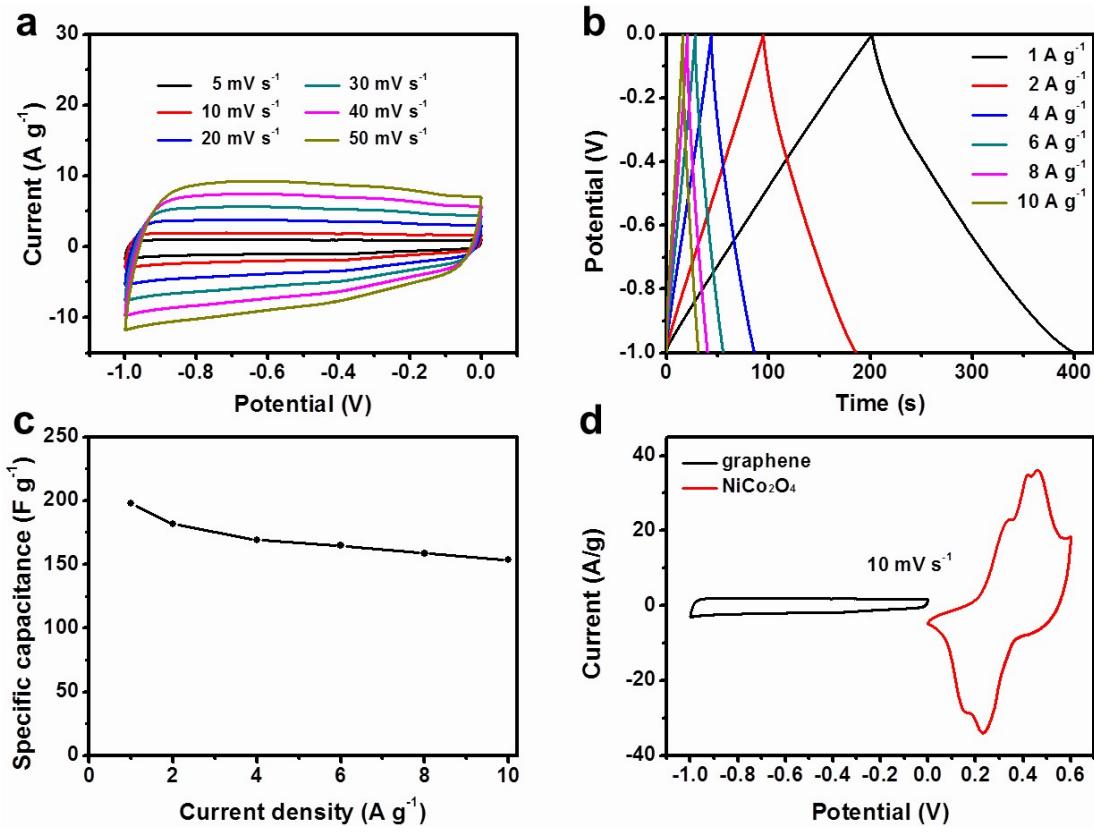
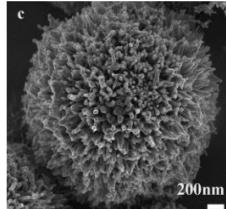
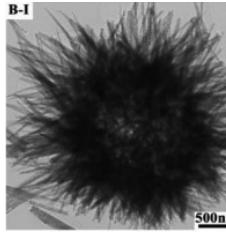
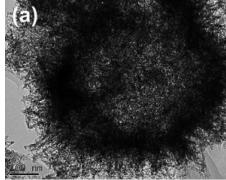
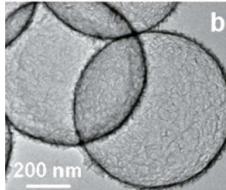
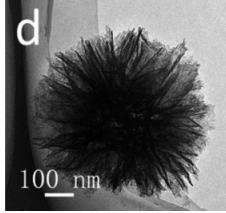
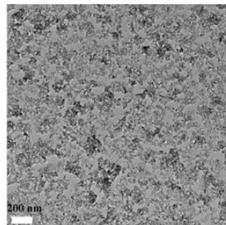
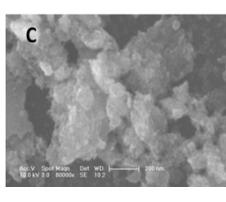
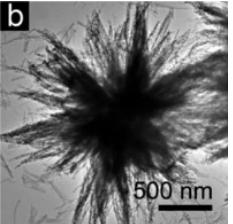
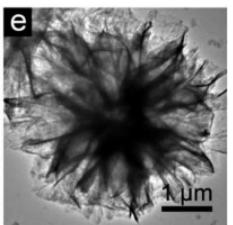
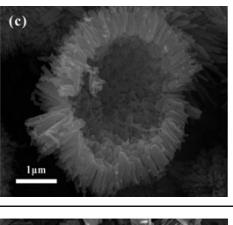
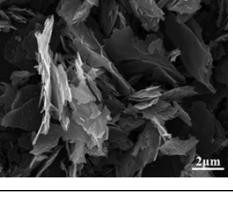
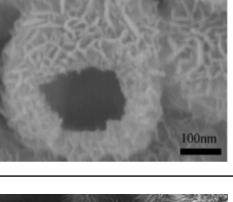
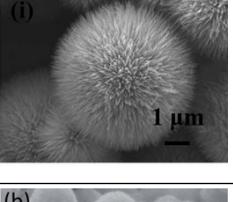
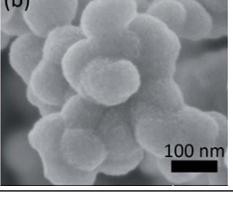
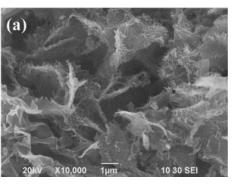
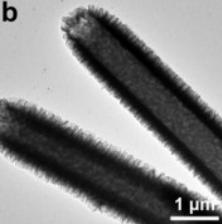
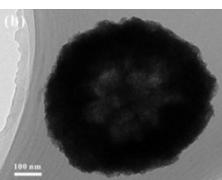
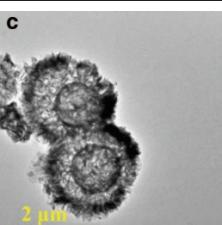
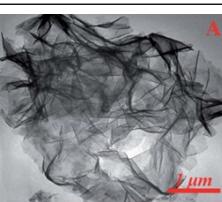
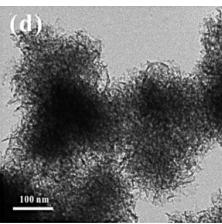
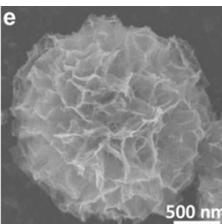


Fig. S10 CV curves at different scan rates (a) and charge-discharge curves at different current densities (b) of the graphene electrode. (c) The corresponding specific capacitances at different current densities of the graphene electrode. (d) Compared CV curves of the IH-NiCo₂O₄ and graphene at a scan rate of 10 mV s^{-1} .

Table S1 A comparison with previously reported NiCo₂O₄ nanomaterials.

Material	Morphology	Mass loading (mg cm ⁻²)	Potential Window (V)	Specific capacitance@current density	Capacity retention (%)
Rambutan-like NiCo ₂ O ₄ ¹		2.0	0-0.4	798 F g ⁻¹ @0.5 A g ⁻¹	91.7(1500 cycles@2 A g ⁻¹)
Urchin like NiCo ₂ O ₄ ²		>1	0-0.45	658 F g ⁻¹ @1 A g ⁻¹	98.4(1000 cycles@10 A g ⁻¹)
Hollow urchin-like NiCo ₂ O ₄ microspheres ³		2.5-3.5	0-0.5	950 F g ⁻¹ @1 A g ⁻¹	93.6(1500 cycles@6 A g ⁻¹)
Hollow NiCo ₂ O ₄ sub-microspheres ⁴		8	0-0.4	678 F g ⁻¹ @1 A g ⁻¹	87(3500 cycles@10 A g ⁻¹)
Flower-like NiCo ₂ O ₄ hierarchitectures ⁵		—	0-0.55	1191.2 F g ⁻¹ @1 A g ⁻¹	78(1200 cycles@1 A g ⁻¹)
Spinel NiCo ₂ O ₄ nanostructure ⁶		1	0-0.4	1362 F g ⁻¹ @1 A g ⁻¹	41(1500 cycles@4 A g ⁻¹)
NiCo ₂ O ₄ nanoflake composites ⁷		2	0-0.4	1468 F g ⁻¹ @4 A g ⁻¹	85.5(5000 cycles@4 A g ⁻¹)

Nanowires building NiCo_2O_4 architectures ⁸		1.3	0-0.5	1080 F g^{-1} @ 2 A g^{-1}	86.5(1500 cycles@ 4 A g^{-1})
Nanosheets building NiCo_2O_4 architectures ⁸		1.3	0-0.5	1400 F g^{-1} @ 5 A g^{-1}	94(1500 cycles@ 4 A g^{-1})
Nanorod-assembled NiCo_2O_4 hollow microspheres ⁹		—	0-0.5	764 F g^{-1} @ 2 A g^{-1}	101.7(1500 cycles@ 2 A g^{-1})
NiCo_2O_4 nanosheets ¹⁰		—	0-0.45	876 F g^{-1} @ 1 A g^{-1}	88(1000 cycles@ 1 A g^{-1})
Hierarchical mesoporous NiCo_2O_4 hollow nanocubes ¹¹		1	0-0.45	795.6 F g^{-1} @ 1 A g^{-1}	97.5(2000 cycles@ 1 A g^{-1}) 96.1(2000 cycles@ 2 A g^{-1})
Urchin like NiCo_2O_4 ¹²		2.1	0-0.55	436.1 F g^{-1} @ 1 A g^{-1}	No decay(1000 cycles@ 10 A g^{-1})
Mesoporous NiCo_2O_4 nanospheres ¹³		2	0-0.4	842 F g^{-1} @ 2 A g^{-1}	107(1000 cycles@ 30 mV s^{-1})
Multiple hierarchical NiCo_2O_4 ¹⁴		5.0-6.0	0-0.45	1393 F g^{-1} @ 0.5 A g^{-1}	—

Hierarchical NiCo ₂ O ₄ tetragonal microtubes ¹⁵		1.0	0-0.53	1387.9 F g ⁻¹ @2 A g ⁻¹	89.4(2000 cycles@10 A g ⁻¹)
Hollow NiCo ₂ O ₄ submicrospheres ¹⁶		—	0-0.5	987 F g ⁻¹ @1 A g ⁻¹	No decay(5000 cycles@5 A g ⁻¹)
NiCo ₂ O ₄ double- shell hollow spheres ¹⁷		3.76	0-0.4	781 F g ⁻¹ @1 A g ⁻¹	85.8(2000 cycles@2 A g ⁻¹)
Mesoporous NiCo ₂ O ₄ nanosheets ¹⁸		1	0-0.35	292 F g ⁻¹ @1 A g ⁻¹	90(2000 cycles@8 A g ⁻¹)
3D network-like mesoporous NiCo ₂ O ₄ ¹⁹		1.0	0-0.5	931 F g ⁻¹ @3 A g ⁻¹	125.5(1000 cycles@3 A g ⁻¹)
IH-NiCo ₂ O ₄ (This work)		2.1	0-0.55	1822.3 F g ⁻¹ @2 A g ⁻¹	87.6(7000 cycles@10 A g ⁻¹)

References

- Y. Shang, Y. Gai, L. Wang, L. Hao, H. Lv, F. Dong and L. Gong, *Eur. J. Inorg. Chem.*, 2017, **2017**, 2340.
- J. Xiao and S. Yang, *RSC Adv.*, 2011, **1**, 588.
- Y. Lei, Y. Wang, W. Yang, H. Yuan and D. Xiao, *RSC Adv.*, 2015, **5**, 7575.
- C. Yuan, J. Li, L. Hou, J. Lin, G. Pang, L. Zhang, L. Lian and X. Zhang, *RSC Adv.*, 2013, **3**, 18573.
- C. An, Y. Wang, Y. Huang, Y. Xu, C. Xu, L. Jiao and H. Yuan, *CrystEngComm*, 2014, **16**, 385.
- S. Jiang, Y. Sun, H. Dai, P. Ni, W. Lu, Y. Wang, Z. Li and Z. Li, *Electrochim. Acta*, 2016, **191**, 364.
- Y. Sun, X. Xiao, P. Ni, Y. Shi, H. Dai, J. Hu, Y. Wang, Z. Li and Z. Li, *Electrochim. Acta*, 2014, **121**,

270.

8. L. Yu, H. Wu, T. Wu and C. Yuan, *RSC Adv.*, 2013, **3**, 23709.
9. Y. Zhu, X. Ji, R. Yin, Z. Hu, X. Qiu, Z. Wu and Y. Liu, *RSC Adv.*, 2017, **7**, 11123.
10. L. Zhang, W. Zheng, H. Jiu, C. Ni, J. Chang and G. Qi, *Electrochim. Acta.*, 2016, **215**, 212.
11. C. Zheng, C. Cao, R. Chang, J. Hou and H. Zhai, *Phys. Chem. Chem. Phys.*, 2016, **18**, 6268.
12. J. Wang, Y. Zhang, J. Ye, H. Wei, J. Hao, J. Mu, S. Zhao and S. Hussain, *RSC Adv.*, 2016, **6**, 70077.
13. M. J. Pang, S. Jiang, G. H. Long, Y. Ji, W. Han, B. Wang, X. L. Liu, Y. L. Xi, F. Z. Xu and G. D. Wei, *RSC Adv.*, 2016, **6**, 67839.
14. S. Wang, S. Sun, S. Li, F. Gong, Y. Li, Q. Wu, P. Song, S. Fang and P. Wang, *Dalton T.*, 2016, **45**, 7469.
15. F.-X. Ma, L. Yu, C.-Y. Xu and X. W. Lou, *Energy Environ. Sci.*, 2016, **9**, 862.
16. Y. Zhu, J. Wang, Z. Wu, M. Jing, H. Hou, X. Jia and X. Ji, *J. Power Sources*, 2015, **287**, 307.
17. X. Li, L. Jiang, C. Zhou, J. Liu and H. Zeng, *NPG Asia Mater.*, 2015, **7**, e165.
18. S. Khalid, C. Cao, A. Ahmad, L. Wang, M. Tanveer, I. Aslam, M. Tahir, F. Idrees and Y. Zhu, *RSC Adv.*, 2015, **5**, 33146.
19. Y. Zhu, Z. Wu, M. Jing, W. Song, H. Hou, X. Yang, Q. Chen and X. Ji, *Electrochim. Acta*, 2014, **149**, 144.