

Electronic Supplementary Information

Rational design and synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles derived from MOF-74 as high-performance supercapacitor electrodes

Siru Chen, Ming Xue*, Yanqiang Li, Liangkui Zhu, Ying Pan and Shilun Qiu*

^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012 (P. R. China)
E-mail: xueming@jlu.edu.cn; sqiu@jlu.edu.cn.

Table of Contents

1. SEM images of MOF-74	S2
2. Elemental Mappings of mix-metal MOF-74	S2
3. EDS of MOF-74	S3
4. Thermogravimetric Analysis	S4
5. SEM images of metal oxide	S5
6. TEM images of metal oxides	S5
7. Elemental Mappings of mix-metal oxides	S6
8. EDS analysis of mix-metal oxides	S7
9. XPS Analysis	S8
10. PXRD of MOF-74-CoNi ₂ , MOF-74-CoNi ₄ and synthesized metal oxides	S9
11. HRTEM images of metal oxides	S10
12. Low-Pressure N ₂ Sorption measurements of MOF-74	S11
13. Low-Pressure N ₂ Sorption measurements of metal oxides	S12
14. Cyclic voltammetry (CV) measurements	S13
15. Galvanostatic charge–discharge measurements	S14
16. Comparison with some NiCo ₂ O ₄ materials from literature	S15
17. References	S16

1. SEM images of MOF-74

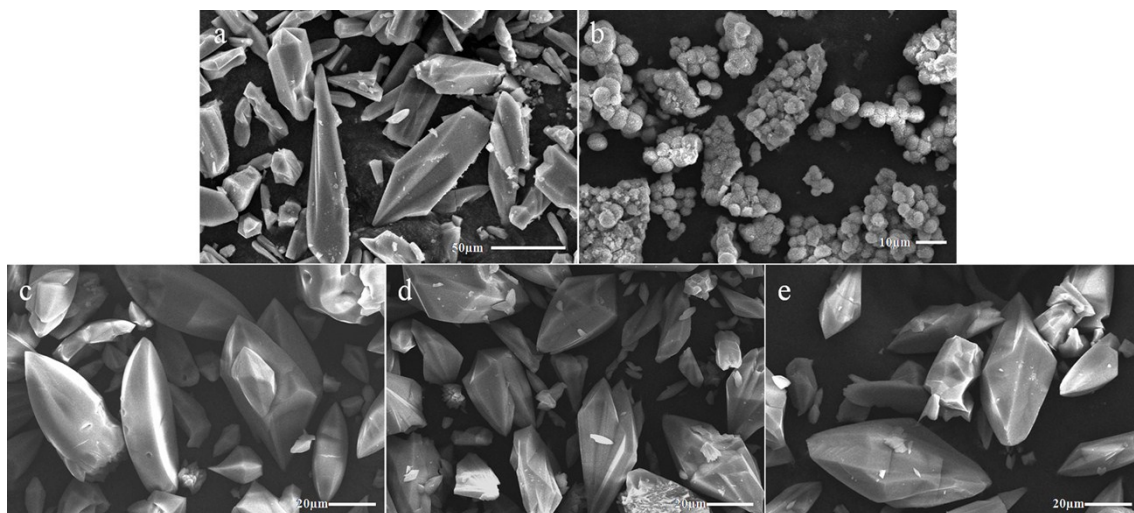


Figure S1. SEM images of: (a) MOF-74-Co, (b) MOF-74-Ni, (c) MOF-74-NiCo1, (d) MOF-74-NiCo2 and (e) MOF-74-NiCo4 samples.

2. Elemental Mappings of mix-metal MOF-74

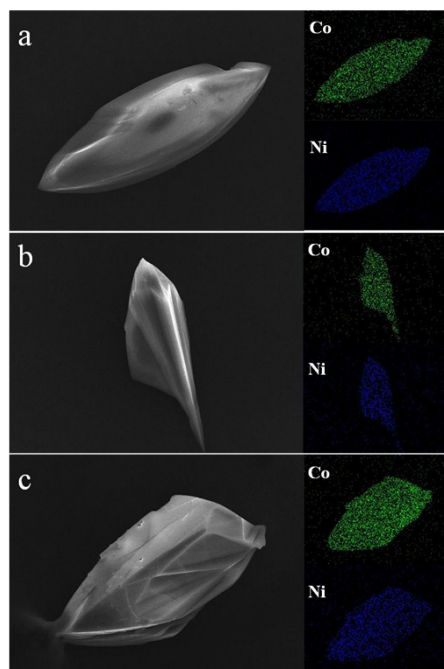


Figure S2. Elemental Mappings of: (a) MOF-74-NiCo1, (b) MOF-74-NiCo2 and (c) MOF-74-NiCo4.

3. EDS of MOF-74

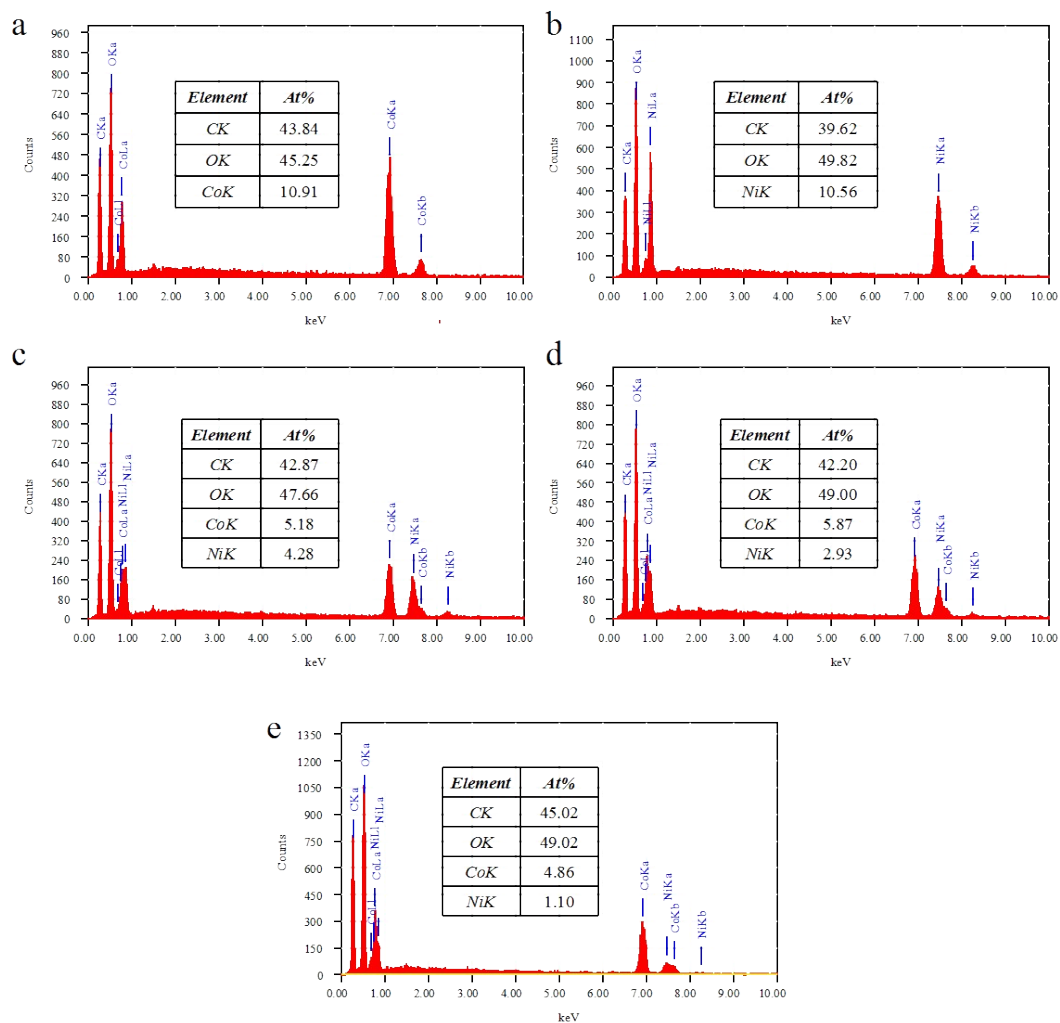


Figure S3. EDS of: (a) MOF-74-Co, (b) MOF-74-Ni, (c) MOF-74-NiCo1, (d) MOF-74-NiCo2 and (e) MOF-74-NiCo4 samples.

4. Thermogravimetric Analysis

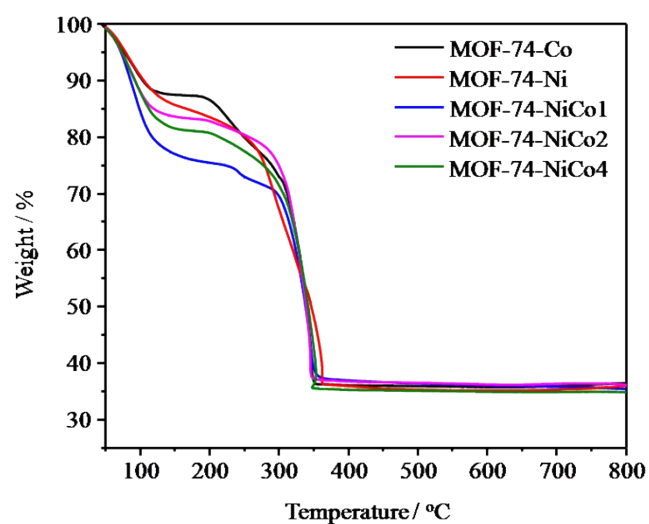


Figure S4. TGA curves of: MOF-74-Co, MOF-74-Ni, MOF-74-NiCo1, MOF-74-NiCo2 and MOF-74-NiCo4 samples under air atmosphere.

5. SEM images of metal oxide

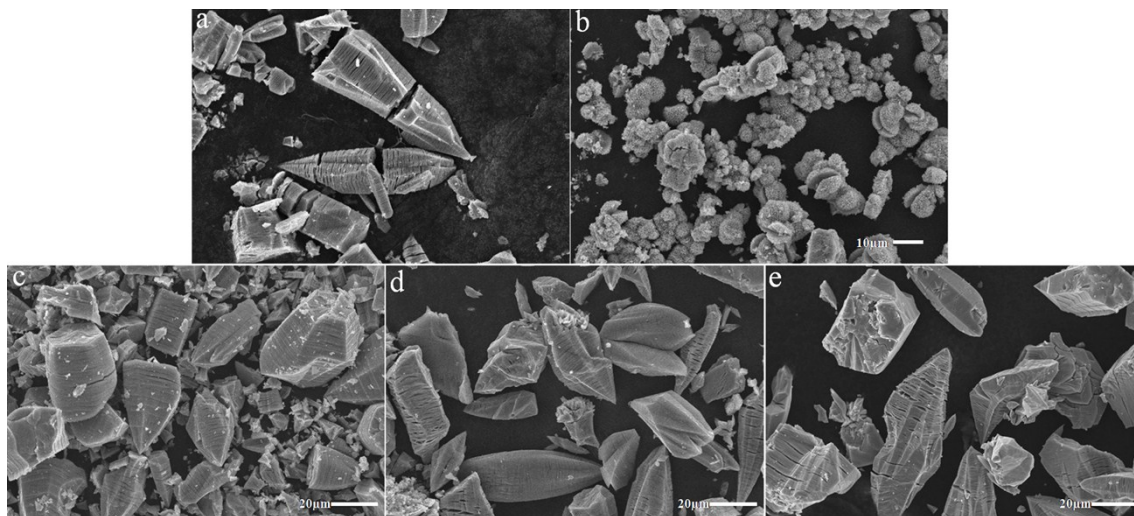


Figure S5. SEM images of: (a) Co_3O_4 , (b) NiO , (c) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -1, (c) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -2 and (d) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -4 samples.

6. TEM images of metal oxides

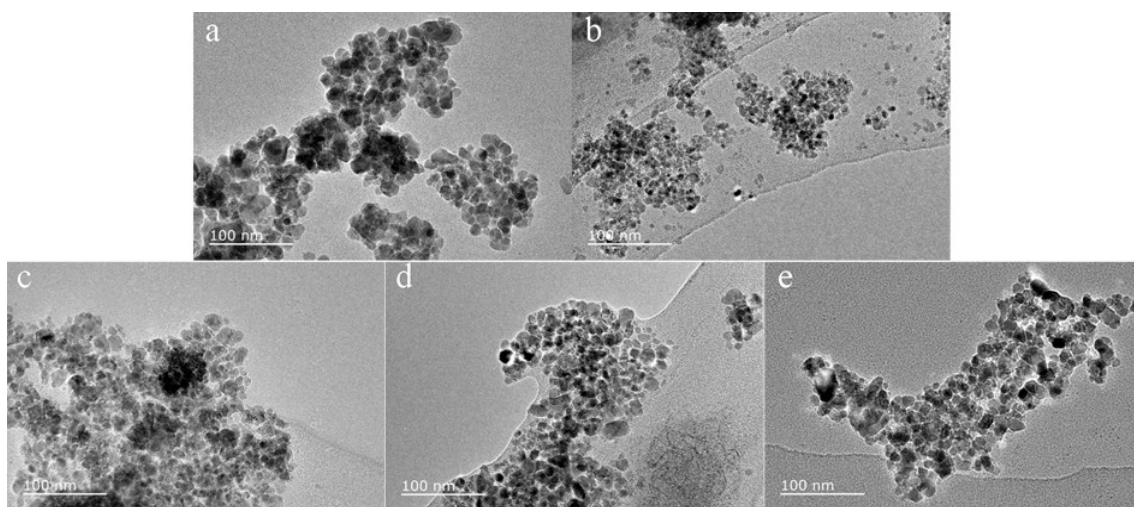


Figure S6 TEM images of: (a) Co_3O_4 , (b) NiO , (c) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -1, (c) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -2 and (d) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -4 samples.

7. Elemental Mappings of mix-metal oxides

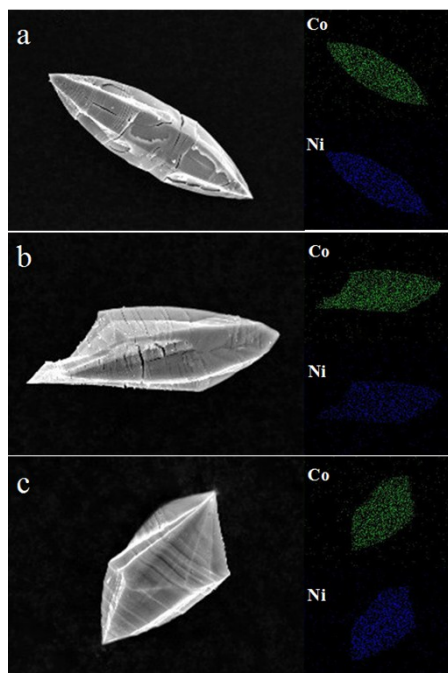


Figure S7. Elemental Mappings of: (a) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -1, (b) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -2 and (c) $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ -4 samples.

8. EDS analysis of metal oxides.

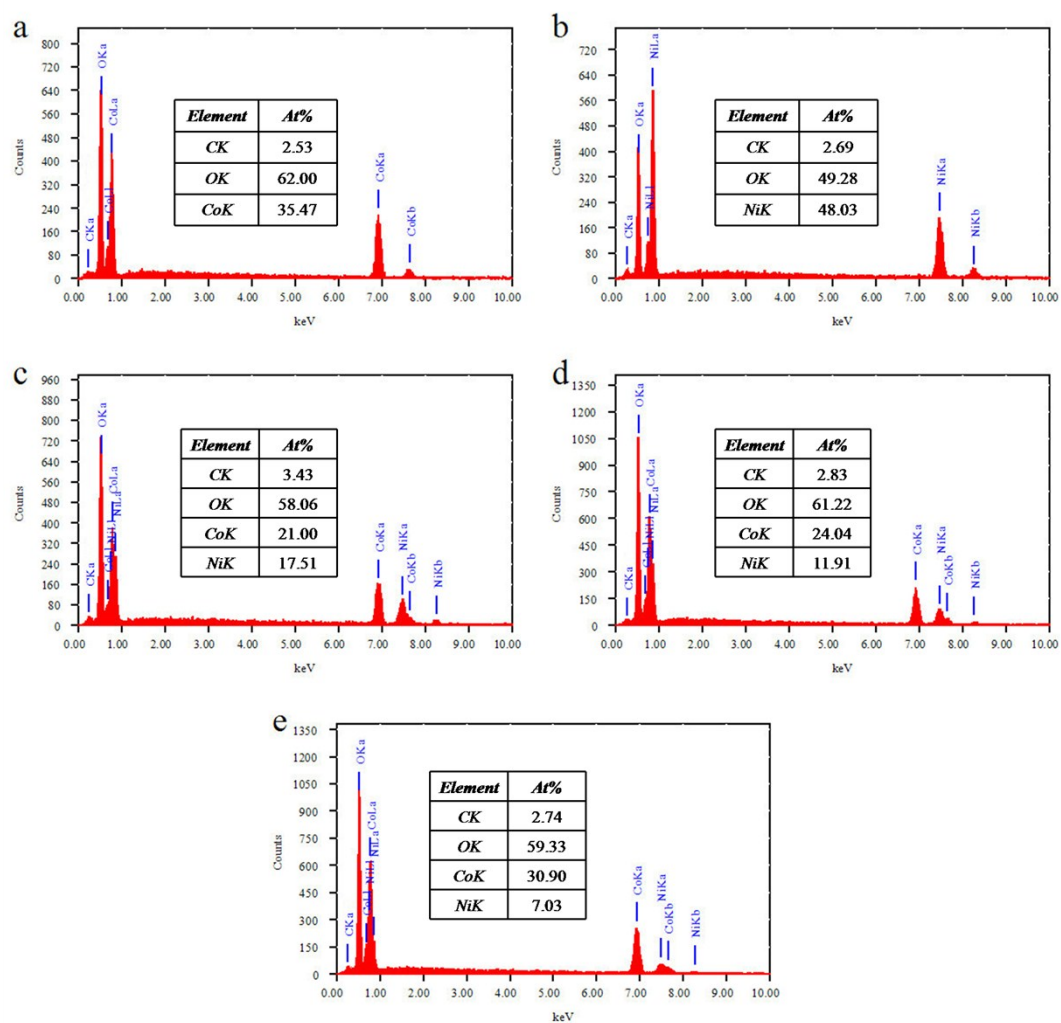


Figure S8. EDS of: (a) Co_3O_4 , (b) NiO , (c) $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-1}$, (d) $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-2}$ and (e) $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-4}$ samples.

9. XPS Analysis

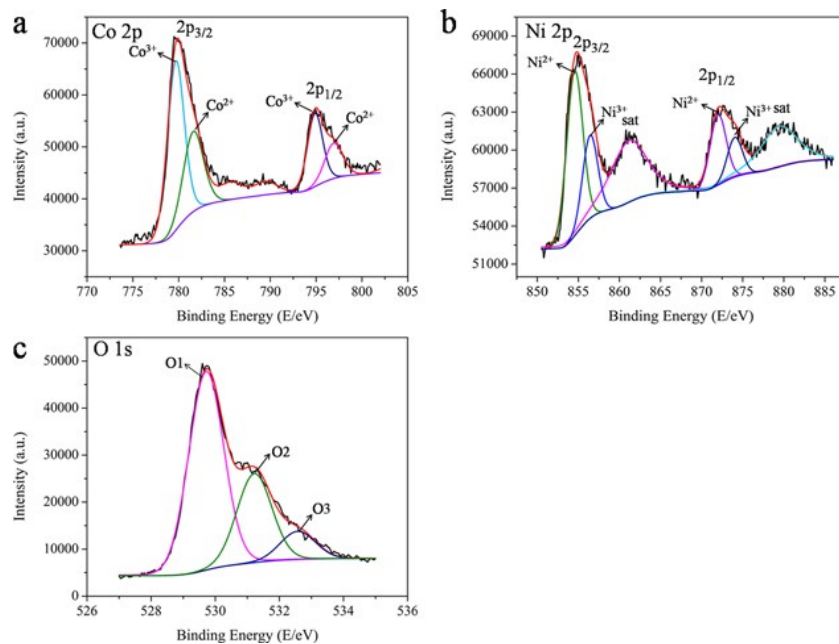


Figure S9. (a) Co 2p; (b) Ni 2p; and (c) O 1s XPS spectra of the as-prepared $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-2}$ sample.

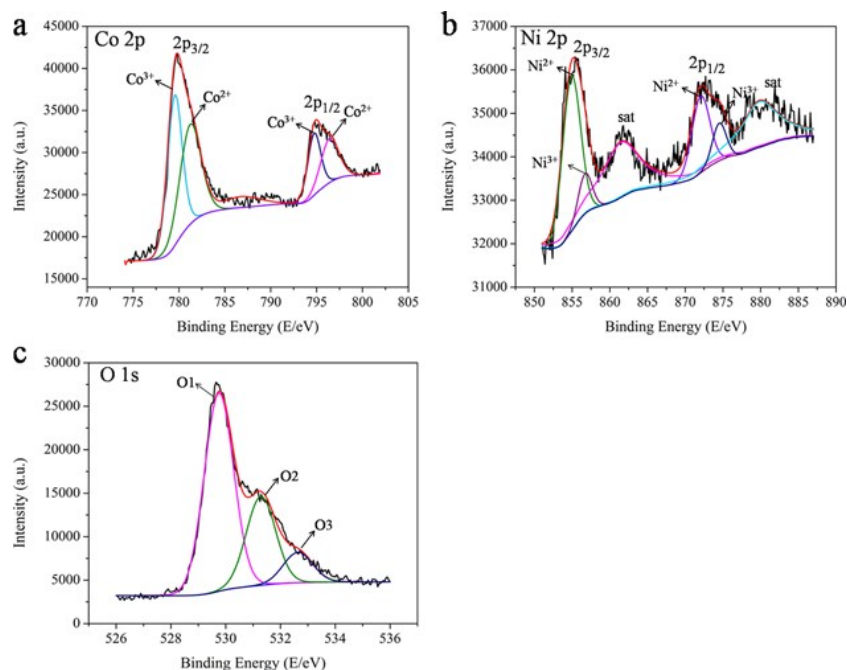


Figure S10. (a) Co 2p; (b) Ni 2p; and (c) O 1s XPS spectra of the as-prepared $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-4}$ sample.

10. PXRD of MOF-74-CoNi₂, MOF-74-CoNi₄ and synthesized metal oxides.

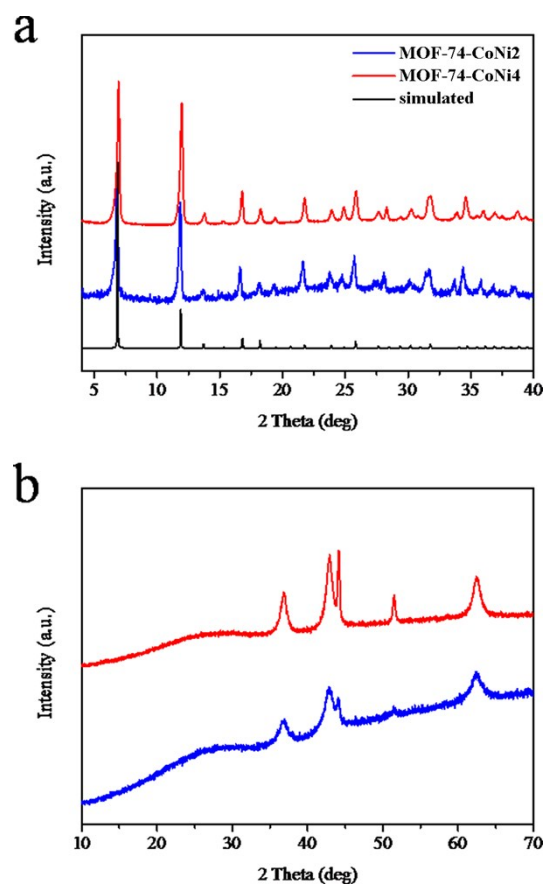


Figure S11. PXRD of (a) MOF-74-CoNi₂ and MOF-74-CoNi₄; (b) the synthesized metal oxides.

11. HRTEM images

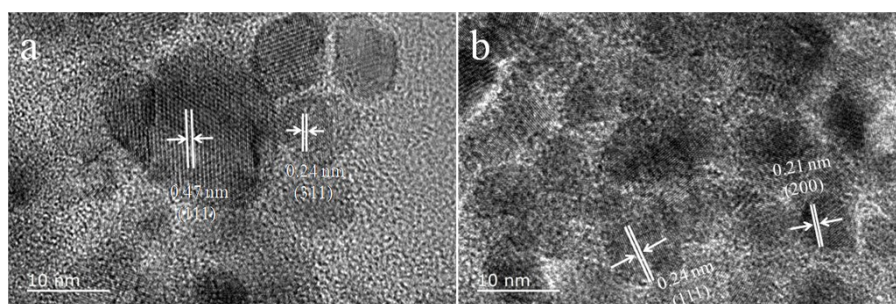


Figure S12. HRTEM images: (a) Co₃O₄ and (b) NiO samples.

12. Low-Pressure N₂ Sorption measurements of MOF-74

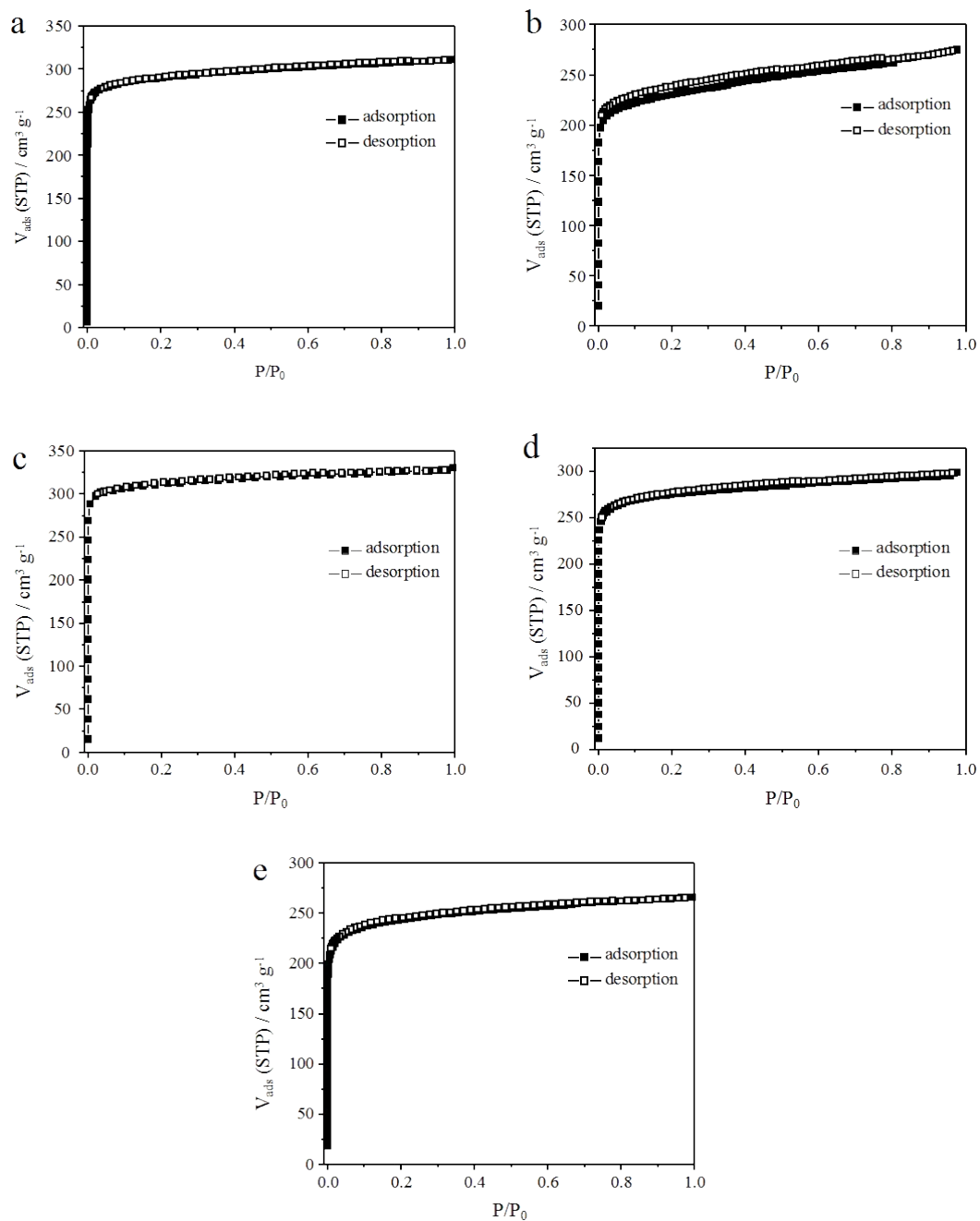


Figure S13. Nitrogen sorption isotherms of: (a) MOF-74-Co, (b) MOF-74-Ni, (c) MOF-74-NiCo1, (d) MOF-74-NiCo2 and (e) MOF-74-NiCo4.

13. Low-Pressure N₂ Sorption measurements of metal oxides.

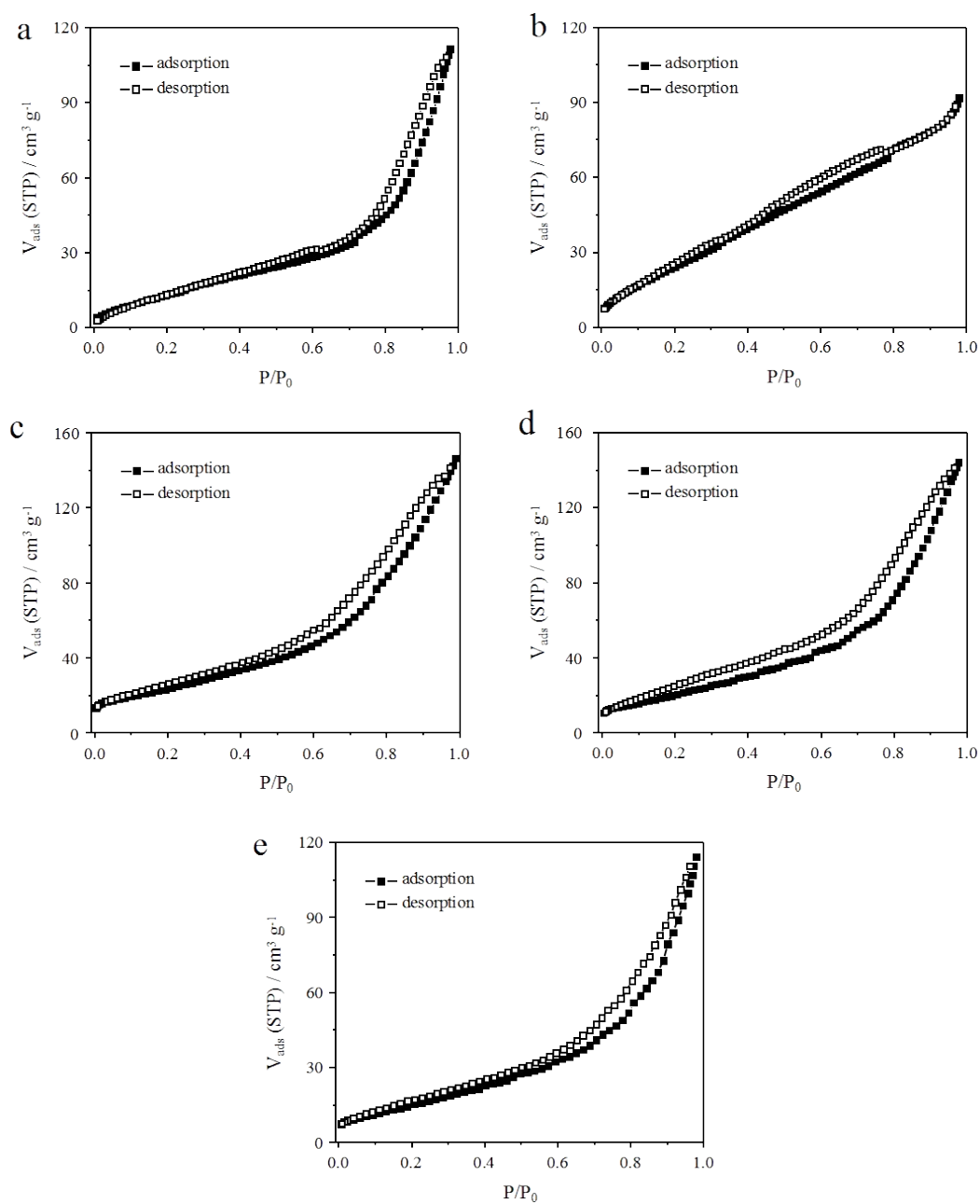


Figure S14. Nitrogen sorption isotherms of: (a) Co_3O_4 , (b) NiO , (c) $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-1}$, (d) $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-2}$ and (e) $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-4}$ samples.

14. Cyclic voltammetry (CV) measurements

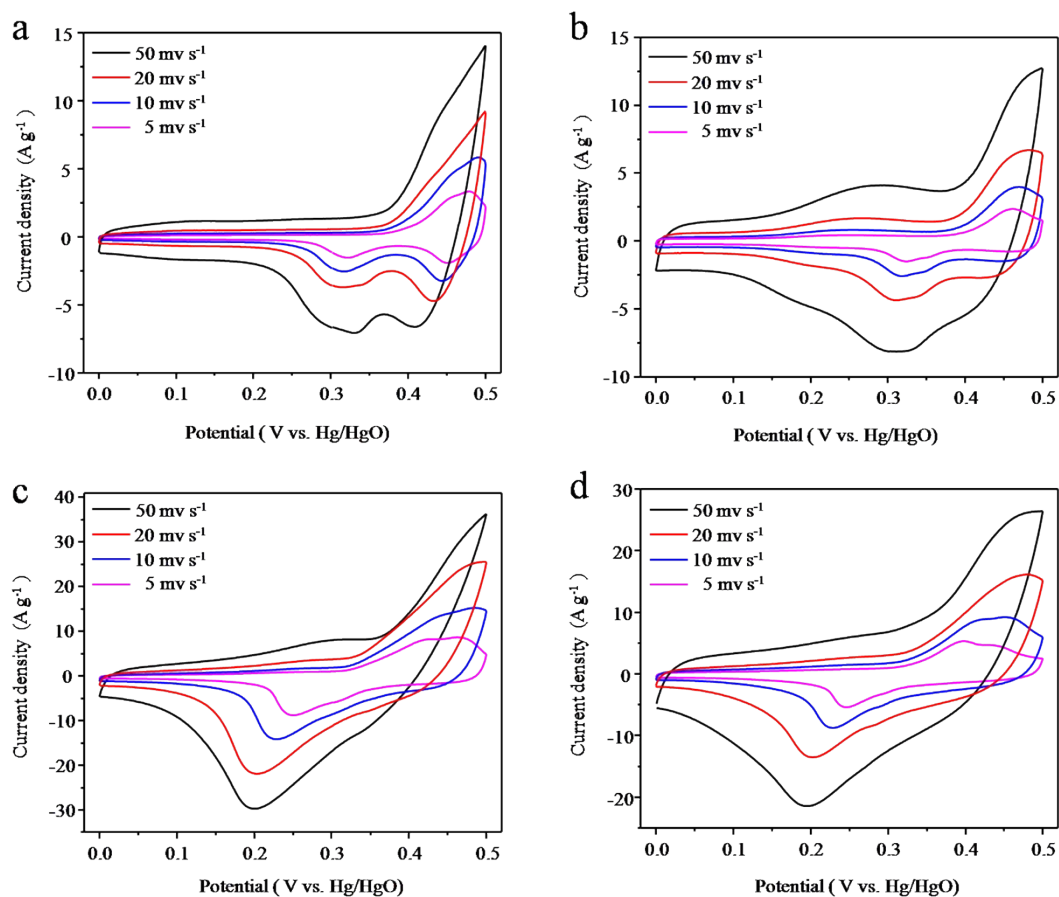


Figure S15. Cyclic voltammetry (CV) measurements of: (a) Co_3O_4 , (b) NiO , (c) $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-2}$ and (d) $\text{Ni}_x\text{Co}_{3-x}\text{O}_{4-4}$ within 0.0–0.50 V at a scan rate from 5 to 50 mV s^{-1} in 6.0 M KOH electrolyte at room temperature.

15. Galvanostatic charge–discharge measurements

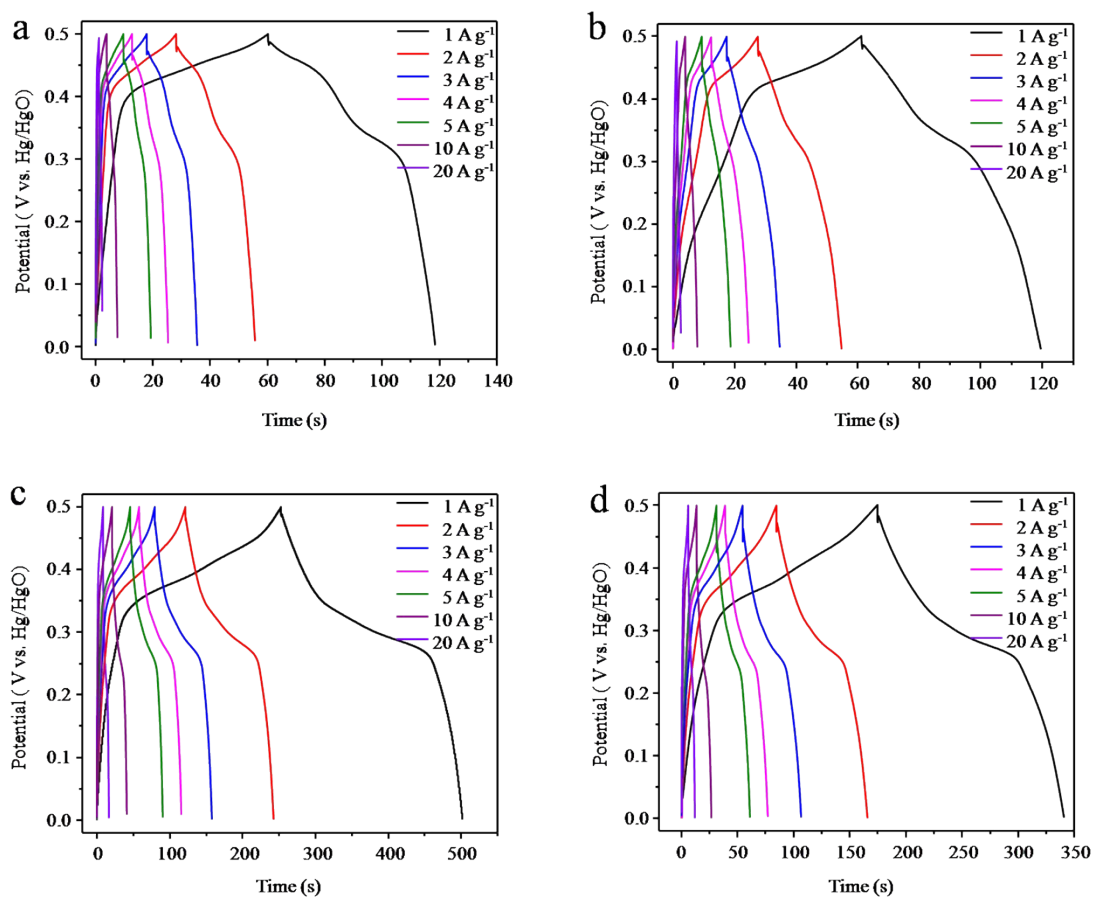


Figure S16. The galvanostatic charge–discharge curves of: (a) Co₃O₄, (b) NiO, (c) Ni_xCo_{3-x}O₄₋₂ and (d) Ni_xCo_{3-x}O₄₋₄ with current densities of 1, 2, 3, 4, 5, 10 and 20 A g⁻¹ in 6.0 M KOH electrolyte at room temperature.

16. Comparison with some NiCo₂O₄ materials from literature.

Table S1. Comparison of electrochemical performance of as-prepared Ni_xCo_{3-x}O₄ nanoparticles with some NiCo₂O₄ materials from literature.

Material	Specific Capacitance (F g ⁻¹) 1)	Rate performance	Capacitance retention	Reference
Ni _x Co _{3-x} O ₄ -1	797 (1 A g ⁻¹)	74.9% (20 A g ⁻¹)	80% (10000 cycles)	This work
Ni _x Co _{3-x} O ₄ -2	498 (1 A g ⁻¹)	67.1% (20A g ⁻¹)	72% (10000 cycles)	This work
Ni _x Co _{3-x} O ₄ -4	333 (1 A g ⁻¹)	67.3% (20A g ⁻¹)	75% (10000 cycles)	This work
NiCo ₂ O ₄ nanowires	245 (1 A g ⁻¹)	78% (10 A g ⁻¹)	115% (1000 cycles)	1
NiCo ₂ O ₄ nanosheets	123 (1 A g ⁻¹)	73% (10 A g ⁻¹)	95% (2200 cycles)	1
Porous NiCo ₂ O ₄ nanowires	743 (1 A g ⁻¹)	78.6% (40A g ⁻¹)	93.8% (3000 cycles)	2
NiCo ₂ O ₄ nanoflake@nanowire	891(1 A g ⁻¹)	69.5% (40 A g ⁻¹)	97.2% (8000 cycles)	3
Mesoporous Ni _{0.3} Co _{2.7} O ₄ hierarchical structures	960 (0.625 A g ⁻¹)	83.9% (6.25 A g ⁻¹)	98.1% (3000 cycles)	4
NiCo ₂ O ₄ nanoplates	294 (1 A g ⁻¹)	48% (10 A g ⁻¹)	89.8% (2200 cycles)	5
Hollow NiCo ₂ O ₄ microsphere	678 (1 A g ⁻¹)	79.6% (10 A g ⁻¹)	87% (3500 cycles)	6
NiCo ₂ O ₄ nanosheets on carbon nanofibers	1002 (1 A g ⁻¹)	67.3% (10 A g ⁻¹)	92.75% (2400 cycles)	7
NiCo ₂ O ₄ nanowires	760 (1 A g ⁻¹)	70% (20 A g ⁻¹)	81% (3000 cycles)	8
NRGO-NiCoO ₂	508 (0.5 A g ⁻¹)	No data	93% (2000 cycles)	9
NiCo ₂ O ₄ @graphene	778 (1 A g ⁻¹)	48% (80 A g ⁻¹)	90% (10000 cycles)	10
NiCo ₂ O ₄ on carbon	660 (2 A g ⁻¹)	58.2% (16 A g ⁻¹)	91.8% (3000 cycles)	11

17. References

1. H. W. Wang and X. F. Wang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 6255.
2. H. Jiang, J. Ma, C. Z. Li, *Chem. Commun.*, 2012, **48**, 4465
3. X. Liu, Y. Zhang, X. Xia, S. Shi, Y. Lu, X. Wang, C. Gu and J. Tu, *J. Power Sources*, 2013, **239**, 157.
4. H. B. Wu, H. Pang and X. W. Lou, *Energy Environ. Sci.*, 2013, **6**, 3619.
5. J. Pu, J. Wang, X. Q. Jin, F. Cui, E. H. Sheng and Z. H. Wang, *Electrochim. Acta*, 2013, **106**, 226.
6. C. Yuan, J. Li, L. Hou, J. Lin, G. Pang, L. Zhang, L. Lian, X. Zhang, *RSC Adv.*, 2013, **3**, 18573.
7. G. Q. Zhang, X. W. Lou, *Sci. Rep.*, 2013, **3**, 1470.
8. H. L. Wang, Q. M. Gao, L. Jiang, *Small*, 2011, **7**, 2454.
9. Y. Xu, J. Wei, L. Tan, J. Yua and Y. Chen, *J. Mater. Chem. A*, 2015, **3**, 7121.
10. Y. Wei, S. Chen, D. Su, B. Sun, J. Zhu and G. Wang, *J. Mater. Chem. A*, 2014, **2**, 8103.
11. D. Zhang, H. Yan, Y. Lu, K. Qiu, C. Wang, C. Tang, Y. Zhang, C. Cheng and Y. Luo, *Nanoscale Res. Lett.*, 2014, **9**, 139.