Supporting Information

Multilayer NiO@Co_3O_4@Graphene Quantum Dots Hollow Spheres for High-Performance Lithium-Ion Batteries and Supercapacitors

Xiaojie Yin[1],† Chuanwei Zhi[1],† Weiwei Sun[2], Li-Ping Lv[2]* and Yong Wang[1]*

[1]*School of Environmental and Chemical Engineering*

[2]*Institute of Green Chemical Engineering and Clean Energy*

Shanghai University, 99 Shangda Road, Shanghai, P. R. China, 200444

*Corresponding authors: Tel: +86-21-66137723/66138091

Email address: yongwang@shu.edu.cn; liping_lv@shu.edu.cn

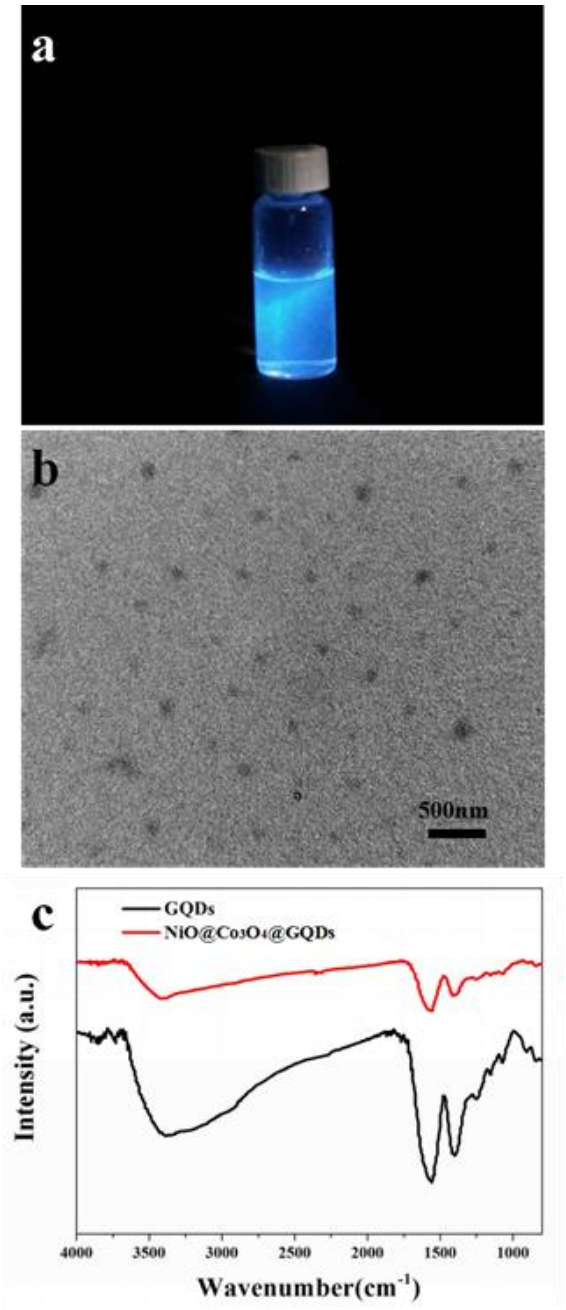

Figure S1. a) the digital photo of GQDs solution under UV light (365 nm). b) TEM image of GQDs. c) FTIR curves of GQDs and NiO@Co_3O_4@GQDs.

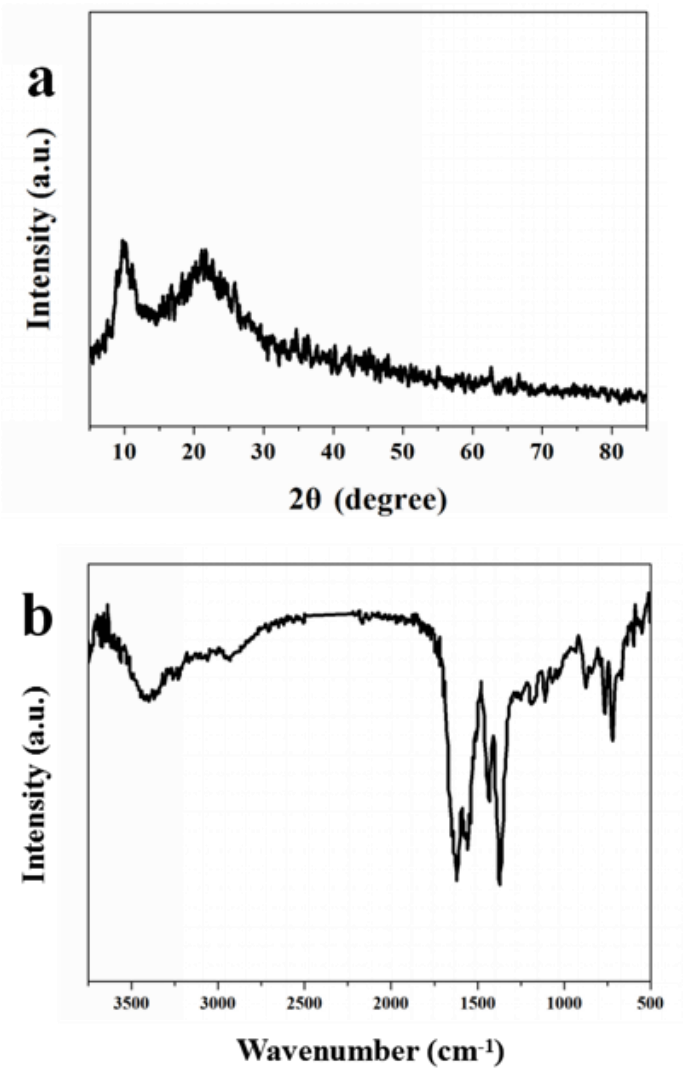

Figure S2. a) XRD and b) FTIR curves of Co-Ni-BTC MOF.

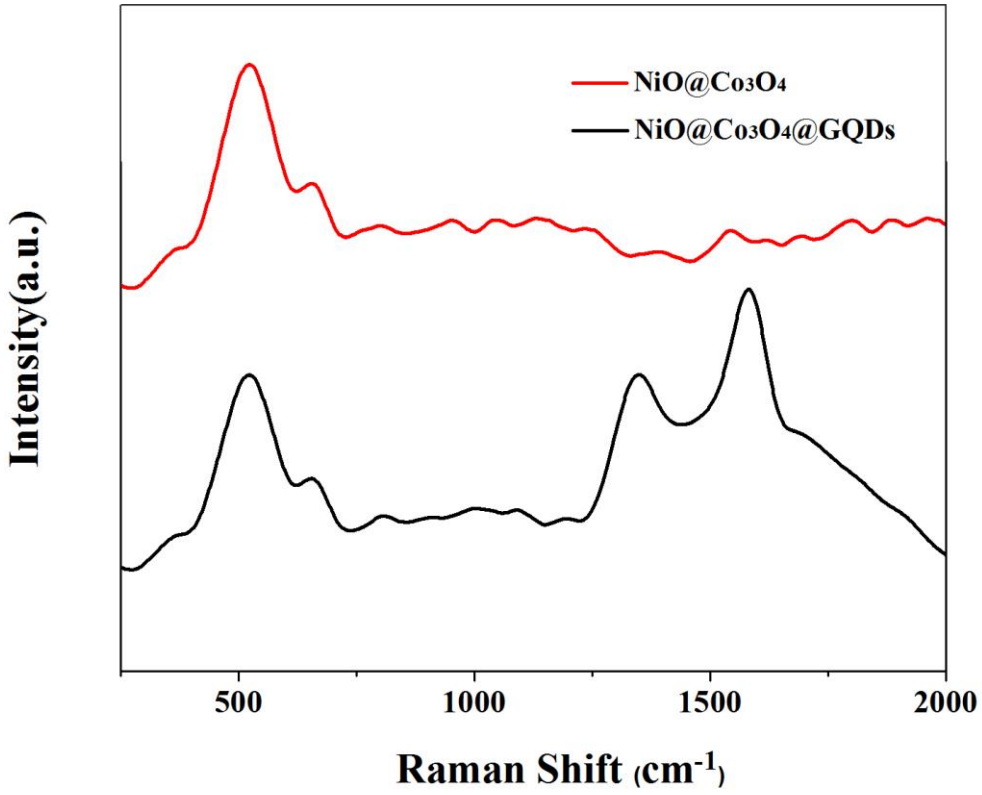

Figure S3. Raman spectra for NiO@Co_3O_4@GQDs and NiO@Co_3O_4.

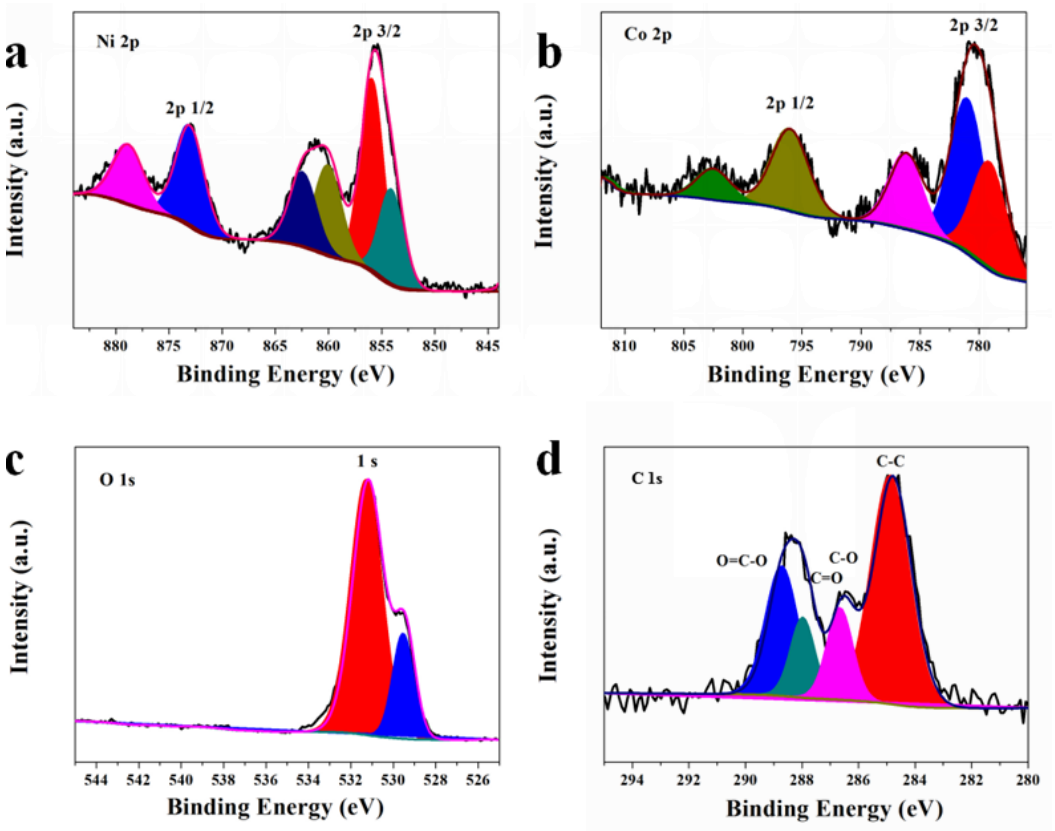

Figure S4. XPS spectra of NiO@Co_3O_4@GQDs: a) Ni 2p, b) Co 2p, c) O 1s and d) C 1s.

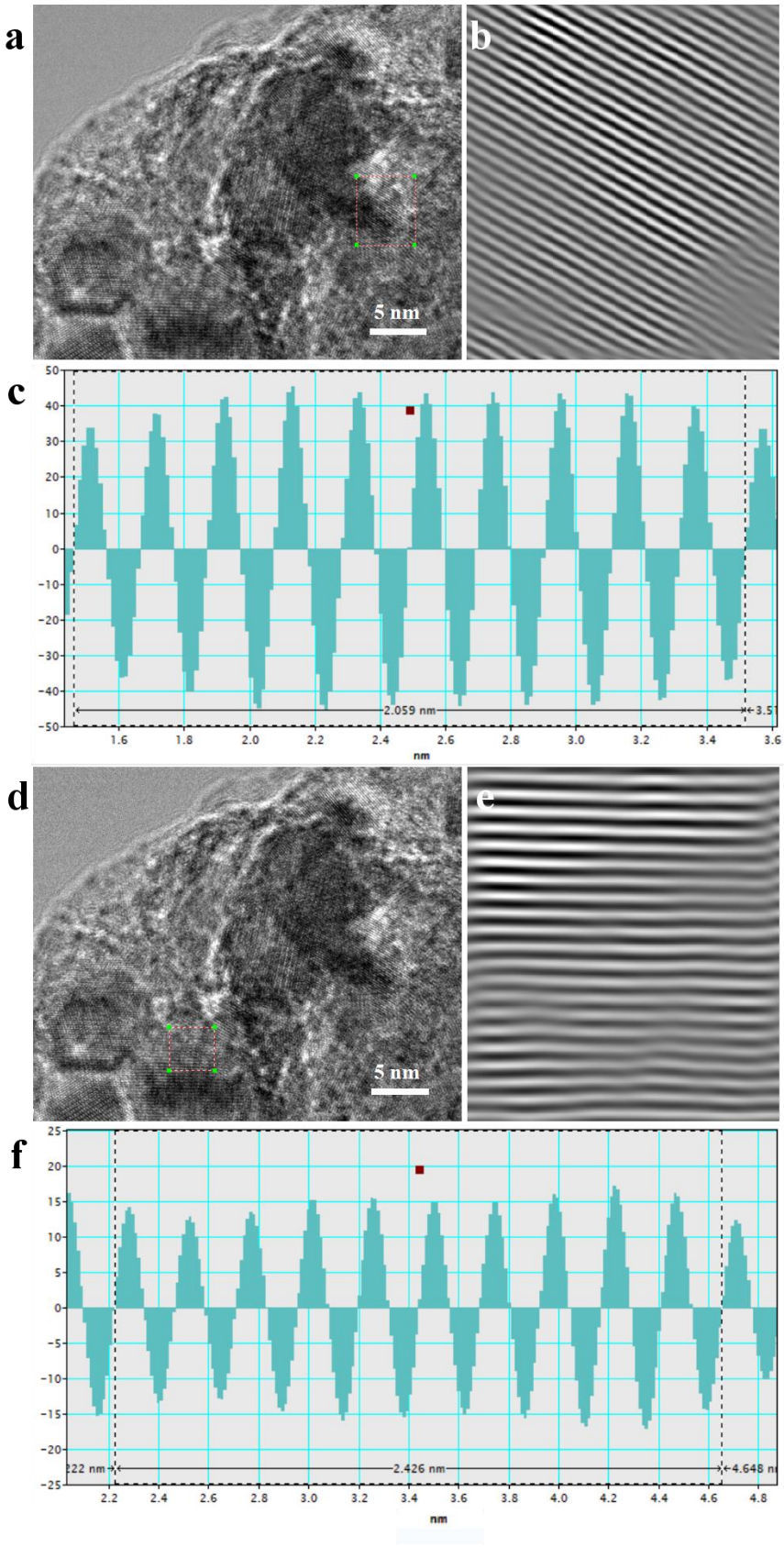

Figure S5. a, d) HRTEM images of NiO@Co_3O_4@GQDs. Lattice fringes of b) (100) plane of graphene and e) (111) plane of NiO. Images in c, f) indicate the lattice spacing of ten lattice fringes of the two phases, respectively.

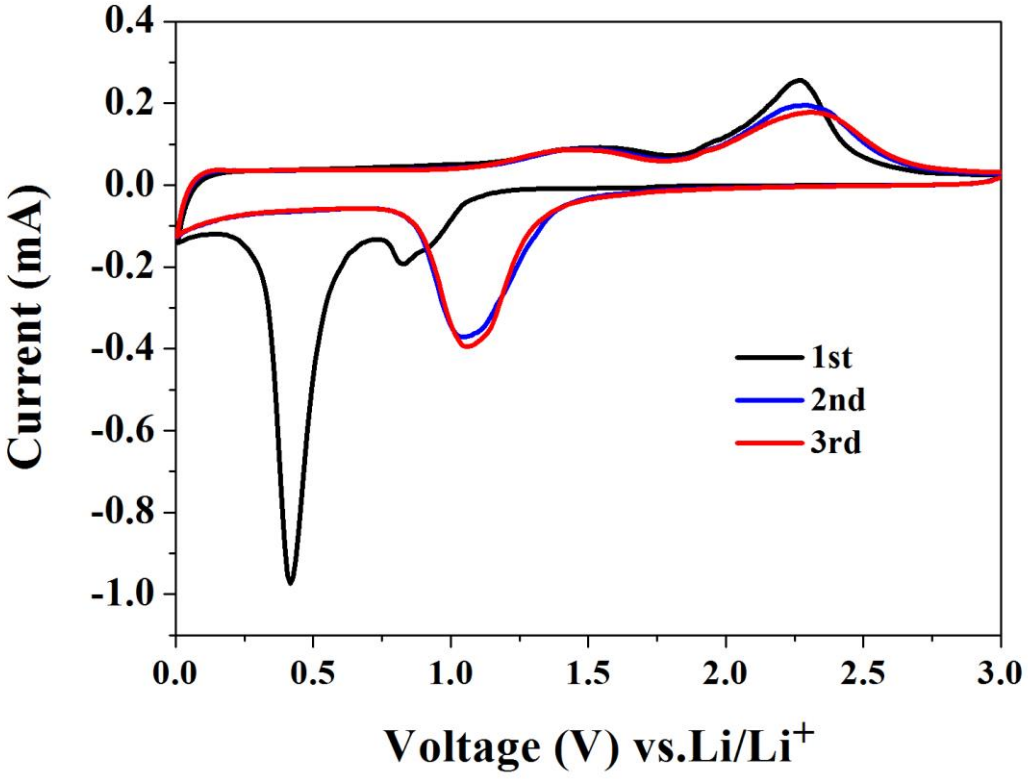

Figure S6. CV profiles of the first three cycles of NiO@Co_3O_4 at a scan rate of 0.1 mV s^{-1}.

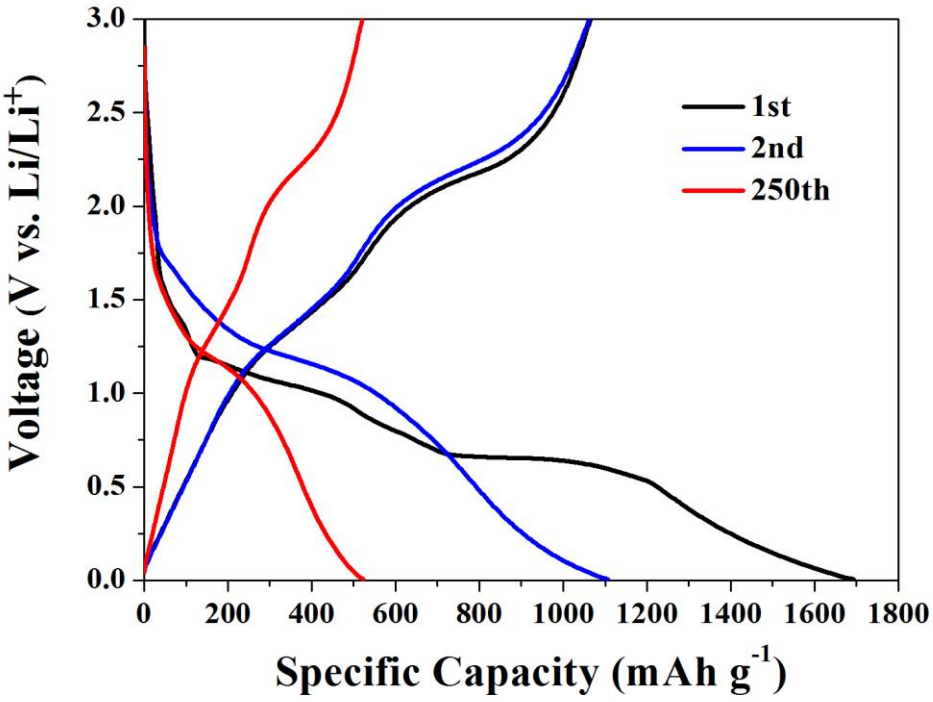

Figure S7. Discharging/charging profiles of 1st, 2nd and 250th cycle of NiO@Co_3O_4.

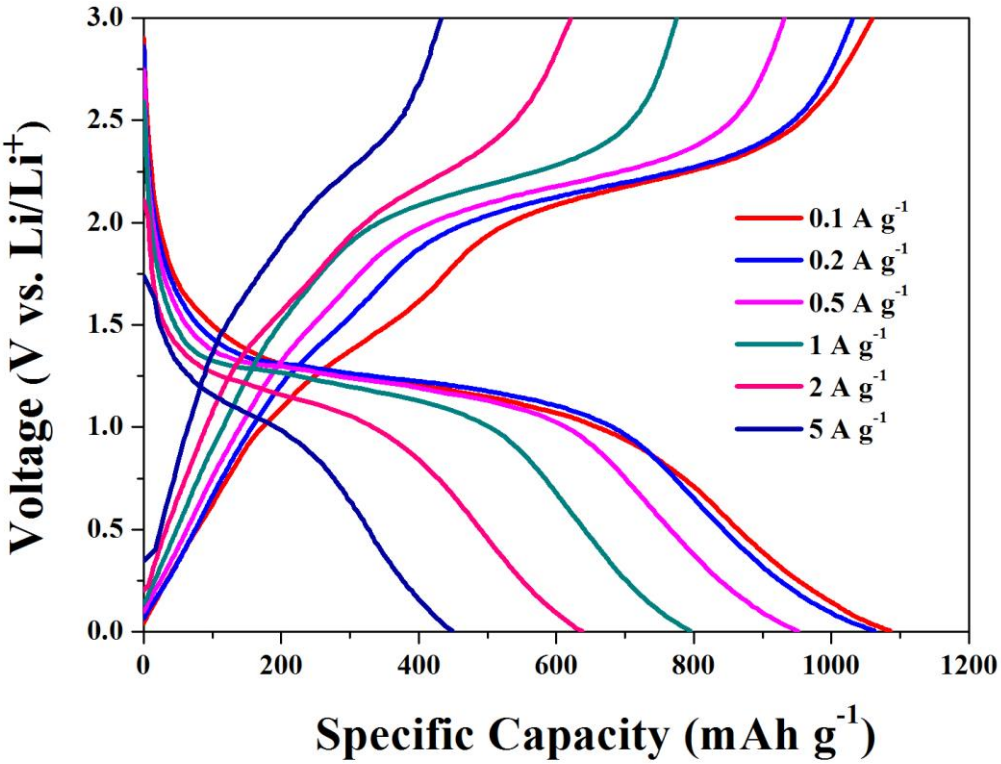

Figure S8. The voltage profile at different C-rates (0.1, 0.2, 0.5, 1, 2 and 5 A g^{-1}) of $NiO@Co_3O_4@GQDs$.

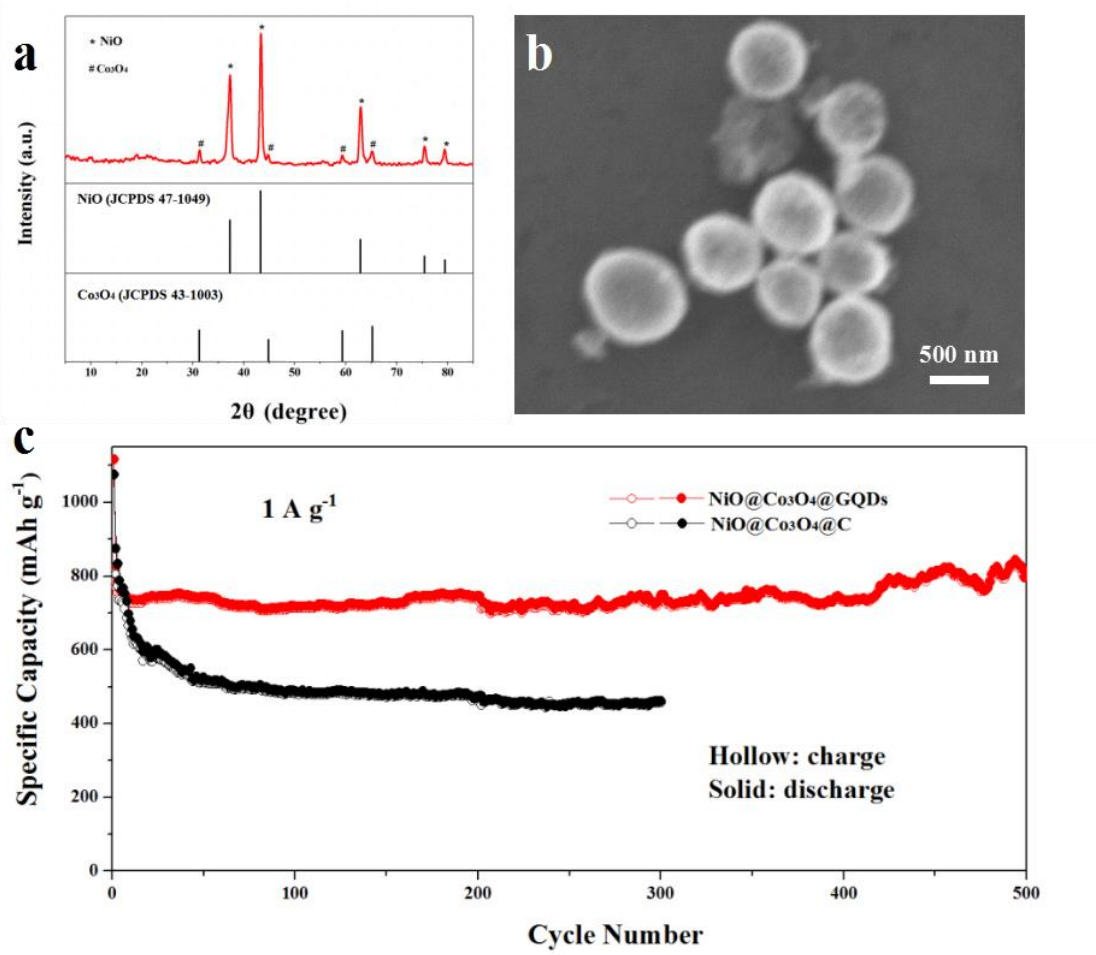

Figure S9. a) XRD patterns and b) SEM image of NiO@Co_3O_4@C. c) cycling performance of NiO@Co_3O_4@GQDs and NiO@Co_3O_4@C at 1 A g^{-1}.

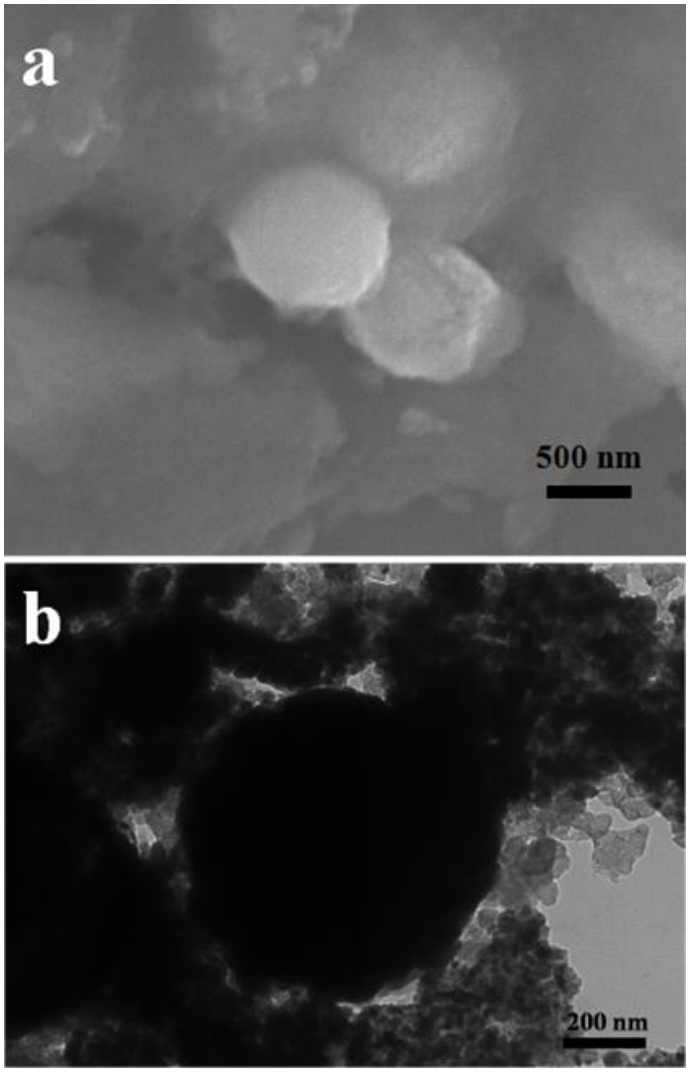

Figure S10. a) SEM and b) TEM image of NiO@Co_3O_4@GQDs anode for LIBs after 250 cycles.

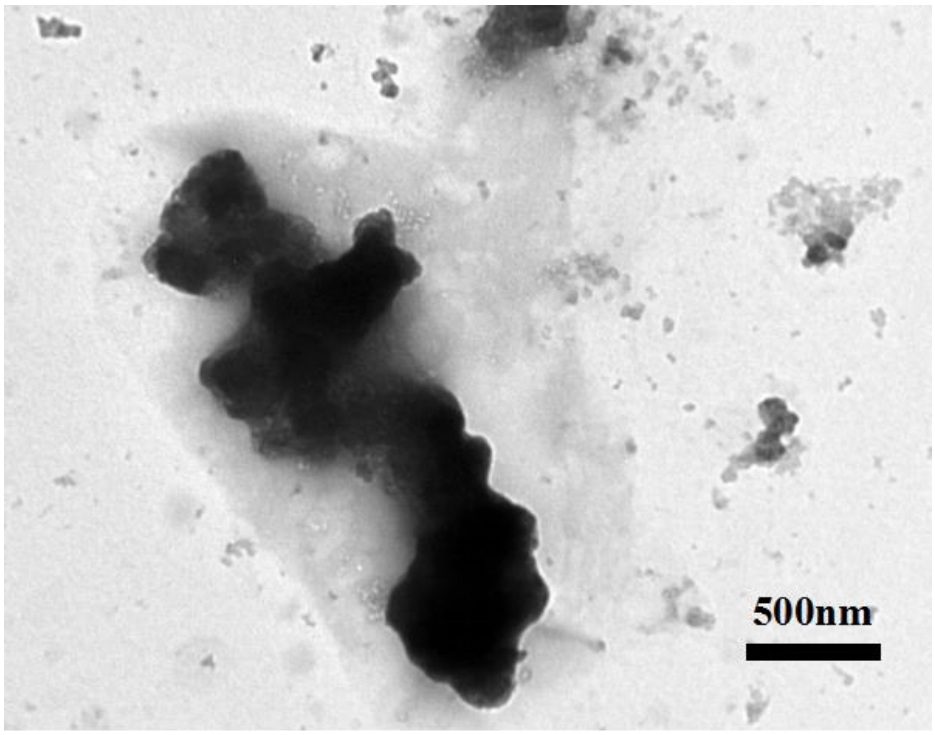

Figure S11. TEM image of $NiO@Co_3O_4$ anode for LIBs after 250 cycles.

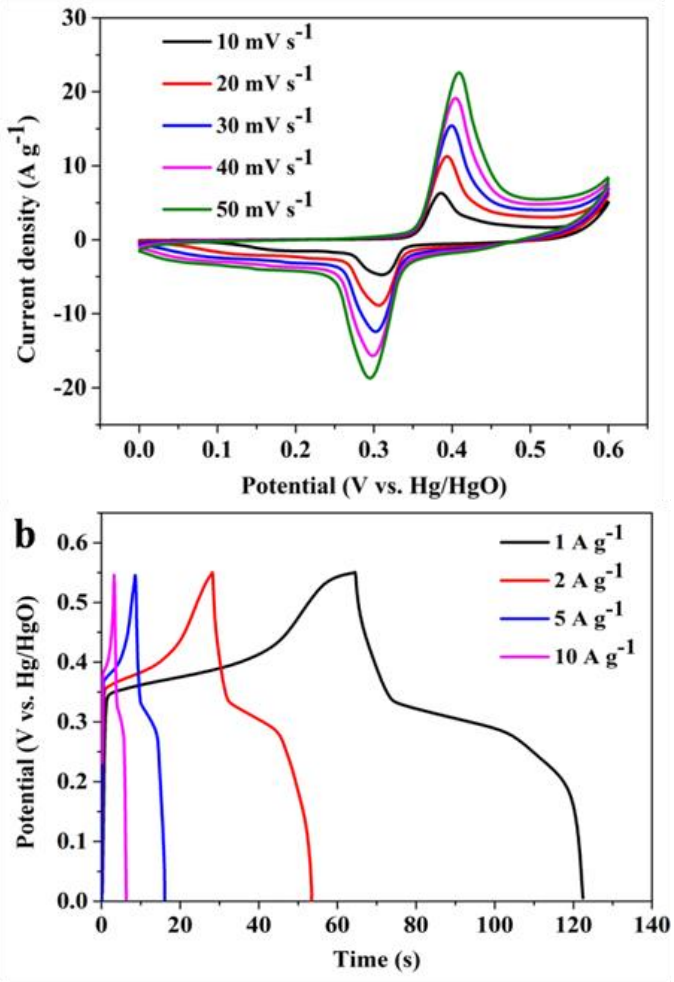

Figure S12. a) CV curves of the GQDs electrode at various scan rates. b) Galvanostatic charge-discharge curves of the GQDs electrode at different current densities.

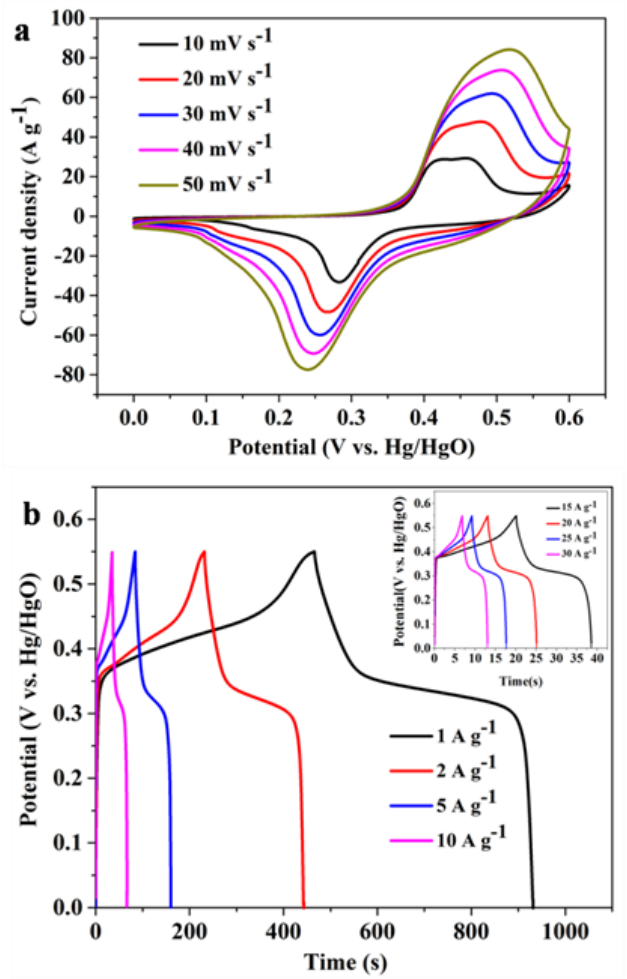

Figure S13. a) CV curves of the NiO@Co_3O_4 electrode at various scan rates. b) Galvanostatic charge-discharge curves of the NiO@Co_3O_4 electrode (1-10 A g^{-1} and 15-30 A g^{-1}, the inset).

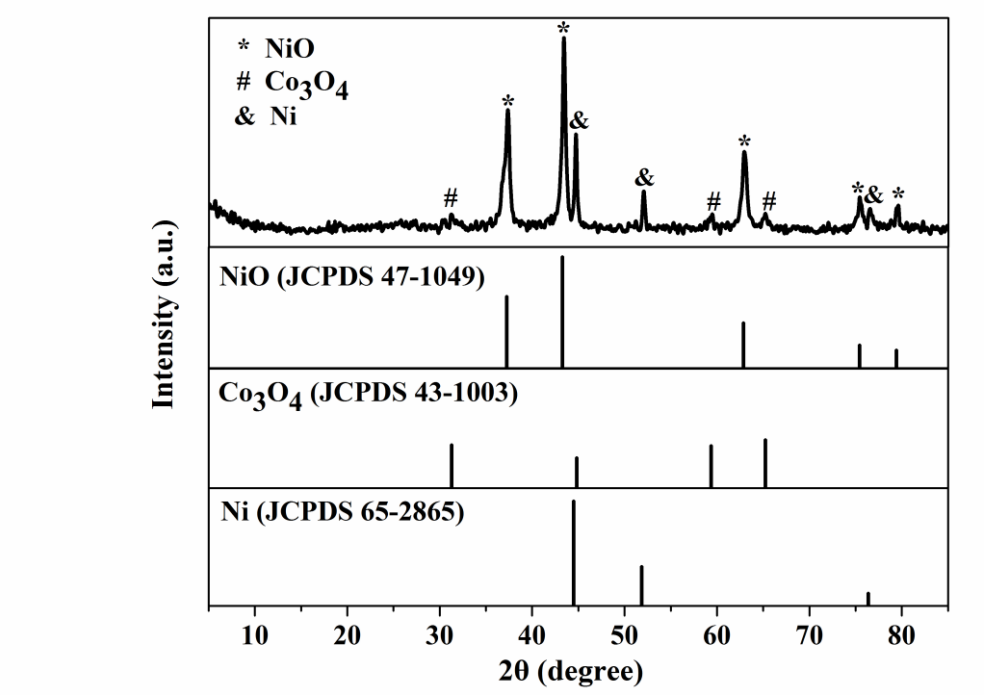

Figure S14. XRD data of NiO@Co_3O_4@GQDs after 3000 cycling tests of supercapacitor performance in three-electrode system.

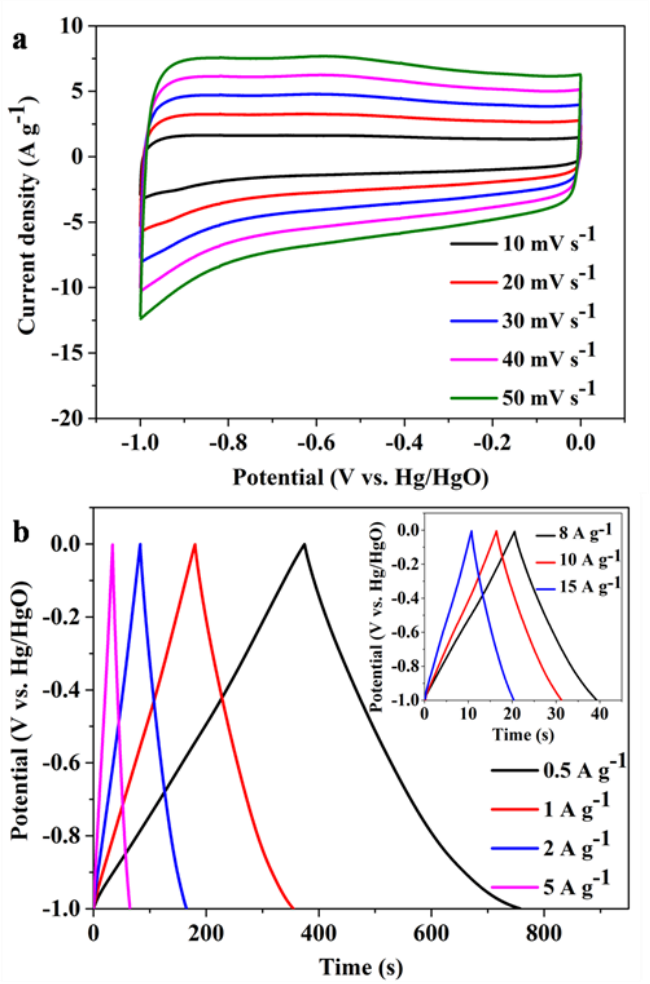

Figure S15. a) CV curves of the AC electrode at various scan rates. b) Galvanostatic charge-discharge curves of the AC electrode (0.5-5 A g^{-1} and 8-15 A g^{-1}, the inset).

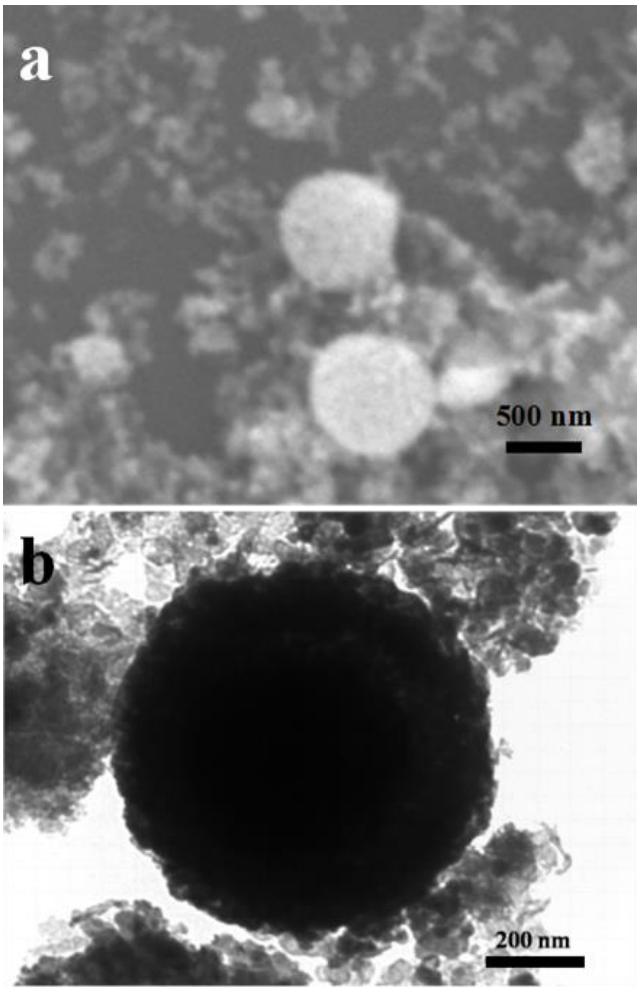

Figure S16. a) SEM and b) TEM image of the NiO@Co_3O_4@GQDs cathode for ASC device after 10000 cycles.

Table S1. The element analysis data of the NiO@Co_3O_4@GQDs composite.

Samples	Elemental contents (wt%)		
	C	N	H
NiO@Co_3O_4@GQDs	15.12	0.04	1.15

Table S2. Electrochemical properties comparison of $NiO@Co_3O_4@GQDs$ of this work and previous Co-Ni bimetal-oxide based anode for LIBs. (IRC: initial reversible capacity, mAh g^{-1}; RRC: retained reversible capacity, mAh g^{-1}; CN: cycle number; CD: current density, mA g^{-1}; V: voltage, V)

Composite	Morphology	IRC	RRC/CN	CD	V	References
$NiO@Co_3O_4@GQDs$	Multilayer Hollow Microsphere	~ 1300	~ 1327/250	100	0.005-3.0	This work
$Ni_xCo_{3-x}O_4$	Multi-shelled Hollow Sphere	~ 1139	~ 1109/100	100	0.005-3.0	1
$NiCo_2O_4$	Multi-shelled Hollow Spheres	~ 905	~ 706/100	200	0.01-3.0	2
$NiCo_2O_4$	Nanosheet	1015	988/50	200	0.01-3.0	3
$NiCo_2O_4$	Microrods	1046	857/100	100	0.01-3.0	4
$NiCo_2O_4$	Nanocube	1161	1058/200	100	0.01-3.0	5
$NiCo_2O_4$	Nanorod	~ 1095	~ 1000/400	500	0-3.0	6
$NiCo_2O_4$/CNT	Nanoparticle	1281	~ 1020/200	300	0-3.0	7
$NiCo_2O_4$-C	Nanorod	~ 1252	~ 1081/200	100	0.01-3.0	8
NiO−CoO	Nanoneedles	692	801/200	200	0.01-3.0	9
$NiO-Co_3O_4$	Nanoplate	~ 772	633/70	100	0.005-3.0	10
NiCo-$NiCoO_2$/C	Nanoparticle	~ 748	861/100	100	0.01-3.0	11
CoO–NiO–C	Nanoflower	731	562/60	100	0.002-3.0	12
$NiCoO_2$/rGO/ $NiCoO_2$	Sandwich Nanosheets	850	998/60	100	0.01-3.0	13
Ni−Co−Mn−O	Multi-shelled Hollow Spheres	~ 1470	~ 1097/250	200	0.01-3.0	14

References:

1. L. L. Wu, Z. Wang, Y. Long, J. Li, Y. Liu, Q. S. Wang, X. Wang, S. Y. Song, X. G. Liu, H. J. Zhang, Multishelled $Ni_xCo_{3-x}O_4$ Hollow Microspheres Derived from Bimetal-Organic Frameworks as Anode Materials for High-Performance Lithium-Ion Batteries. *Small* **2017**, 1604270.

2. L. F. Shen, L. Yu, X. Y. Yu, X. G. Zhang, X. W. Lou, Self-templated formation of uniform $NiCo_2O_4$ hollow spheres with complex interior structures for lithium-ion batteries and supercapacitors. *Angew. Chem. Int. Ed.* **2015**, *54*, 1868-1872.

3. Z. Y. Fan, B. R. Wang, Y. X. Xi, X. Xu, M. Y. Li, J. Li, P. Coxon, S. D. Cheng, G. X. Gao, C. H. Xiao, G. Yang, K. Xi, S. J. Ding, R. V. Kumar, A $NiCo_2O_4$ nanosheet-mesoporous carbon composite electrode for enhanced reversible lithium storage. *Carbon* **2016**, *99*, 633-641.

4. F. Fu, J. D. Li, Y. Z. Yao, X. P. Qin, Y. B. Dou, H. Y. Wang, J. K. Tsui, K. Y. Chan, M. H. Shao, Hierarchical $NiCo_2O_4$ Micro- and Nanostructures with Tunable Morphologies as Anode Materials for Lithium- and Sodium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2017**, *9*, 16194-16201.

5. H. Guo, L. X. Liu, T. T. Li, W. W. Chen, J. J. Liu, Y. Y. Guo, Y. C. Guo, Accurate hierarchical control of hollow crossed $NiCo_2O_4$ nanocubes for superior lithium storage. *Nanoscale* **2014**, *6*, 5491–5497.
6. H. S. Jadhav, R. S. Kalubarme, C. N. Park, J. Kim, C. J. Park, Facile and cost effective synthesis of mesoporous spinel $NiCo_2O_4$ as an anode for high lithium storage capacity. *Nanoscale* **2014**, *6*, 10071–10076.
7. S. Abouali, M. A. Garakani, Z. L. Xu, J. K. Kim, $NiCo_2O_4$/CNT nanocomposites as bi-functional electrodes for Li ion batteries and supercapacitors. *Carbon* **2016**, *102*, 262-272.
8. L. Peng, H. J. Zhang, Y. J. Bai, J. Yang, Y. Wang, Unique synthesis of mesoporous peapod-like $NiCo_2O_4$–C nanorods array as an enhanced anode for lithium ion batteries. *J. Mater. Chem. A* **2015**, *3*, 22094-22101.
9. Y. H. Wei, F. L. Yan, X. Tang, Y. Z. Luo, M. Zhang, W. F. Wei, L. B. Chen, Solvent-Controlled Synthesis of NiO-CoO/Carbon Fiber Nanobrushes with Different Densities and Their Excellent Properties for Lithium Ion Storage. *ACS Appl. Mater. Interfaces* **2015**, *7*, 21703-21711.
10. Y. P. Zhang, Q. Q. Zhuo, X. X. Lv, Y. Y. Ma, J. Zhong, X. H. Sun, NiO-Co_3O_4 nanoplate composite as efficient anode in Li-ion battery. *Electrochimica Acta* **2015**, *178*, 590-596.
11. Z. W. Zhang, Q. Li, Z. Q. Li, J. Y. Ma, C. X. Li, L. W. Yin, X. P. Gao, Partially Reducing Reaction Tailored Mesoporous 3D Carbon Coated NiCo-$NiCoO_2$/Carbon Xerogel Hybrids as Anode Materials for Lithium Ion Battery with Enhanced Electrochemical Performance. *Electrochimica Acta* **2016**, *203*, 117-127.
12. Y. F. Wang, L. J. Zhang, Simple synthesis of CoO–NiO–C anode materials for lithium-ion batteries and investigation on its electrochemical performance. *Journal of Power Sources* **2012**, *209*, 20-29.
13. X. N. Leng, Y. Shao, L. B. Wu, S. F. Wei, Z. H. Jiang, G. Y. Wang, Q. Jiang, J. S. Lian, A unique porous architecture built by ultrathin wrinkled $NiCoO_2$/rGO/$NiCoO_2$ sandwich nanosheets for pseudocapacitance and Li ion storage. *J. Mater. Chem. A* **2016**, *4*, 10304-10313.
14. D. Luo, Y. P. Deng, X. L. Wang, G. R. Li, J. Wu, J. Fu, W. Lei, R. L. Liang, Y. S. Liu, Y. L. Ding, A. P. Yu, Z. W. Chen, Tuning Shell Numbers of Transition Metal Oxide Hollow Microspheres toward Durable and Superior Lithium Storage. *ACS Nano* **2017**, *11*, 11521−11530.

Table S3. Electrochemical performance comparison of Co-Ni bimetal-oxide based supercapacitor electrodes. (PM: preparation method; SC: specific capacitance; RP: rate performance.)

Ref.	Composite	PM	SC	RP
This work	NiO@Co_3O_4@GQDs	Calcinationand hydrothermal method	1361 F g^{-1} (1 A g^{-1})	55.3% (30 A g^{-1})
1	$NiCo_2O_4$–rGO	Hydrothermal method	1185 F g^{-1} (2 A g^{-1})	86.7% (8 A g^{-1})
2	Layered $NiCo_2O_4$/RGO	Electrostatic self-assembly	1348 F g^{-1} (1 A g^{-1})	62.3% (30 A g^{-1})
3	CKF/CoNiOx	Hydrothermal and calcination method	711.1 F g^{-1} (1 A g^{-1})	64.1% (2 A g^{-1})
4	$NiCo_2O_4$ hollow micro-sphere	Hydrothermal method	942.2 F g^{-1} (0.5 A g^{-1})	75.5% (5 A g^{-1})
5	$NiCo_2O_4$ hollow microspheres	Template method andthermal treatment	720 F g^{-1} (2 A g^{-1})	80.6% (25 A g^{-1})
6	Co_3O_4 nanowire@NiO nanosheet arrays	Hydrothermal and electrodeposition method	230.4 F g^{-1} (0.5 A g^{-1})	59.3%(8 A g^{-1})
7	NiO@Co_3O_4 nanowire arrays	Hydrothermal method	1236.67 F g^{-1} (1 A g^{-1})	67.7%(20 A g^{-1})
8	Rod-like nickel cobaltite/graphene	Hydrothermal method	845 F g^{-1}(0.25 A g^{-1})	33.3% (20 A g^{-1})
9	Hollow $NiCo_2O_4$ nanowall arrays	Calcination method	1055.3 F g^{-1}(2.5 mA cm^{-2})	45.8%(60 mA cm^{-2})
10	$NiCo_2O_4$@MnO_2 nanosheet networks	Electrodeposition method	913.6 Fg^{-1} (0.5A g^{-1})	55.2% (20 A g^{-1})
11	Nickel/cobalt oxide composite hollow spheres	Gasflow atomization and templatemethod	630 F g^{-1} (1 A g^{-1})	54.3% (20 A g^{-1})
12	$NiCo_2O_4$-decorated porous carbon nanosheets	Hydrothermal method	596.8F g^{-1} (2 A g^{-1})	26.8% (20 A g^{-1})
13	PPy-$NiCo_2O_4$	Hydrothermal and electrodeposition method	910 F g^{-1}(1 A g^{-1})	30.8% (5 A g^{-1})
14	$NiCo_2O_4$ hollow spheres	Solvothermal and calcination method	1141 F g^{-1}(1 A g^{-1})	68.7% (15 A g^{-1})

References:

1. S. Al-Rubaye, R. Rajagopalan, S. X. Dou and Z. X. Cheng, Facile synthesis of a reduced graphene oxide wrapped porous $NiCo_2O_4$ composite with superior performance as an electrode material for supercapacitors, J. Mater. Chem. A, 2017, 5, 18989-18997.
2. Q. Li, C. X. Lu, C. M. Chen, L. J. Xie, Y. D. Liu, Y. Li, Q. Q. Kong and H. Wang, Layered $NiCo_2O_4$/reduced graphene oxide composite as an advanced electrode for supercapacitor, Energy Storage Mater., 2017, 8, 59-67.

3. W. B. Xu, B. Mu and A. Q. Wang, Three-dimensional hollow microtubular carbonized kapok fiber/cobalt-nickel binary oxide composites for high-performance electrode materials of supercapacitors, Electrochim. Acta, 2017, 224, 113-124.
4. C. C. Ji, F. Z. Liu, L. Xu and S. C. Yang, Urchin-like $NiCo_2O_4$ hollow microspheres and $FeSe_2$ micro-snowflakes for flexible solid-state asymmetric supercapacitors, J. Mater. Chem. A, 2017, 5, 5568-5576.
5. X. H. Qi, W. J. Zheng, G. H. He, T. F. Tian, N. X. Du and L. Wang, $NiCo_2O_4$ hollow microspheres with tunable numbers and thickness of shell for supercapacitors, Chem. Eng. J., 2017, 309, 426-434.
6. D. D. Han, X. Y. Jing, J. Wang, Y. S. Ding, Z. Y. Cheng, H. Dang and P. C. Xu, Three-dimensional Co_3O_4 Nanowire@NiO Nanosheet Core-shell Construction Arrays as Electrodes for Low Charge Transfer Resistance, Electrochim. Acta, 2017, 241, 220-228.
7. Q. Q. Hu, Z. X. Gu, X. T. Zheng and X. J. Zhang, Three-dimensional NiO@Co3O4 hierarchical nanowire arrays for solid-state symmetric supercapacitor with enhanced electrochemical performances, Chem. Eng. J., 2016, 304, 223-231.
8. Y. Lv, H. L. Wang, X. N. Xu, J. Shi, W. Liu and X. Wang, Balanced mesoporous nickle cobaltite-graphene and doped carbon electrodes for high-performance asymmetric supercapacitor, Chem. Eng. J., 2017, 326, 401-410.
9. C. Guan, X. M. Liu, W. N. Ren, X. Li, C. W. Cheng and J. Wang, Rational Design of Metal-Organic Framework Derived Hollow $NiCo_2O_4$ Arrays for Flexible Supercapacitor and Electrocatalysis, Adv. Energy Mater. 2017, 1602391.
10. Y. B. Zhang, B. Wang, F. Liu, J. P. Cheng, X. W. Zhang and L. Zhang, Full synergistic contribution of electrodeposited three-dimensional $NiCo_2O_4$@MnO_2 nanosheet networks electrode for asymmetric supercapacitors, Nano Energy, 2016, 27, 627-637.
11. N. Wang, P. Zhao, Q. Zhang, M. Q. Yao and W. C. Hu, Monodisperse nickel/cobalt oxide composite hollow spheres with mesoporous shell for hybrid supercapacitor: A facile fabrication and excellent electrochemical performance, Composites Part B, 2017, 113, 144-151.
12. V. Veeramani, R. Madhu, S. M. Chen, M. Sivakumar, C. T. Hung, N. Miyamoto and S. B. Liu, $NiCo_2O_4$-decorated porous carbon nanosheets for high-performance supercapacitors, Electrochim. Acta, 2017, 247, 288-295.
13. T. H. Ko, D. Y. Lei, S. Balasubramaniam, M. K. Seo, Y. S. Chung, H. Y. Kim and B. S. Kim, Polypyrrole-Decorated Hierarchical $NiCo_2O_4$ Nanoneedles/Carbon Fiber Papers for Flexible High-Performance Supercapacitor Applications, Electrochim. Acta, 2017, 247, 524-534.
14. L. F. Shen，L. Yu, X. Y. Yu, X. G. Zhang and X. W. Lou, Self-templated formation of uniform $NiCo_2O_4$ hollow spheres with complex interior structures for lithium-ion batteries and supercapacitors. Angew. Chem. Int. Ed., 2015, 54, 1868-1872.