Supplementary Information

Hierarchical hollow structure of $Ni_xCo_{3-x}O_4$ particles for high-performance hybrid supercapacitors with excellent cyclic stability

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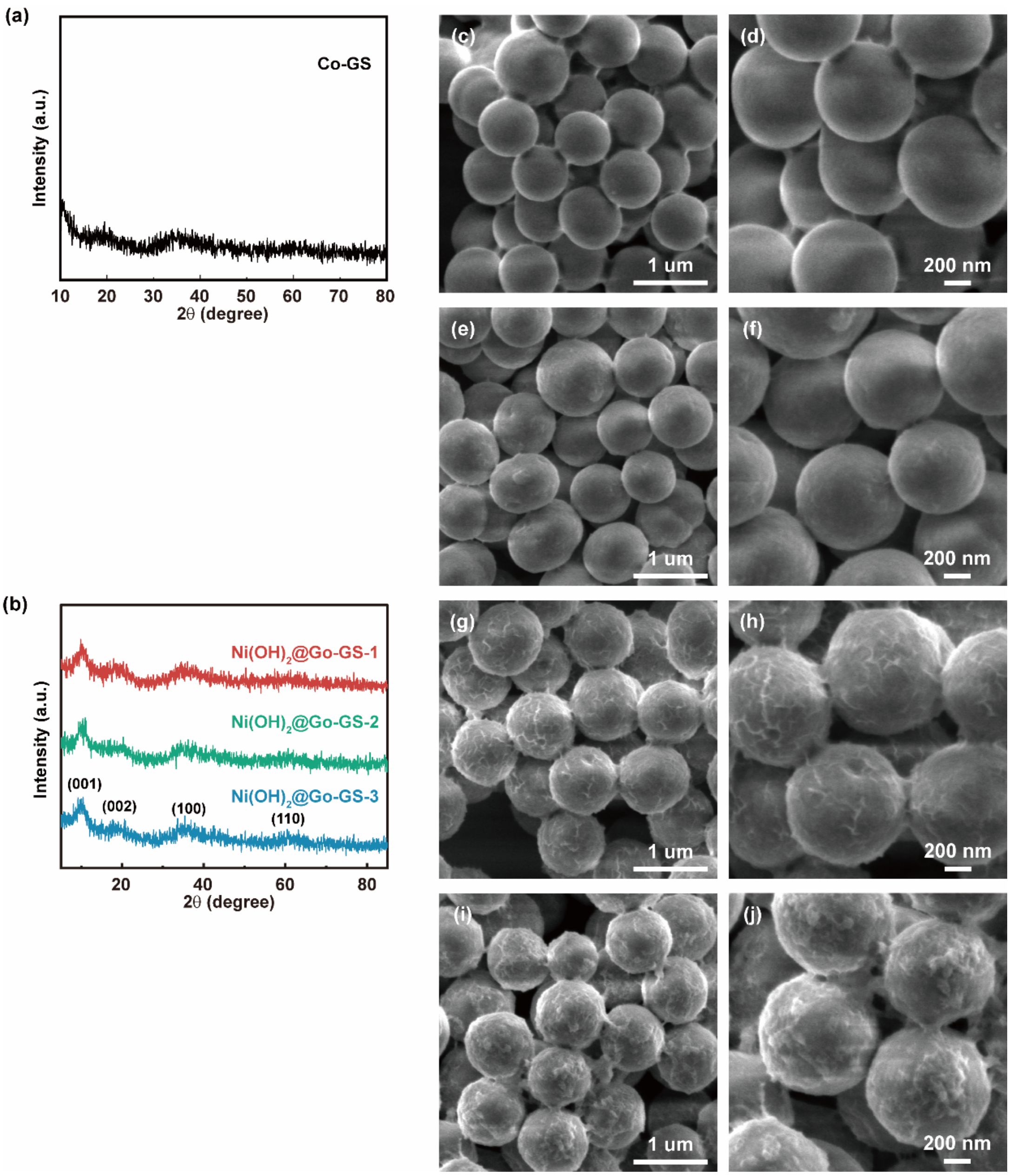

Figure S1 (a, b) XRD diffraction pattern of Co-GSs and $Ni(OH)_2$@Co-GS; SEM images of (c, d) Co-GSs; (e, f) $Ni(OH)_2$@Co-GS-1; (g, h) $Ni(OH)_2$@Co-GS-2; (i, j) $Ni(OH)_2$@Co-GS-3.

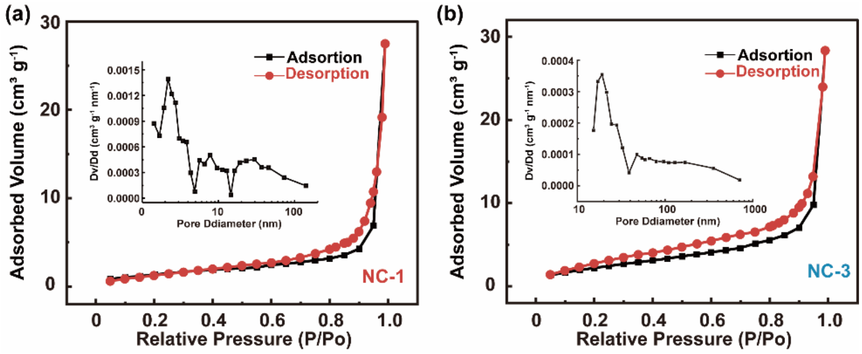

Figure S2 N_2 adsorption-desorption isotherms and corresponding pore size distribution (inset) of (a) NC-HHP-1 and (b) NC-HHP-3.

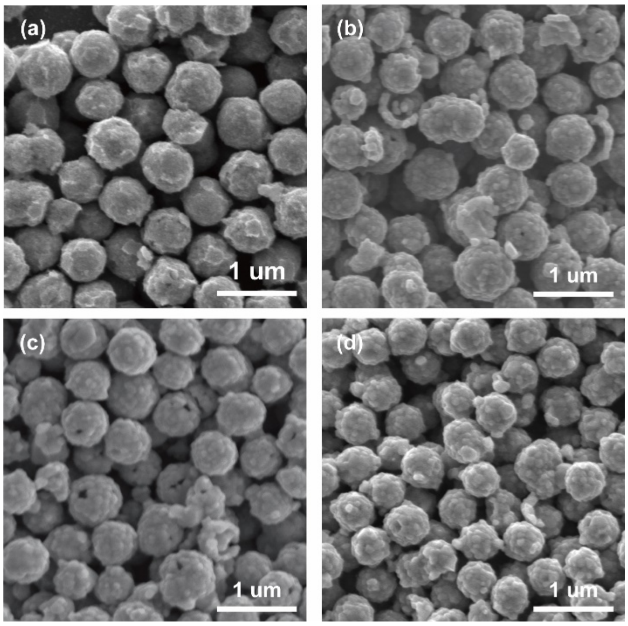

Figure S3 SEM images of NC-HHP-2 at different annealing temperatures: (a) 300 °C; (b) 400 °C; (c) 500 °C; (d) 600 °C.

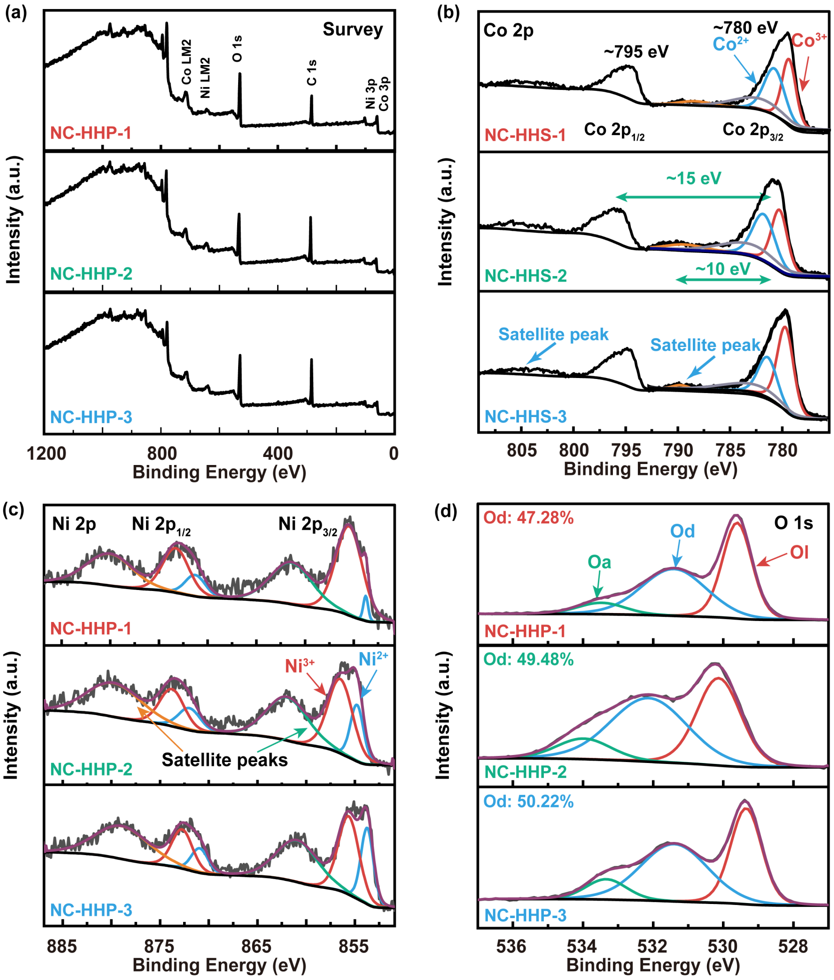

Figure S4 XPS spectra of NC-HHPs.

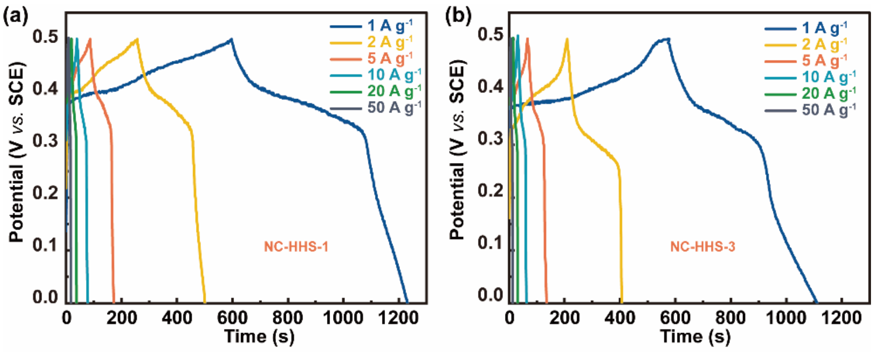

Figure S5 GCD curves of (a) NC-HHP-1 and (b) NC-HHP-3 at various current densities.

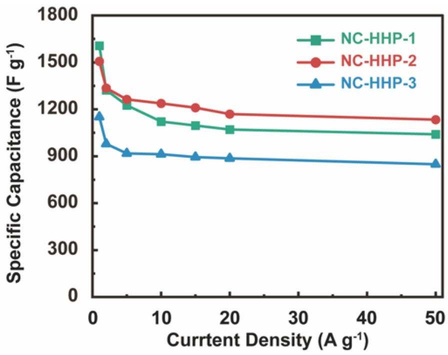

Figure S6 Corresponding specific capacitance of NC-HHPs by using F g^{-1} as the unit.

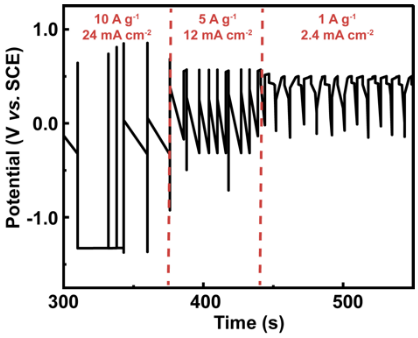

Figure S7 GCD curves of the blank Ni foam sample at different current densities.

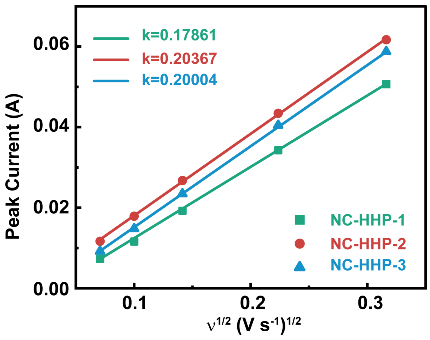

Figure S8 Plot of peak current *vs.* $\nu^{1/2}$ to calculate diffusion coefficient.

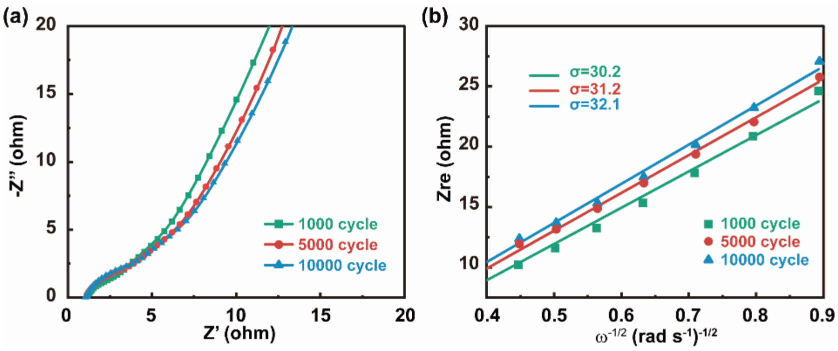

Figure S9 (a) Nyquist plots of HSC device after different cycle; (b) the linear relationship between Zre and $\omega^{-1/2}$ of HSC device after different cycle.

Method to calculate voltametric charge

Trasatti pioneered a method to quantify the surface contribution. As explained by Mousavi and Augustyn,[1,2] the voltammetric charge is related to the scan rate. The value of q(v) can be deconvoluted into two terms: $q_{s,total}$ (surface-controlled) and q_d (diffusion-controlled). Then, the surface-controlled component can be further divided into two terms: (1) "$q_{s,out}$", represents the contribution of the outer surface of the electrode active material to the charge storage (more accessible position such as the region directly accessible to the electrolyte), which is invariant of sweep rate.[1,2] (2) "$q_{s,in}$", comes from the partially accessible sites (less accessible position such as pores, grain boundaries, and cracks), which is sweep rate dependent.[1, 2]

When the scan rate tends to infinity, the part of $q_{s,in}$ equals 0:

$$q=q_{s,out}+q_d, \tag{A}$$

When the scan rate tends to 0:

$$q=q_{s,in}+q_{s,out}+q_d. \tag{B}$$

With these boundary conditions, $q_{s,in}$ and $q_{s,out}$ can be calculated by plotting the relationship between the voltammetric charge and the scan rate as below:

(1) $q_{s,out}$: Assuming semi-infinite linear diffusion and a linear relationship between q_d and $v^{-1/2}$, when the scan rate tends to infinity, eq A can be rewritten as: $q=q_{s,out}+k_1v^{-1/2}$. So when v tends to infinity, that is, $v^{-1/2}$ tends to 0, using the relationship between q and $v^{-1/2}$, we can get the intercept, which is $q_{s,out}$.[2]

(2) $q_{s,in}$: Assuming q^{-1} decreases linearly with $v^{1/2}$, eq B can be rewritten as: $q^{-1}=(q_{s,in}+q_{s,out})^{-1}+k_2v^{1/2}$. So when v tends to 0, that is, $v^{1/2}$ tends to 0, using the relationship between q^{-1} and $v^{1/2}$, we can get the intercept, which is $(q_{s,total})^{-1}$. $q_{s,in}$ then can be obtaind by using eq: $q_{s,total}=q_{s,in}+q_{s,out}$.[2]

References:

1. S. Fleischmann, J. B. Mitchell, R. Wang, C. Zhan, D. E. Jiang, V. Presser and V. Augustyn, *Chem Rev*, 2020, **120**, 6738-6782.
2. A. Noori, M. F. El-Kady, M. S. Rahmanifar, R. B. Kaner and M. F. Mousavi, *Chem Soc Rev*, 2019, **48**, 1272-1341.

Table S1 ICP-OES results of NC-HHP.

NC-HHP	Co (wt%)	Ni (wt%)	O (wt%)	Co (at%)	Ni (at%)	Ni (at%)/ Co (at%)
1	58.78	18.02	23.20	36.21	11.15	0.31
2	56.73	19.53	23.74	34.64	11.97	0.35
3	54.85	20.16	24.99	32.82	12.11	0.37

Table S2 Specific surface area and pore size data for NC-HHP.

NC-HHP	Surface Area		Pore Size	
	Multi BET (m^2 g^{-1})	Langmuir (m^2 g^{-1})	Average (nm)	BJH (nm)
1	5.3	9.2	32.0	2.2
2	12.8	22.5	89.3	17.0
3	8.8	14.9	99.6	19.1

Table S3 XPS analysis results of NC-HHP.

NC-HHP	Co	Ni	O
1	1	0.33	3.30
2	1	0.48	4.01
3	1	0.65	5.15

Table S4 Parameters from equivalent circuit model of NC-HHP.

NC-HHP	Rs	R1	Rct
1	0.41	7.8	52.9
2	0.43	**3.4**	**37.1**
3	0.38	8.6	92.0

Table S5 Specific parameter value of diffusion coefficient from EIS.

	NC-HHP-1	NC-HHP-2	NC-HHP-3
R (J mol^{-1} K^{-1})		8.314	
T (K)		298	
A (cm^2)		1	
n		1	
F (C mol^{-1})		96500	
c (mol cm^3)		0.006	
σ	27.72	27.10	28.02

Table S6 Diffusion coefficients calculated by using EIS data.

Electrode materials	Diffusion coefficient	Ref
NC-HHP-1	1.28×10^{-12}	This work
NC-HHP-2	1.34×10^{-12}	This work
NC-HHP-3	1.25×10^{-12}	This work
NiCo2O4 thin films	4.6×10^{-13}	[1]
NixCo3-xO4 thin films	1.45×10^{-17}	[1]
Co-doped MnO2	1.58×10^{-13}	[2]
Layered NiCo(OH)4	5.50×10^{-12}	[3]
Alkali etching CoSi-3	1.83×10^{-13}	[4]
Hierarchical CoFe2O4 nanorods	1.30×10^{-9}	[5]
Co3(PO4)2 nanoflakes	5.52×10^{-9}	[6]
mesoporous STP	3.27×10^{-13}	[7]

References:

1. R. J. Deokate, R. S. Kalubarme, C.-J. Park and C. D. Lokhande, *Electrochim Acta*, 2017, **224**, 378-385.
2. C.-L. Tang, X. Wei, Y.-M. Jiang, X.-Y. Wu, L. N. Han, K.-X. Wang and J.-S. Chen, *The Journal of Physical Chemistry C*, 2015, **119**, 8465-8471.
3. Y. Chen, W. K. Pang, H. Bai, T. Zhou, Y. Liu, S. Li and Z. Guo, *Nano Lett*, 2017, **17**, 429-436.
4. Y. Zhang, C. Wang, X. Dong, H. Jiang, T. Hu, C. Meng and C. Huang, *Chem Eng J*, 2020, DOI: 10.1016/j.cej.2020.127964.
5. S. Lalwani, R. B. Marichi, M. Mishra, G. Gupta, G. Singh and R. K. Sharma, *Electrochim Acta*, 2018, **283**, 708-717.
6. J. Theerthagiri, K. Thiagarajan, B. Senthilkumar, Z. Khan, R. A. Senthil, P. Arunachalam, J. Madhavan and M. Ashokkumar, *Chemistryselect*, 2017, **2**, 201-210.
7. A. K. Tomar, G. Singh and R. K. Sharma, *J Power Sources*, 2019, **426**, 223-232.

Table S7 Diffusion coefficients calculated by using CV data

Electrode materials	Diffusion coefficient	Ref
NC-HHP-1	1.22×10^{-8}	This work
NC-HHP-2	1.59×10^{-8}	This work
NC-HHP-3	1.54×10^{-8}	This work
NiCo2O4@rGO	2.43×10^{-8}	[1]
Co3O4/NiO	1.60×10^{-12}	[2]
NiCo2O4/NF	5.80×10^{-12}	[3]
NiCo2O4/NF@PPy	8.20×10^{-12}	[3]
NiCo2O4 nanobelt	3.40×10^{-13}	[4]
NixCo3-xO4 nanobelt	4.60×10^{-13}	[4]
Co3O4 nanoneedle	8.55×10^{-11}	[5]
Co3O4/Carbon paper	5.20×10^{-11}	[6]
S-doped Co3O4	1.21×10^{-9}	[7]
Ni-Co-OH@Graphene	1.47×10^{-10}	[8]
CoNiP nanocrystals	2.64×10^{-10}	[9]
NiFe2O4/rGO	2.60×10^{-12}	[10]

References:

1. A. M. Patil, N. Kitiphatpiboon, X. An, X. Hao, S. Li, X. Hao, A. Abudula and G. Guan, *ACS Appl Mater Interfaces*, 2020, **12**, 52749-52762.
2. Y. Liu, Z. Wang, Y. Zhong, X. Xu, J.-P. M. Veder, M. R. Rowles, M. Saunders, R. Ran and Z. Shao, *Chem Eng J*, 2020, **390**.
3. R. BoopathiRaja and M. Parthibavarman, *Electrochim Acta*, 2020, **346**.
4. M. Harilal, S. G. Krishnan, B. L. Vijayan, M. V. Reddy, S. Adams, A. R. Barron, M. M. Yusoff and R. Jose, *Materials & Design*, 2017, **122**, 376-384.
5. I. Hussain, J. M. Lee, S. Iqbal, H. S. Kim, S. W. Jang, J. Y. Jung, H. J. An, C. Lamiel, S. G. Mohamed, Y. R. Lee and J.-J. Shim, *Electrochim Acta*, 2020, **340**.
6. H. Wei, C. He, J. Liu, H. Gu, Y. Wang, X. Yan, J. Guo, D. Ding, N. Z. Shen, X. Wang, S. Wei and Z. Guo, *Polymer*, 2015, **67**, 192-199.
7. S. Lalwani, A. Joshi, G. Singh and R. K. Sharma, *Electrochim Acta*, 2019, **328**.
8. J. Kang, M. Hwang, K.-d. Seong, L. Lyu, D. Ko and Y. Piao, *Electrochim Acta*, 2020, **346**.
9. N. Zhang, Y. Li, J. Xu, J. Li, B. Wei, Y. Ding, I. Amorim, R. Thomas, S. M. Thalluri, Y. Liu, G. Yu and L. Liu, *ACS Nano*, 2019, **13**, 10612-10621.
10. K. Hareesh, B. Shateesh, R. P. Joshi, S. S. Dahiwale, V. N. Bhoraskar, S. K. Haram and S. D. Dhole, *Electrochim Acta*, 2016, **201**, 106-116.

Table S8 Comparison of the capacitance and cyclic stability data of NC-HHP with published work.

Electrode	**Current density (A g^{-1})**	**Specific capacity (F g^{-1})**	**Cycling stability**	**Reference**
Hierarchical hollow $Ni_xCo_{3-x}O_4$ particles	10	1192	99%@40000 cycles	This work
$NiCo_2O_4$ nanoneedles	10	820	114%@1000 cycles	[1]
$NiCo_2O_4$-CNT nanoparticles	5	557	89.3%@5000 cycles	[2]
Hierarchical $Ni(OH)_2$ nanoflakes	5	508	65.0%@4500 cycles	[3]
N-doped carbon@$NiCo_2O_4$ nanowire	10	984	91.3%@5000 cycles	[4]
NiO@Co_3O_4@graphene quantum dots	10	748	76.4%@3000 cycles	[5]
Multilevel $NiCoO_2$/Ni nanoporous	10	708	90.8%@5000 cycles	[6]
CC/$NiCo_2O_4$@NiO nanosheets	6.15	690	90.9%@10000 cycles	[7]
$NiCo_2O_4$ nanosheets	10	1093	85.8%@10000 cycles	[8]
Hexagonal $NiCo_2O_4$ nanostructures	10	600	98.0%@2000 cycles	[9]
Ultrathin $NiCo_2O_4$ nanosheets	10	635	91.4%@5000 cycles	[10]
Core-shell $NiCo_2O_4$@$Ni_xCo_yMoO_4$	5	826	99.5%@10000 cycles	[11]
Core-shell $NiCo_2O_4$@$NiCo_2O_4$ nanocones	4	887	85.3%@21000 cycles	[12]
Yolk-shelled $NiCo_2O_4$ spheres	10	558	98.0%@10000 cycles	[13]

References:

1. Z. Cao, C. Liu, Y. Huang, Y. Gao, Y. Wang, Z. Li, Y. Yan and M. Zhang, *J Power Sources*, 2020, **449**.
2. Y. Xue, T. Chen, S. Song, P. Kim and J. Bae, *Nano Energy*, 2019, **56**, 751-758.
3. S. Zhang, Z. Yang, K. Gong, B. Xu, H. Mei, H. Zhang, J. Zhang, Z. Kang, Y. Yan and D. Sun, *Nanoscale*, 2019, **11**, 9598-9607.
4. Z. Xu, J. Ren, Q. Meng, X. Zhang, C. Du and J. Chen, *Acs Sustain Chem Eng*, 2019, **7**, 12447-12456.
5. X. Yin, C. Zhi, W. Sun, L.-P. Lv and Y. Wang, *J Mater Chem A*, 2019, **7**, 7800-7814.
6. B. Liu, J. Hou, T. Zhang, C. Xu and H. Liu, *J Mater Chem A*, 2019, **7**, 16222-16230.
7. Y. Ouyang, R. Huang, X. Xia, H. Ye, X. Jiao, L. Wang, W. Lei and Q. Hao, *Chem Eng J*, 2019, **355**, 416-427.
8. Z. Qu, M. Shi, H. Wu, Y. Liu, J. Jiang and C. Yan, *J Power Sources*, 2019, **410**, 179-187.
9. J. Bhagwan, G. Nagaraju, B. Ramulu, S. C. Sekhar and J. S. Yu, *Electrochim Acta*, 2019, **299**, 509-517.
10. J. Nan, Y. Shi, Z. Xiang, S. Wang, J. Yang and B. Zhang, *Electrochim Acta*, 2019, **301**, 107-116.
11. P. Sun, W. He, H. Yang, R. Cao, J. Yin, C. Wang and X. Xu, *Nanoscale*, 2018, **10**, 19004-19013.
12. X. Wang, Y. Fang, B. Shi, F. Huang, F. Rong and R. Que, *Chem Eng J*, 2018, **344**, 311-319.
13. L. Wang, X. Jiao, P. Liu, Y. Ouyang, X. Xia, W. Lei and Q. Hao, *Appl Surf Sci*, 2018, **427**, 174-181.

Table S9 Comparison of the capacitance and cyclic stability data of NC-HHP//AC HSC device with other transition metal oxides based hybrid supercapacitors.

Electrode	**Current density ($A\ g^{-1}$)**	**Specific capacity ($F\ g^{-1}$)**	**Cycling stability**	**Reference**
NC-HHP//AC	10	161	~100%@50000 cycles	This work
NiS-$NiCo_2O_4$@C//AC	2	82.5	89%@5000 cycles	**[1]**
$NiCo_2O_4$@HfC//AC	10	132.7	94.8%@5000 cycles	**[2]**
P-doped $NiCo_2O_4$//rGO	5	92.9	88.5%@10000 cycles	**[3]**
$NiCo_2O_4$// $NiCo_2O_4$	2	73.1	86%@500 cycles	**[4]**
$NiCo_2O_4$@N-doped Carbon//AC	5	105.1	97.3%@15000 cycles	**[5]**
CNTs@NiCo LDH//rGO-Fe2O3	2	97.1	93.5%@1000 cycles	**[6]**
$NiCo_2O_4$-CNT//AC	5	95	81.2%@5000 cycles	**[7]**
$NiCo_2O_4$@GQDs//AC	4	75	71.8%@3000 cycles	**[8]**
Ni(OH)2//AC	1	64	75.3%@7000 cycles	**[9]**
NiO@Co_3O_4@graphene//AC	5	74.2	84.3%@10000 cycles	**[10]**
$NiCoO_2$/Ni//AC	10	70.8	90.5%@20000 cycles	**[11]**
CC/$NiCo_2O_4$@NiO//graphene	4	99.8	95.2%@10000 cycles	**[12]**
$NiCo_2O_4$/NiO/Co_3O_4//AC	1	100	83%@2000 cycles	**[13]**
Co_9S_8@$NiCo_2O_4$/AC	8	62.1	88.9%@6000 cycles	**[14]**
$NiCo_2O_4$//carbonized melamine	5	87.8	83.6%@10000 cycles	**[15]**
$NiCo_2O_4$/$CoMoO_4$//AC	4	49.27	71.4%@9000 cycles	**[16]**
$NiCo_2O_4$//superactivated carbon	5	21	87%@10000 cycles	**[17]**
$NiCo_2O_4$//graphene hydrogel	2	230	92%@5000 cycles	**[18]**
$NiCo_2O_4$//AC	0.25	82.5	90%@2000 cycles	**[19]**
$NiCo_2O_4$//PD-PC carbon	5	114.6	95.5%@5000 cycles	**[20]**
$NiMoO_4$/NiO//AC	0.5	95	95.5%@5000 cycles	**[21]**
$NiCo_2O_4$@rGO//rGO	6	61.2	81.1%@10000 cycles	**[22]**
$NiCo_2O_4$/graphene	5	62.2	70.5%@10000 cycles	**[23]**
$Ni_xCo_{3-x}O_4$//graphene hydrogel	1	130	80%@5000 cycles	**[24]**

References:

1. S. Ahmad, C. Yang, W. Xie, Z. Deng, H. Zhang, Y. Zhao and X. Su, *Carbon*, 2020, **158**, 912-921.
2. X. Yin, H. Li, Y. Fu, R. Yuan and J. Lu, *Chem Eng J*, 2020, **392**.
3. W. Chu, Z. Shi, Y. Hou, D. Ma, X. Bai, Y. Gao and N. Yang, *ACS Appl Mater Interfaces*, 2020, **12**, 2763-2772.
4. Z. Cao, C. Liu, Y. Huang, Y. Gao, Y. Wang, Z. Li, Y. Yan and M. Zhang, *J Power Sources*, 2020, **449**.
5. Z. Xu, J. Ren, Q. Meng, X. Zhang, C. Du and J. Chen, *Acs Sustain Chem Eng*, 2019, **7**, 12447-12456.
6. Y. Wang, H. Wei, H. Lv, Z. Chen, J. Zhang, X. Yan, L. Lee, Z. M. Wang and Y. L. Chueh, *ACS Nano*, 2019, **13**, 11235-11248.
7. Y. Xue, T. Chen, S. Song, P. Kim and J. Bae, *Nano Energy*, 2019, **56**, 751-758.
8. J. Luo, J. Wang, S. Liu, W. Wu, T. Jia, Z. Yang, S. Mu and Y. Huang, *Carbon*, 2019, **146**, 1-8.
9. S. Zhang, Z. Yang, K. Gong, B. Xu, H. Mei, H. Zhang, J. Zhang, Z. Kang, Y. Yan and D. Sun,

Nanoscale, 2019, **11**, 9598-9607.

10. X. Yin, C. Zhi, W. Sun, L.-P. Lv and Y. Wang, *J Mater Chem A*, 2019, **7**, 7800-7814.
11. B. Liu, J. Hou, T. Zhang, C. Xu and H. Liu, *J Mater Chem A*, 2019, **7**, 16222-16230.
12. Y. Ouyang, R. Huang, X. Xia, H. Ye, X. Jiao, L. Wang, W. Lei and Q. Hao, *Chem Eng J*, 2019, **355**, 416-427.
13. X. Feng, Y. Huang, C. Li, X. Chen, S. Zhou, X. Gao and C. Chen, *Chem Eng J*, 2019, **368**, 51-60.
14. F. Zhu, W. Liu, Y. Liu and W. Shi, *Inorg Chem Front*, 2019, **6**, 982-987.
15. Z. Qu, M. Shi, H. Wu, Y. Liu, J. Jiang and C. Yan, *J Power Sources*, 2019, **410**, 179-187.
16. W. Guo, Y. Wu, Y. Tian, X. Lian, J. Li and S. Wang, *Chemelectrochem*, 2019, **6**, 4645-4652.
17. T. Panja, N. Diez, R. Mysyk, D. Bhattacharjya, E. Goikolea and D. Carriazo, *Chemelectrochem*, 2019, **6**, 2536-2545.
18. H. Feng, S. Gao, J. Shi, L. Zhang, Z. Peng and S. Cao, *Electrochim Acta*, 2019, **299**, 116-124.
19. J. Bhagwan, G. Nagaraju, B. Ramulu, S. C. Sekhar and J. S. Yu, *Electrochim Acta*, 2019, **299**, 509-517.
20. J. Nan, Y. Shi, Z. Xiang, S. Wang, J. Yang and B. Zhang, *Electrochim Acta*, 2019, **301**, 107-116.
21. R. Xu, J. Lin, J. Wu, M. Huang, L. Fan, Z. Xu and Z. Song, *Appl Surf Sci*, 2019, **463**, 721-731.
22. K. H. Oh, G. S. Gund and H. S. Park, *J Mater Chem A*, 2018, **6**, 22106-22114.
23. L. Wang, X. Jiao, P. Liu, Y. Ouyang, X. Xia, W. Lei and Q. Hao, *Appl Surf Sci*, 2018, **427**, 174-181.
24. A. Jayakumar, R. P. Antony, R. H. Wang and J. M. Lee, *Small*, 2017, **13**, 1603102.