

Supplementary information

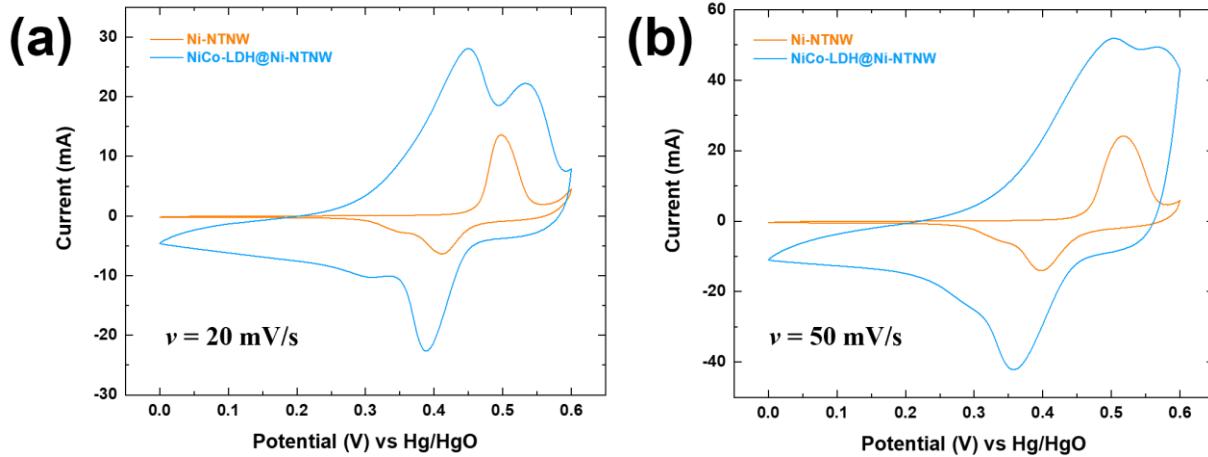


Fig. S1 CV of Ni-NTNW and NiCo-LDH@Ni-NTNW electrodes at scan rates of (a) 20 mV/s and (b) 50 mV/s.

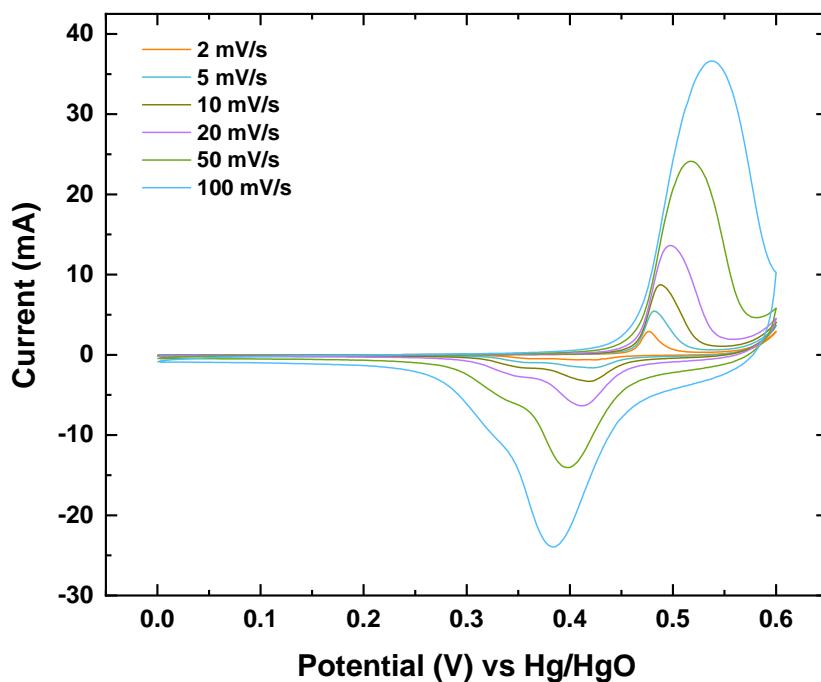


Fig. S2 CV curves of Ni-NTNW at different scan rates between 2-100 mV/s.

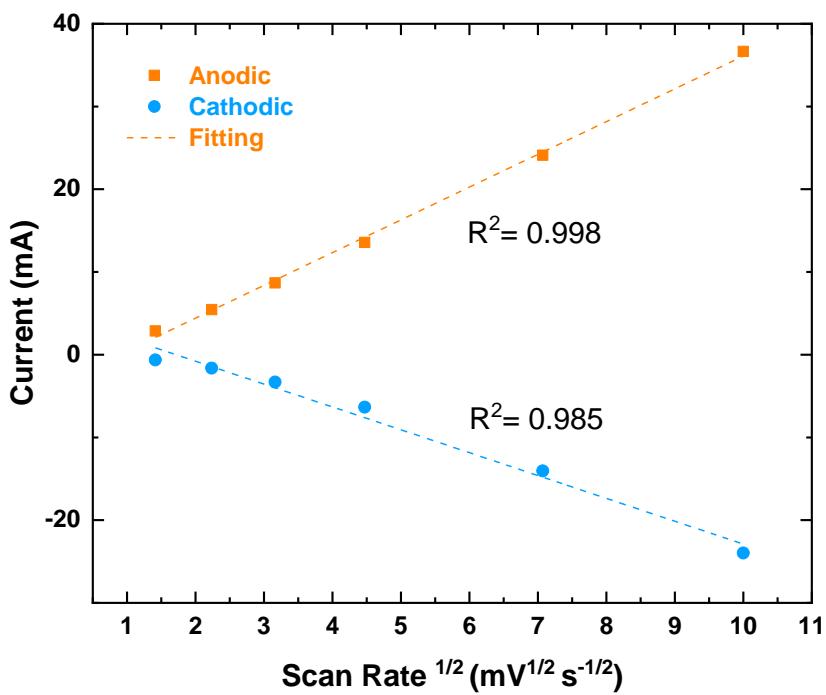


Fig. S3 The oxidation and reduction peak currents as a function of $v^{1/2}$ of Ni-NTNW electrode.

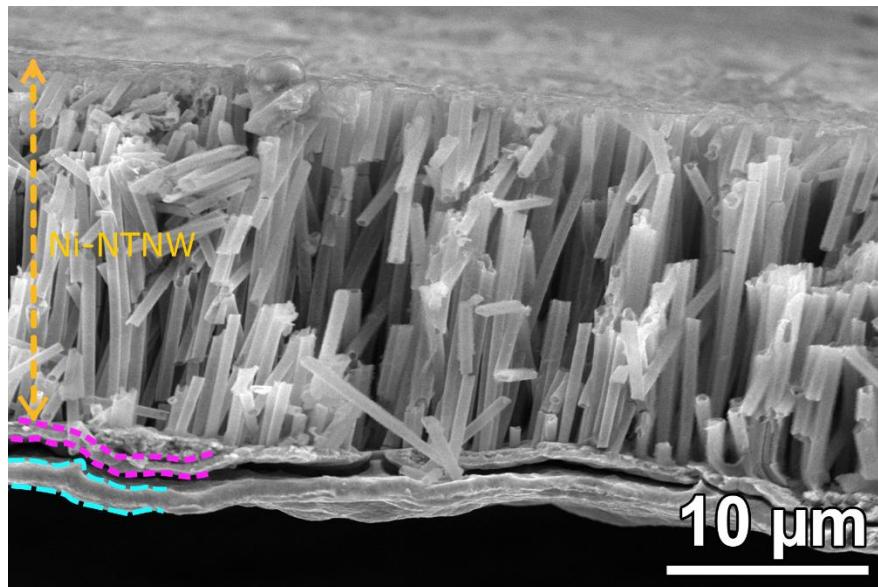


Fig. S4 SEM cross-sectional micrograph of the Ni-NTNW based electrode (with 400 nm nanotubes).

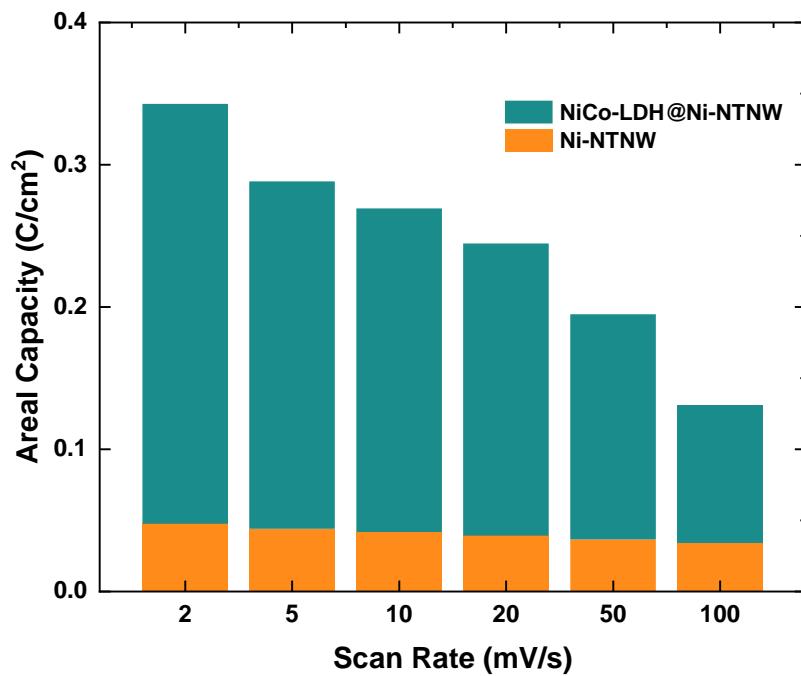


Fig. S5 Areal capacities of Ni-NTNW and NiCo-LDH@Ni-NTNW electrodes estimated from CV curves at different scan rates.

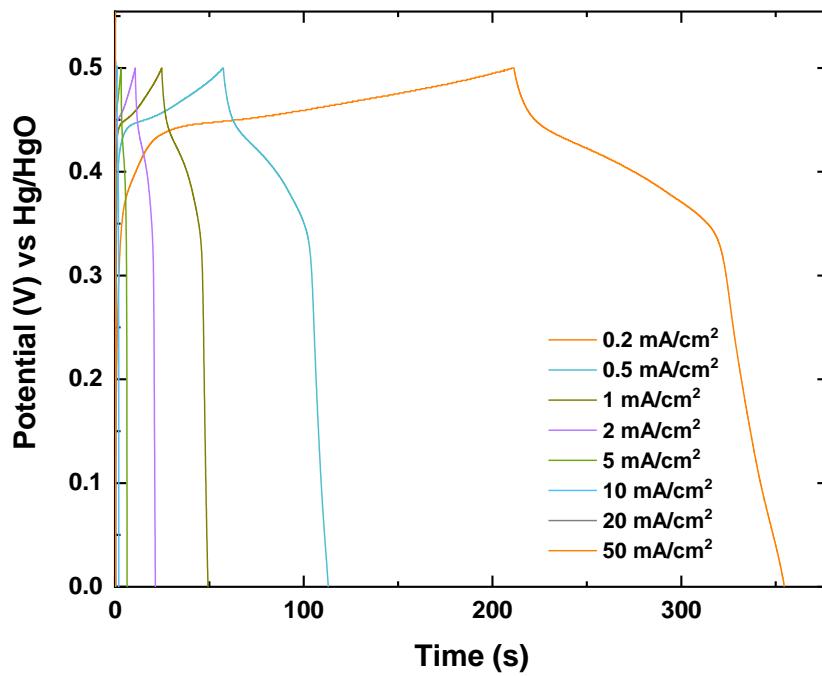


Fig. S6 GCD curves for Ni-NTNW electrode at different current densities between 0.2 and 50 mA/cm².

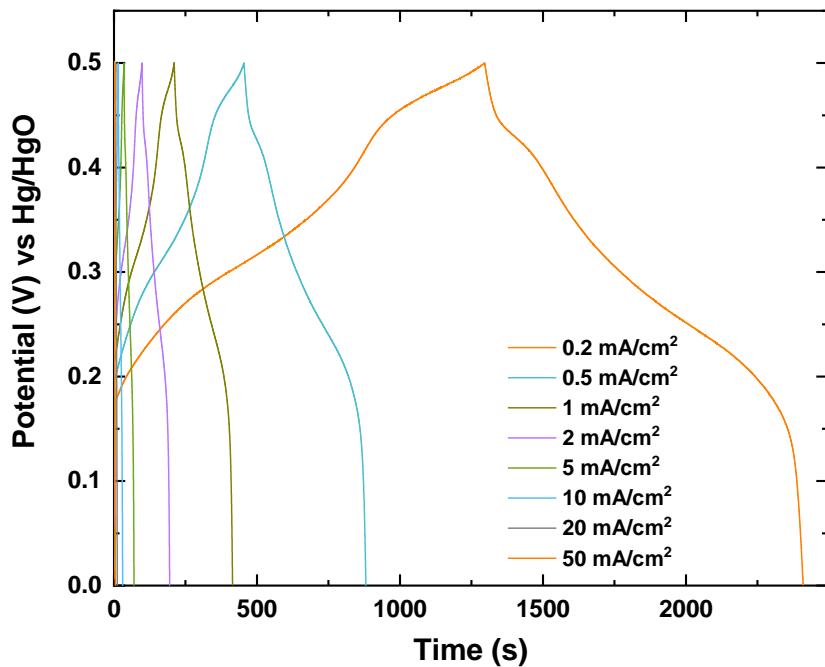


Fig. S7 GCD curves for NiCo-LDH@Ni-NTNW electrode at different current densities between 0.2 and 50 mA/cm².

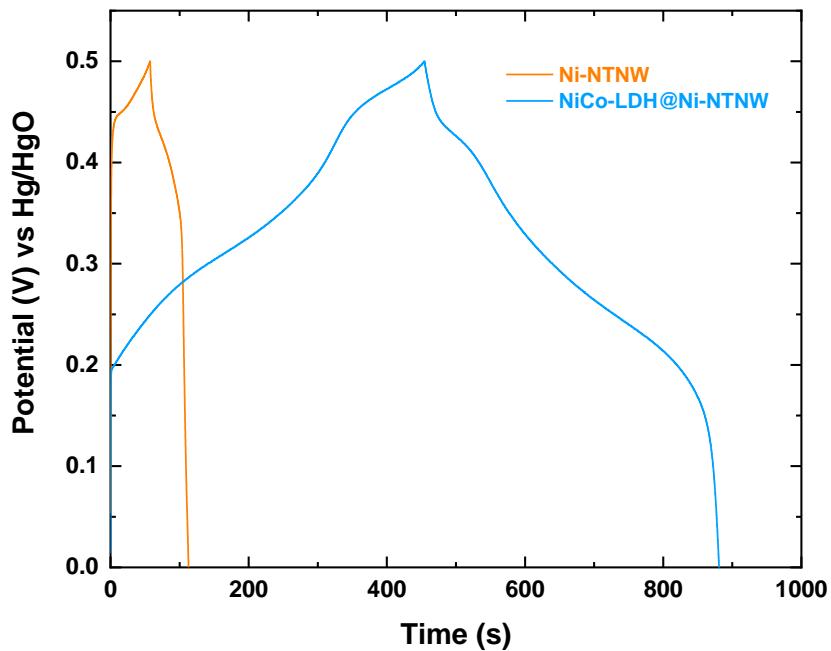


Fig. S8 GCD curves of Ni-NTNW and NiCo-LDH@Ni-NTNW electrodes at 0.5 mA/cm².

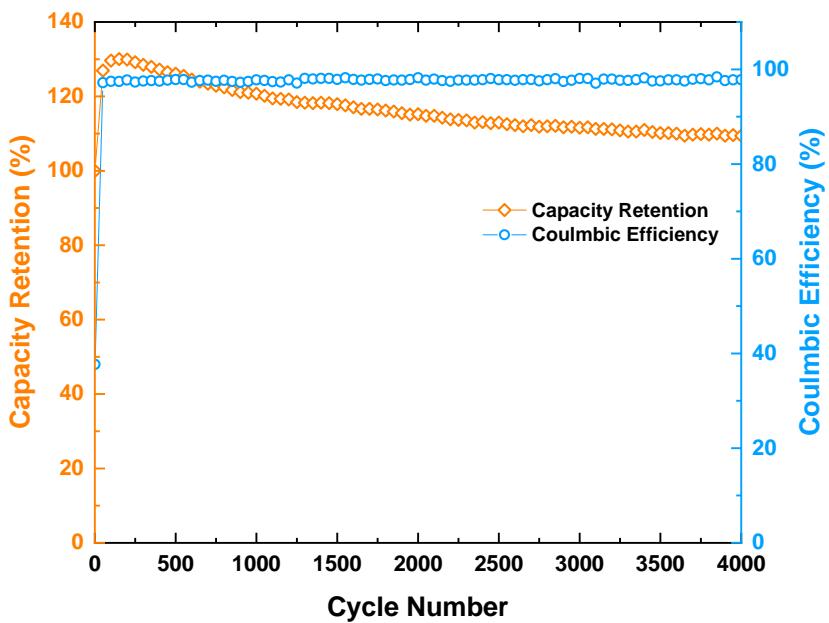


Fig. S9 Cycling stability of the Ni-NTNW electrode at current density of 10 mA/cm^2 .

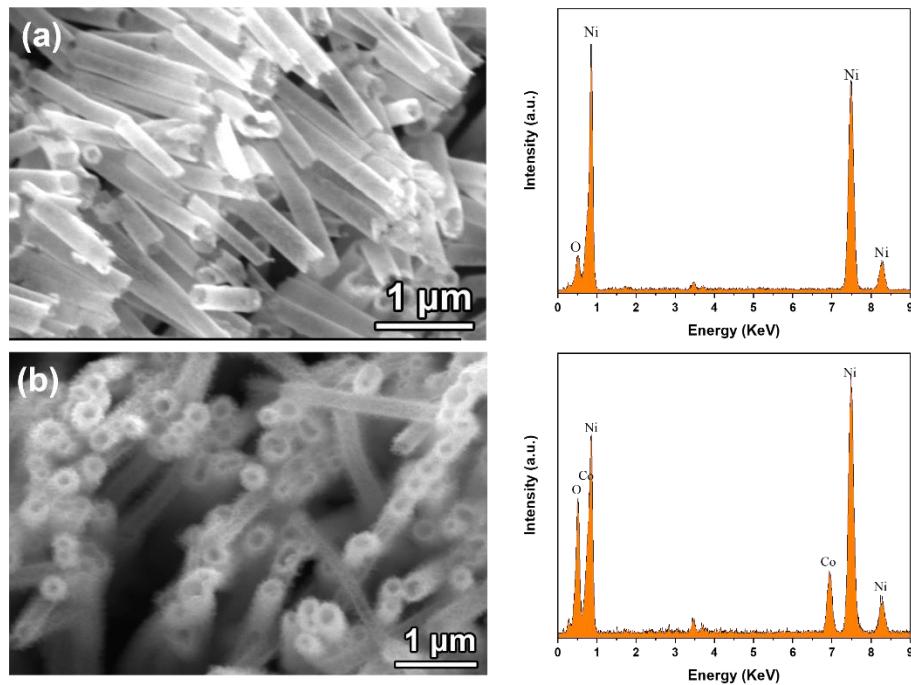


Fig. S10 SEM and EDX of (a) Ni-NTNW and (b) NiCo-LDH@Ni-NTNW electrodes after cycling test.

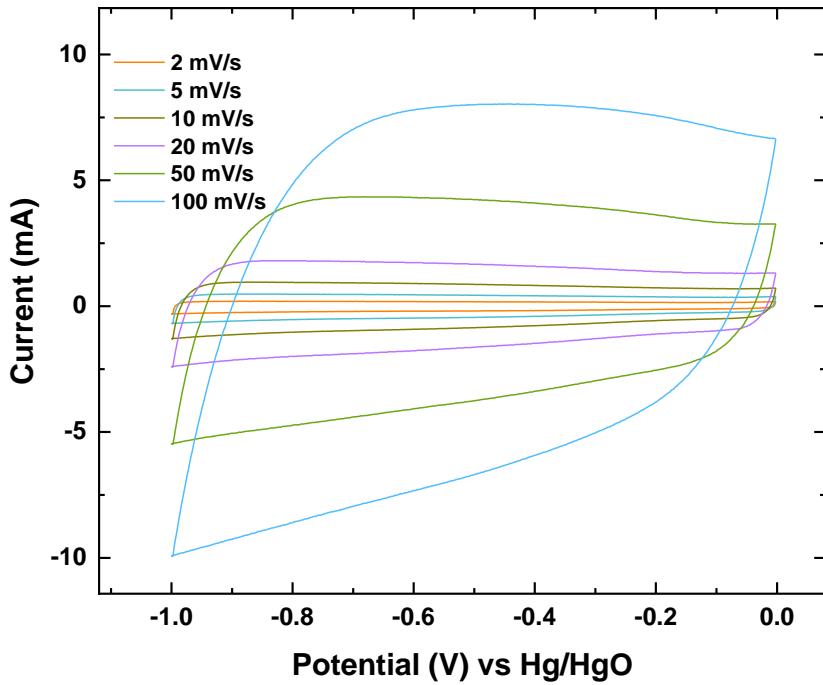


Fig. S11 CV curves of AC electrode at different scan rates between 2-100 mV/s.

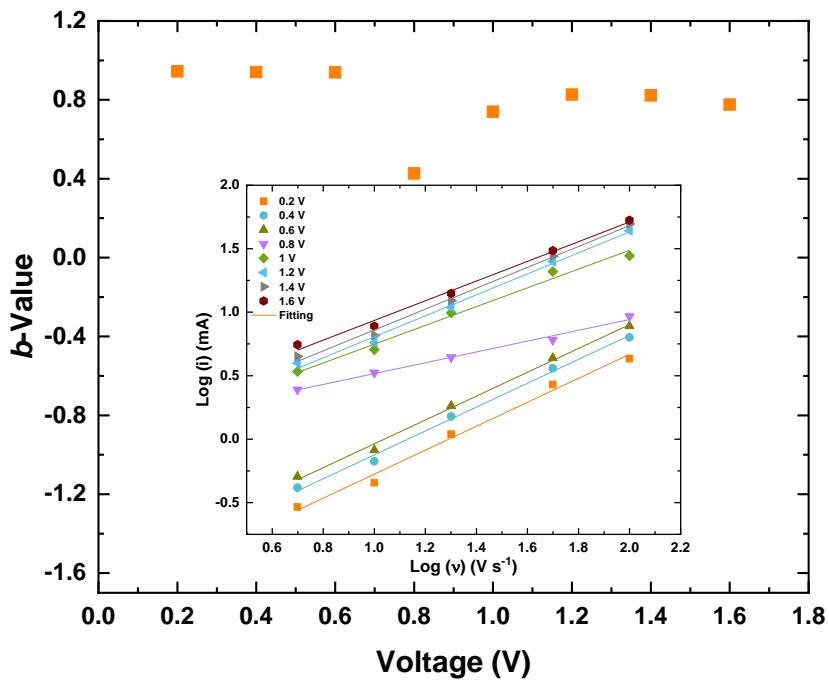


Fig. S12 b -Values for the assembled HSC at different voltages (Inset: the plots of $\log I$ as a function of $\log v$ at different stages of the CV potential window).

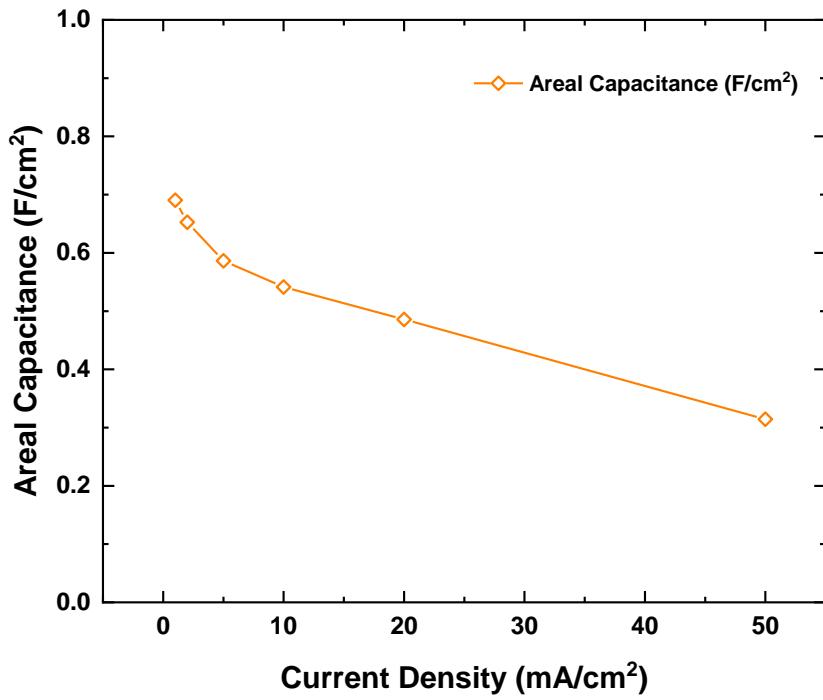


Fig. 13 Areal capacitance the HSC device at different current densities.

Table S1. Performance comparison of NiCo-LDH@Ni-NTNW electrode with recently reported NiCo-based battery-type electrodes in three-electrode setup.

| Electroactive material | Current collector | Current density | Electrolyte | Capacity | Ref. |
|--|--------------------------------|-------------------------|-------------|---|-----------|
| NiCoP/Ti ₃ C ₂ MXene | 3D printed CNT based ink | - | 2 M KOH | 68.5 C/cm ³ 10 C/cm ² | [1] |
| NiCo-LDH | Ni-coated textile | 1 A/g | 1 M KOH | 420 C/g | [2] |
| Ag@NiCo ₂ S ₄ | WC | 1 mA/cm ² | 6 M KOH | 341 C/g 3.04 C/cm ² | [3] |
| Co(OH) ₂ | CW | 1 mA/cm ² | 2 M KOH | 261 C/g 1.48 C/cm ² | [4] |
| NiO/ZnO | Ni foam | 1.3 A/g | 3 M KOH | 248.5 C/g | [5] |
| NiCo-LDH/Co ₉ S ₈ | Ni foam | 4 A/g | 1 M KOH | ~742 C/g * | [6] |
| Co-doped Ni ₁₁ (HPO ₃) ₈ (OH) ₆ | Ni foam | 0.5 A/g | 3 M KOH | 300.6 C/g | [7] |
| NiCo ₂ S ₄ | Ni foam | 2 A/g | 6 M KOH | 508 C/g | [8] |
| 2D/2D NiCo-MOF@GO | - | 0.5 A/g | 2 M KOH | 413.6 C/g | [9] |
| Honeycomb Co@Co(OH) ₂ sheets | Cellulose paper | 2 mA/cm ² | 6 M KOH | 479 C/g 0.321 C/cm ² | [10] |
| Ni-Co LDH nanorods | Carbon nanofiber | 0.02 mA/cm ² | 1 M NaOH | 551.2 C/g 0.011 C/cm ² | [11] |
| mesoporous network-like NiCo ₂ O ₄ | Carbon cloth | 0.33 mA/cm ² | 3 M KOH | 16.2 C/cm ³ 0.29 C/cm ² | [12] |
| NiCo-LDH@Ni-NTNW electrode | Integrated Ni supporting layer | 0.2 mA/cm ² | 1 M KOH | 126.4 C/cm ³ 601.0 C/g 0.252 C/cm ² | This work |

* Estimated from specific capacitance figure

WC: wood-derived carbon

CW: carbonized wood

NGP: Ni/graphite/paper

Table S2. Comparison of electrochemical performance of our NiCo-LDH@Ni-NTNW//AC hybrid supercapacitor with state-of-the-art symmetric/asymmetric and hybrid supercapacitors with high volumetric capacitance and energy density.

| Positive electrode | Negative electrode | Current density (mA/cm ²) | Gravimetric capacitance (F/g) | Areal capacitance (F/cm ²) | Volumetric capacitance (F/cm ³) | Capacitance Retention/Cycles | Voltage (V) | Energy Density (mWh/cm ³) | Ref. |
|--|--|---------------------------------------|-------------------------------|--|---|------------------------------|-------------|---------------------------------------|------|
| Mesoporous network-like NiCo ₂ O ₄ | Mesoporous network-like NiCo ₂ O ₄ | 0.33 | 269 | 0.09 | 5 | 89% 4000 | 1 | 0.69 * | [12] |
| CuCo ₂ O ₄ | AC | 1 | - | 0.262 ** | 2.62 ** | 82% 3000 | 1.5 | 0.81 | [13] |
| MnO ₂ /TCC | TCC | 2 | 45.3 | 1.5 | 16.8 | 96% 20000 | 2 | 9.4 | [14] |
| NiCoP/Ti ₃ C ₂ MXene | AC | 2 | - | 3.29 | 10.97 | 87.5% 5000 | 1.4 | 2.2 | [1] |
| NiCo-LDH@Ni-coated textile | NiCo-LDH@Ni-coated textile | - | - | - | - | - | 0.65 | 1.25 | [2] |
| Co ₉ S ₈ | Co ₃ O ₄ @RuO ₂ | 2.5 | - | 0.34 | 4.28 | 90.2% 2000 | 1.6 | 1.44 | [15] |
| WC@Ag@NiCo ₂ S ₄ | WC@Ag | 1 | 40.2 | 1.87 | 11.3 | 87.7% 10000 | 1.5 | 3.93 | [3] |
| Co(OH) ₂ @CW | CW | 1 | 34.8 | 2.2 | 14.19 | 85% 10000 | 1.5 | 4.45 | [4] |

| | | | | | | | | | |
|-------------------------------------|--------------------------------|-----|-------|-------|------|----------------|-----|------|--------------|
| Ni(OH) ₂ | Mn ₃ O ₄ | 1 | - | - | 2.07 | 83.3% 12000 | 1.3 | 0.35 | [16] |
| GF/NiCo ₂ S ₄ | GF | 0.5 | - | 0.568 | 39.4 | 92% 2000 | 1.5 | 12.3 | [17] |
| NiCo-LDH@Ni- NTNW | AC | 1 | 142.6 | 0.69 | 76.7 | 124% 20000 | 1.6 | 14.8 | This work |

* calculated based on the mass loading

** estimated from specific capacitance figure

TCC: porous carbon cloth

GF: graphene fiber

Table S3. Cyclic stability comparison of our NiCo-LDH@Ni-NTNW//AC hybrid supercapacitor with recently reported asymmetric and hybrid supercapacitors with high-capacitance retention.

| Device composition | Current density | Cycles | Retention | Ref. |
|---|-------------------------|--------|-----------|-----------|
| CNTs/NiCo LDH //AC | 5 A/g | 10000 | 99.4 % | [18] |
| PPNF@Co–Ni MOF//CNF-G | 10 A/g | 10000 | 100 % | [19] |
| Layered CuCo hydroxide//ACC | 8.33 mA/cm ² | 3500 | 96.55% | [20] |
| NiCoP/Ti ₃ C ₂ MXene//AC | 12 mA/cm ² | 5000 | 87.5% | [1] |
| WC@Ag@NiCo ₂ S ₄ //WC@Ag | 50 mA/cm ² | 10000 | 87.7% | [3] |
| Co(OH) ₂ @CW//CW | 50 mA/cm ² | 10000 | 85% | [4] |
| Ni(OH) ₂ /Mn ₃ O ₄ | - | 12000 | 83.3% | [16] |
| NiCo-LDH//CNT | 4 A/g | 5000 | 103.9 % | [21] |
| NiCo-LDH//graphene | - | 700 | 110 % | [22] |
| NiCo-LDH@Ni-NTNW//AC | 20 mA/cm ² | 20000 | 124 % | This work |

AC: activated carbon

ACC: activated carbon cloth

References

- [1] L. Yu, W. Li, C. Wei, Q. Yang, Y. Shao, J. Sun, 3D Printing of NiCoP/Ti₃C₂ MXene Architectures for Energy Storage Devices with High Areal and Volumetric Energy Density, Nano-Micro Lett. 12 (2020) 1–13. <https://doi.org/10.1007/s40820-020-00483-5>.
- [2] Y.M. Jeong, I. Son, S.H. Baek, Binder-free of NiCo-layered double hydroxides on Ni-coated textile for wearable and flexible supercapacitors, Appl. Surf. Sci. 467–468 (2019) 963–967. <https://doi.org/10.1016/j.apsusc.2018.10.252>.
- [3] F. Wang, X. Liu, G. Duan, H. Yang, J.Y. Cheong, J. Lee, J. Ahn, Q. Zhang, S. He, J. Han,

Y. Zhao, I.D. Kim, S. Jiang, Wood-Derived, Conductivity and Hierarchical Pore Integrated Thick Electrode Enabling High Areal/Volumetric Energy Density for Hybrid Capacitors, *Small.* 17 (2021) 1–10. <https://doi.org/10.1002/smll.202102532>.

- [4] Y. Wang, X. Lin, T. Liu, H. Chen, S. Chen, Z. Jiang, J. Liu, J. Huang, M. Liu, Wood-Derived Hierarchically Porous Electrodes for High-Performance All-Solid-State Supercapacitors, *Adv. Funct. Mater.* 28 (2018). <https://doi.org/10.1002/ADFM.201806207>.
- [5] G.-C. Li, P.-F. Liu, R. Liu, M. Liu, K. Tao, S.-R. Zhu, M.-K. Wu, F.-Y. Yi, L. Han, MOF-derived hierarchical double-shelled NiO/ZnO hollow spheres for high-performance supercapacitors, *Dalt. Trans.* 45 (2016) 13311–13316.
<https://doi.org/10.1039/C6DT01791F>.
- [6] G. Yilmaz, K.M. Yam, C. Zhang, H.J. Fan, G.W. Ho, In Situ Transformation of MOFs into Layered Double Hydroxide Embedded Metal Sulfides for Improved Electrocatalytic and Supercapacitive Performance, *Adv. Mater.* 29 (2017).
<https://doi.org/10.1002/ADMA.201606814>.
- [7] B. Li, Y. Shi, K. Huang, M. Zhao, J. Qiu, H. Xue, H. Pang, Cobalt-Doped Nickel Phosphite for High Performance of Electrochemical Energy Storage, *Small.* 14 (2018).
<https://doi.org/10.1002/SMML.201703811>.
- [8] B.Y. Guan, L. Yu, X. Wang, S. Song, X.W.D. Lou, Formation of Onion-Like NiCo₂S₄ Particles via Sequential Ion-Exchange for Hybrid Supercapacitors, *Adv. Mater.* 29 (2017).
<https://doi.org/10.1002/ADMA.201605051>.
- [9] S. Li, C. Shi, Y. Pan, Y. Wang, 2D/2D NiCo-MOFs/GO hybrid nanosheets for high-performance asymmetrical supercapacitor, *Diam. Relat. Mater.* 115 (2021) 108358.
<https://doi.org/10.1016/j.diamond.2021.108358>.
- [10] C. Wan, Y. Jiao, D. Liang, Y. Wu, J. Li, A Geologic Architecture System-Inspired Micro-/Nano-Heterostructure Design for High-Performance Energy Storage, *Adv. Energy Mater.* 8 (2018). <https://doi.org/10.1002/AENM.201802388>.
- [11] F. Lai, Y. Huang, Y.E. Miao, T. Liu, Controllable preparation of multi-dimensional hybrid materials of nickel-cobalt layered double hydroxide nanorods/nanosheets on electrospun carbon nanofibers for high-performance supercapacitors, *Electrochim. Acta.* 174 (2015)

456–463. <https://doi.org/10.1016/J.ELECTACTA.2015.06.031>.

- [12] S. Gao, F. Liao, S. Ma, L. Zhu, M. Shao, Network-like mesoporous NiCo₂O₄ grown on carbon cloth for high-performance pseudocapacitors, *J. Mater. Chem. A.* 3 (2015) 16520–16527. <https://doi.org/10.1039/C5TA02876K>.
- [13] Q. Wang, D. Chen, D. Zhang, Electrospun porous CuCo₂O₄ nanowire network electrode for asymmetric supercapacitors, *RSC Adv.* 5 (2015) 96448–96454. <https://doi.org/10.1039/C5RA21170K>.
- [14] H. Wang, C. Xu, Y. Chen, Y. Wang, MnO₂ nanograsses on porous carbon cloth for flexible solid-state asymmetric supercapacitors with high energy density, *Energy Storage Mater.* 8 (2017) 127–133. <https://doi.org/10.1016/J.ENS.2017.05.007>.
- [15] J. Xu, Q. Wang, X. Wang, Q. Xiang, B. Liang, D. Chen, G. Shen, Flexible Asymmetric Supercapacitors Based upon Co₉S₈ Nanorod//Co₃O₄@RuO₂ Nanosheet Arrays on Carbon Cloth, *ACS Nano.* 7 (2013) 5453–5462. <https://doi.org/10.1021/NN401450S>.
- [16] J.-X. Feng, S.-H. Ye, X.-F. Lu, Y.-X. Tong, G.-R. Li, Asymmetric Paper Supercapacitor Based on Amorphous Porous Mn₃O₄ Negative Electrode and Ni(OH)₂ Positive Electrode: A Novel and High-Performance Flexible Electrochemical Energy Storage Device, *ACS Appl. Mater. Interfaces.* 7 (2015) 11444–11451. <https://doi.org/10.1021/ACSAM.5B02157>.
- [17] W. Cai, T. Lai, J. Lai, H. Xie, L. Ouyang, J. Ye, C. Yu, Transition metal sulfides grown on graphene fibers for wearable asymmetric supercapacitors with high volumetric capacitance and high energy density, *Sci. Reports* 2016 61. 6 (2016) 1–9. <https://doi.org/10.1038/srep26890>.
- [18] M. Huang, Y. Wang, J. Chen, D. He, J. He, Y. Wang, Biomimetic design of Ni Co LDH composites linked by carbon nanotubes with plant conduction tissues characteristic for hybrid supercapacitors, *Electrochim. Acta.* 381 (2021) 138289. <https://doi.org/10.1016/J.ELECTACTA.2021.138289>.
- [19] D. Tian, N. Song, M. Zhong, X. Lu, C. Wang, Bimetallic MOF Nanosheets Decorated on Electrospun Nanofibers for High-Performance Asymmetric Supercapacitors, (2019). <https://doi.org/10.1021/acsami.9b16420>.

- [20] A.D. Deshmukh, A.R. Urade, A.P. Nanwani, K.A. Deshmukh, D.R. Peshwe, P. Sivaraman, S.J. Dhoble, B.K. Gupta, Two-Dimensional Double Hydroxide Nanoarchitecture with High Areal and Volumetric Capacitance, *ACS Omega.* 3 (2018) 7204–7213.
<https://doi.org/10.1021/acsomega.8b00596>.
- [21] R. Ramachandran, Y. Lan, Z.X. Xu, F. Wang, Construction of NiCo-Layered Double Hydroxide Microspheres from Ni-MOFs for High-Performance Asymmetric Supercapacitors, *ACS Appl. Energy Mater.* 3 (2020) 6633–6643.
<https://doi.org/10.1021/acsaem.0c00790>.
- [22] X. Sun, G. Wang, H. Sun, F. Lu, M. Yu, J. Lian, Morphology controlled high performance supercapacitor behaviour of the Ni–Co binary hydroxide system, *J. Power Sources.* 238 (2013) 150–156. <https://doi.org/10.1016/J.JPOWSOUR.2013.03.069>.