Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Alternately electrodeposited mesoporous $NiCoSe_2$@MnO_2 nanocomposite-anchored Ni-Co layered double hydroxide nanoneedles for hybrid supercapacitors

Fangqiao Wang, Zhibo Zhao, Xiaoguang Fu, Baobao Li, Zhuomin Chen, Senjing Wang, Qiaoling Huang, Qingchi Xu*, and Meidan Ye*

Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Lab for Soft Functional Materials Research, Department of Physics, College of Physical Science and Technology, Xiamen University, Xiamen 361005, China

*Author to whom correspondence should be addressed: xuqingchi@xmu.edu.cn, mdye@xmu.edu.cn

1. Experimental section

1.1 Synthesis of (Co, Ni)$(CO_3)_{0.5}OH\cdot 0.11H_2O$ nanoneedle electrodes

All the chemicals with analytical grade were commercially purchased and used without further purification. The (Co, Ni)$(CO_3)_{0.5}OH\cdot 0.11H_2O$ (NiCoLDH) electrodes were in-situ grown on carbon fibers (diameter: 200 μm; length: 4 cm) by a hydrothermal process. Firstly, the carbon fibers were soaked in concentrated sulfuric for 60 min to improve its surface hydrophilicity, then successively cleaned by ultrasonication in acetone for 15 min, ethanol for 15 min and deionized water for 15 min to remove dust stains on the surface. Secondly, 50 mg $NiCl_2\cdot 6H_2O$, 100 mg $CoCl_2\cdot 6H_2O$, and 80 mg urea were dissolved in 60 mL deionized water and thoroughly stirred for 10 min until a clear and uniform pink solution was formed. The mixed solution was transferred to a 100 mL Teflonlined stainless autoclave. The pre-treated carbon fiber wires were immersed in the aqueous solution noted above and heated at 120 °C for 7 h, yielding NiCoLDH nanoneedles directly grown on the carbon fiber wires. Finally, the resulting product was washed with deionized water and ethanol, and then dried in a vacuum at 60 °C for 30 min.

1.2 Synthesis of NiCoLDH@$NiCoSe_2$ electrodes

$NiCoSe_2$ was in-situ grown on the NiCoLDH electrodes to form the NiCoLDH@$NiCoSe_2$ electrodes via an electrodeposition method. Firstly, 950.8 mg $NiCl_2\cdot 6H_2O$, 951.6 mg $CoCl_2\cdot 6H_2O$, 1110 mg SeO_2, 200 mg $LiCl\cdot H_2O$ and 50 mg polyethylene glycol (PEG) were dissolved in 200 ml deionized water to serve as the electrolyte A for the electrodeposition process, where $LiCl\cdot H_2O$ was employed to increase the conductivity of the electrolyte and PEG was used as the electrolyte additive. Secondly, all the electrochemical experiments were performed in a conventional three-electrode system with the NiCoLDH electrode as the working electrode, Pt foil as the counter electrode and an Ag/AgCl electrode as the reference electrode. The electrodeposition was carried out at a chronoamperometry measurement mode on an Electrochemical Workstation at a polarization voltage of -0.8 V for 300 s at room temperature.

1.3 Synthesis of NiCoLDH@$NiCoSe_2$@MnO_2 electrodes

MnO_2 was also in-situ grown on the NiCoLDH@$NiCoSe_2$ electrodes to form the NiCoLDH@$NiCoSe_2$@MnO_2 electrodes via another electrodeposition process. Firstly, 4.9 g $Mn(CH_3COO)_2$ and 2.84 g Na_2SO_4 were dissolved in 200 ml deionized water to serve as the electrolyte B for the electrodeposition process. Secondly, the NiCoLDH electrode was also carried out at a chronoamperometry measurement mode in the electrolyte A at a polarization voltage of -0.8 V for 60 s by the same three-electrode system. Thirdly, the corresponding NiCoLDH@$NiCoSe_2$ electrode was transferred to the electrolyte B for secondary chronoamperometry electrodeposition with the polarization voltage of 1V and duration of 40 s, yielding the NiCoLDH@$NiCoSe_2$@MnO_2-1 nanocomposite electrode. Then, other NiCoLDH@$NiCoSe_2$@MnO_2 nanocomposite electrodes (i.e., NiCoLDH@$NiCoSe_2$@MnO_2-2 and NiCoLDH@$NiCoSe_2$@MnO_2-3) were finally obtained by repeating the electrodeposition processes alternately in the electrolytes A and B, respectively. All resulting electrodes were carefully washed several times with deionized water to eliminate surface ions and then dried in the air.

1.4 Assembly of the fiber-shaped asymmetric supercapacitors

The flexible fiber-shaped asymmetric supercapacitors were assembled with the NiCoLDH@$NiCoSe_2$@MnO_2 nanocomposite electrodes as the positive electrodes, the activated carbon electrodes as the negative electrodes, and the polyvinyl alcohol (PVA)/KOH gel as the electrolyte. Firstly, the activated carbon was mixed with conductive carbon black and polyvinylidene difluoride (PVDF) with a ratio of 80 wt %: 10 wt%: 10 wt% in N-methylpyrrolidone to form uniform slurry. Then, the slurry was coated onto carbon fiber wires and dried in an oven overnight before being pressed under 10 M Pa for the preparation of activated carbon electrodes. Secondly, the PVA/KOH gel electrolyte was prepared as follows: 2 g KOH and 2 g PVA powder were dissolved in

20 mL deionized water. After that, the mixed solution was heated at 80 °C in an oil bath until the solution became clear and slightly yellow. Thirdly, the $NiCoLDH@NiCoSe_2@MnO_2$ nanocomposite electrode and the activated carbon electrode were put into a tubular mold, and then the gel electrolyte, which had not been cooled, was injected into the mold through a syringe, and it was ensured that the two fiber electrodes did not short-circuit because of contacting with each other, and finally the device was placed in the room temperature to cool down naturally for 24 h, waiting for the electrolyte to become a gel to solidify and then the device was taken out.

1.5 Characterization and performance measurement

The samples were observed by the scanning electron microscopy (SEM, Carl Zeiss, Sigma-HD, Germany) and transmission electron microscope (TEM, FEI 200kV Netherlands) to characterize their morphology, microstructure and elemental composition. X-ray diffraction (XRD, Rigaku, Ultima-IV, Japan) with a Cu Kα source was applied to characterize the phase structure of samples. An X-ray photoelectron spectroscope (XPS, Physical electronics, Quantum 2000, America) was used to analyze near-surface chemical compositions and valence states of elements of samples.

Electrochemical measurements were performed using an electrochemical workstation (Zahner, Germany). In order to investigate their electrochemical properties, cyclic voltammetry (CV), constant current charge-discharge curve (GCD) and electrochemical impedance (EIS) of the as-prepared electrodes were tested in a three-electrode system with a platinum foil counter electrode and an Hg/HgO reference electrode in a 3 M KOH aqueous electrolyte at room temperature. CV scans were recorded from 0 to 0.5 V (vs. Hg/HgO) at scan rates from 1 to 10 mV s^{-1}. Moreover, the EIS analysis was conducted over a frequency range from 10^{-2} to 10^{5} Hz.

Electrochemical performances of the individual electrodes and the supercapacitor device were calculated from the GCD measurement according to the following Equations: [1-3]

Specific capacity: $C_{pA} = \frac{2 * I\int V\,dt}{3.6 * A * \Delta V}$ for three electrode system (1)

Specific capacitance: $C_A = \frac{I * \Delta t}{A * \Delta V},$ (2)

Specific capacitance: $C_{A,device} = \frac{I * \Delta t}{2 * A * \Delta V}$, for two electrode system (3)

Energy density: $E_{A\ device} = \frac{1}{2} C_{A,device} \Delta V^2$ (4)

Power density: $P_{A\ device} = \frac{E\ *3600}{\Delta t}$ (5)

where C_A is the area capacitance, C_{pA} is the areal capacity, A is the surface areal of the electrode, $E_{A\ device}$ is the areal energy density, $P_{A\ device}$ is the power density, I is the discharge current (mA), ΔV (V), and Δt (s) are the working potential window and discharge time, respectively. The coulombic efficiency, η, was determined according to the following relation:

$$\eta = \frac{t_1}{t_2} \qquad (6)$$

where t_1 is the discharging time and t_2 is the charging time.

Figures

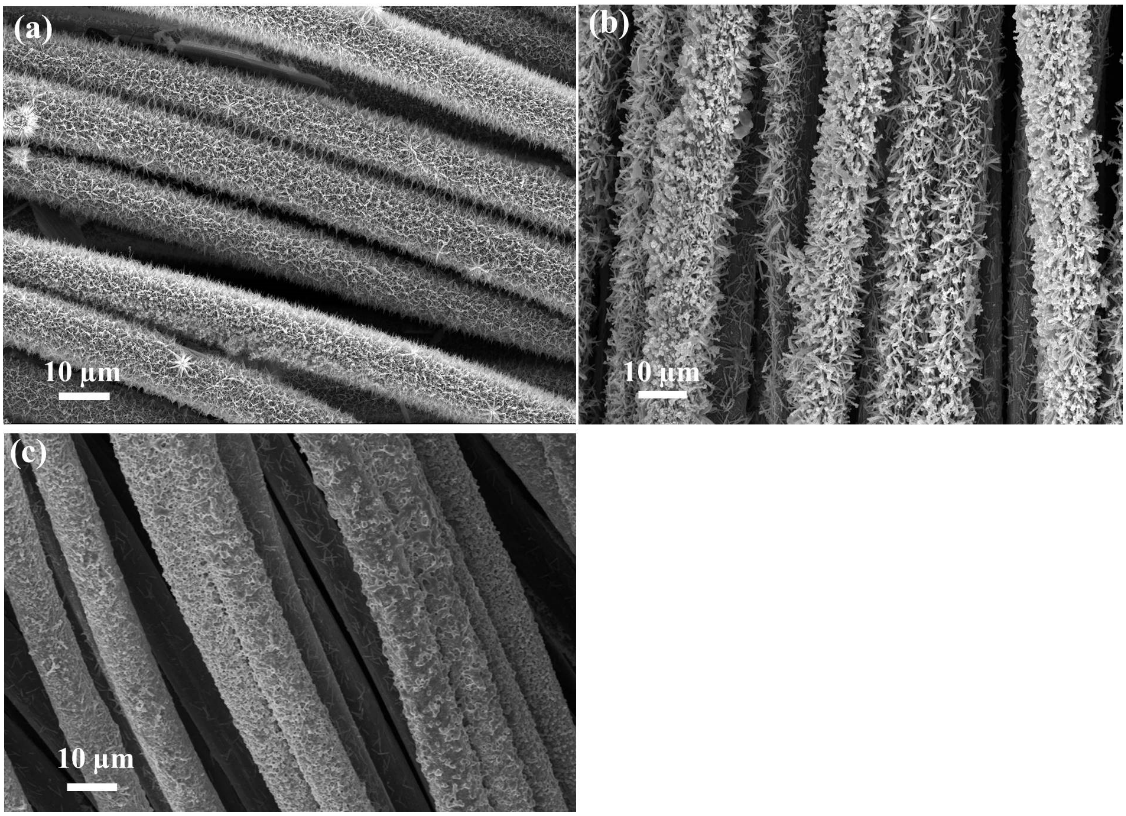


Figure S1. SEM images of (a) NiCoLDH, (b) NiCoLDH@NiCoSe$_2$, (c) NiCoLDH@NiCoSe$_2$@MnO$_2$-1.

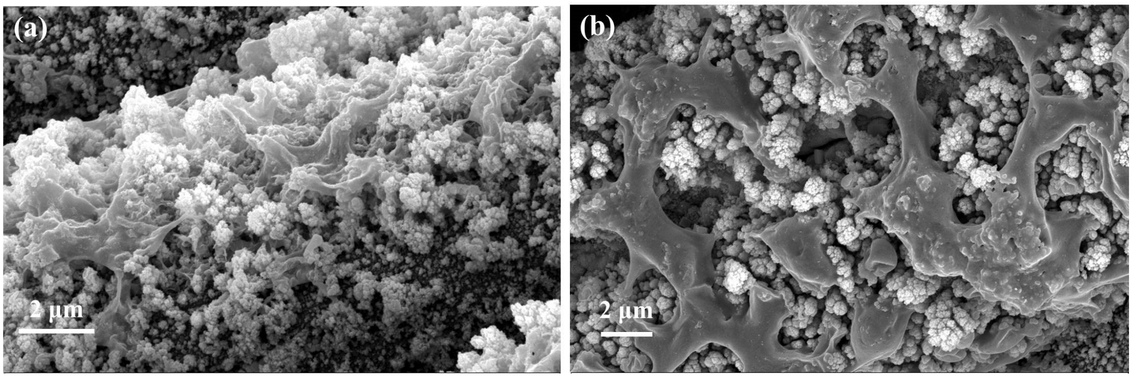


Figure S2. SEM images of (a) NiCoLDH@NiCoSe$_2$@MnO$_2$-2 and (b) NiCoLDH@NiCoSe$_2$@MnO$_2$-3.

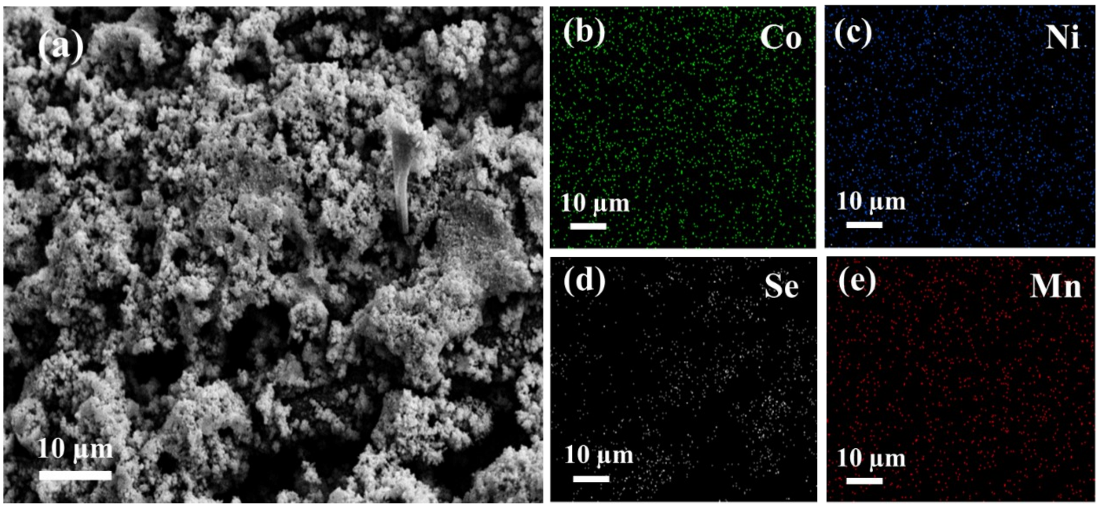
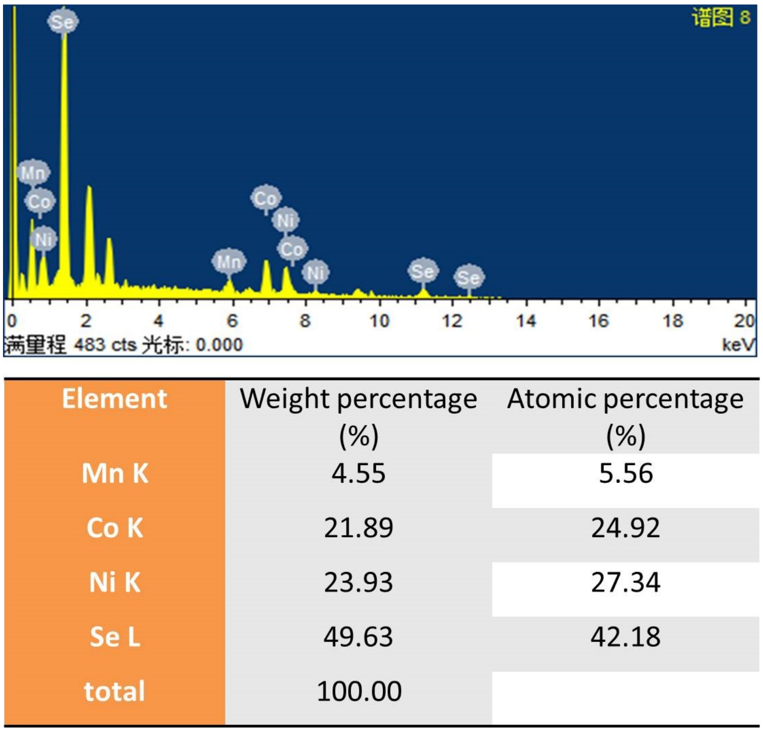


Figure S3. (a) SEM images of NiCoLDH@NiCoSe$_2$@MnO$_2$-3. (b-e) Elemental mappings of NiCoLDH@NiCoSe$_2$@MnO$_2$-3.



Element	Weight percentage (%)	Atomic percentage (%)
Mn K	4.55	5.56
Co K	21.89	24.92
Ni K	23.93	27.34
Se L	49.63	42.18
total	100.00	

Figure S4. The EDS mapping and element ratios of NiCoLDH@NiCoSe$_2$@MnO$_2$.

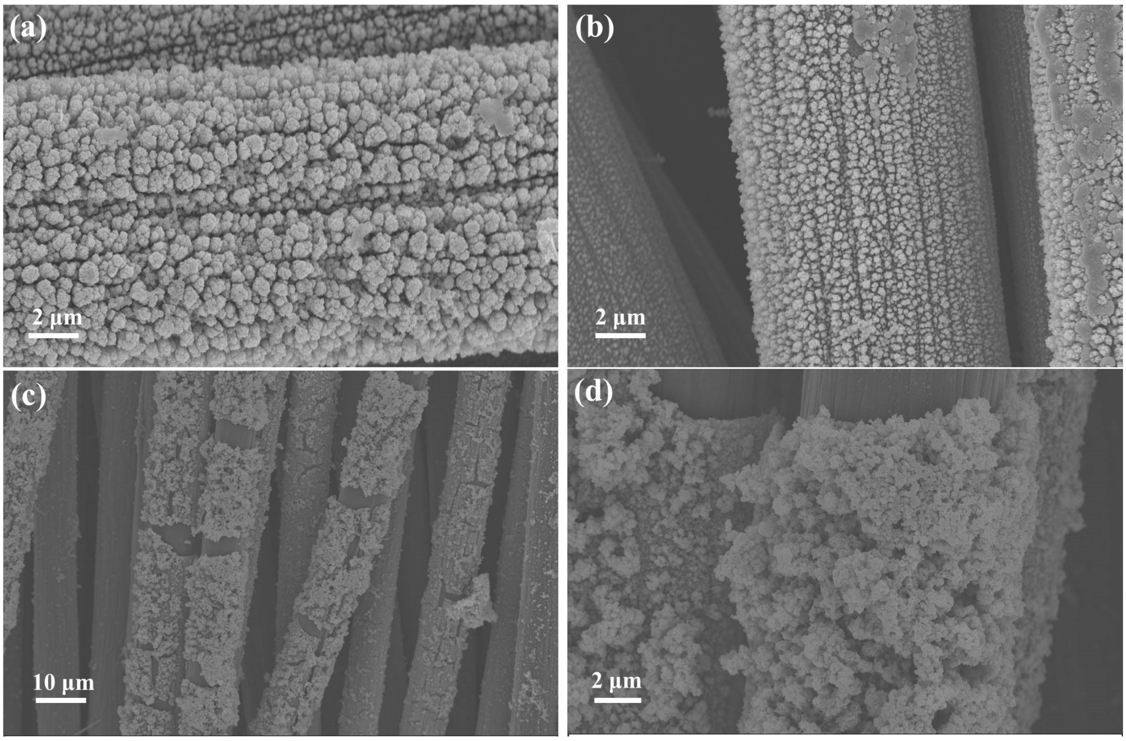


Figure S5. SEM images of $NiCoSe_2$ films on carbon cloth via single-step electrodeposition at -0.8 V for 300 s.

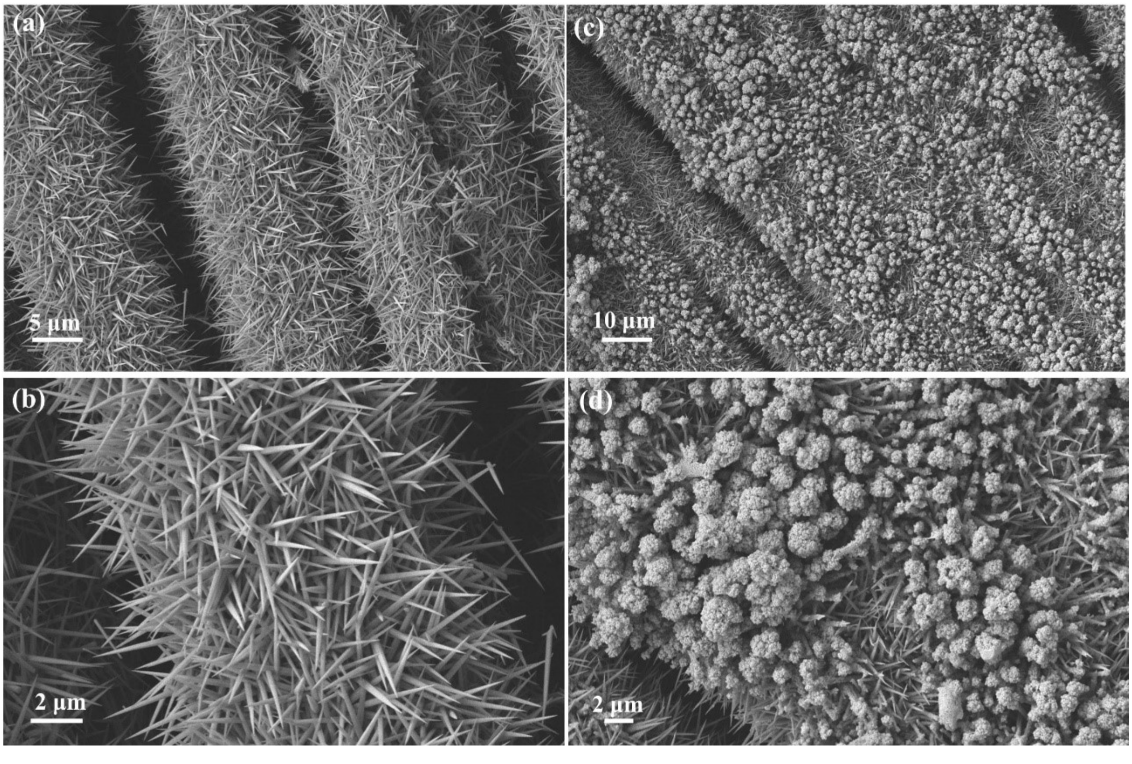


Figure S6. SEM images of NiCoLDH@$NiCoSe_2$ films on carbon cloth via (a-b) hydrothermal growth of NiCoLDH and (c-d) electrodeposition of $NiCoSe_2$ at -0.8 V for 300 s.

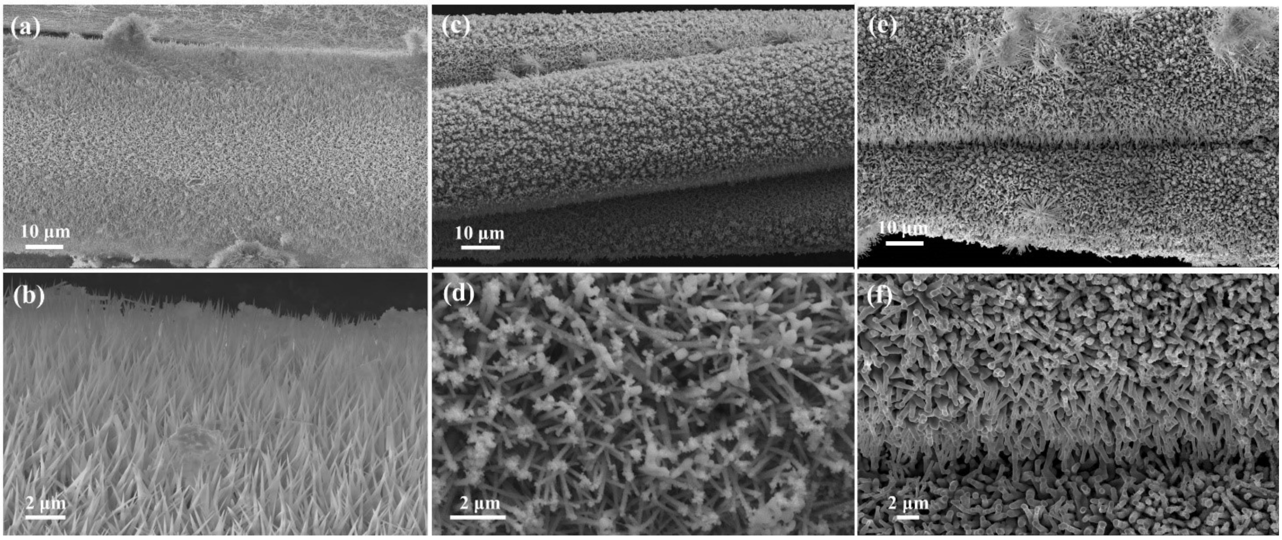


Figure S7. SEM images of NiCoLDH@NiCoSe$_2$@MnO$_2$ films on stainless steel wires via (a-b) hydrothermal growth of NiCoLDH and electrodeposition of (c-d) NiCoSe$_2$ at -0.8 V for 60 s and (e-f) MnO$_2$ at 1 V for 40 s.

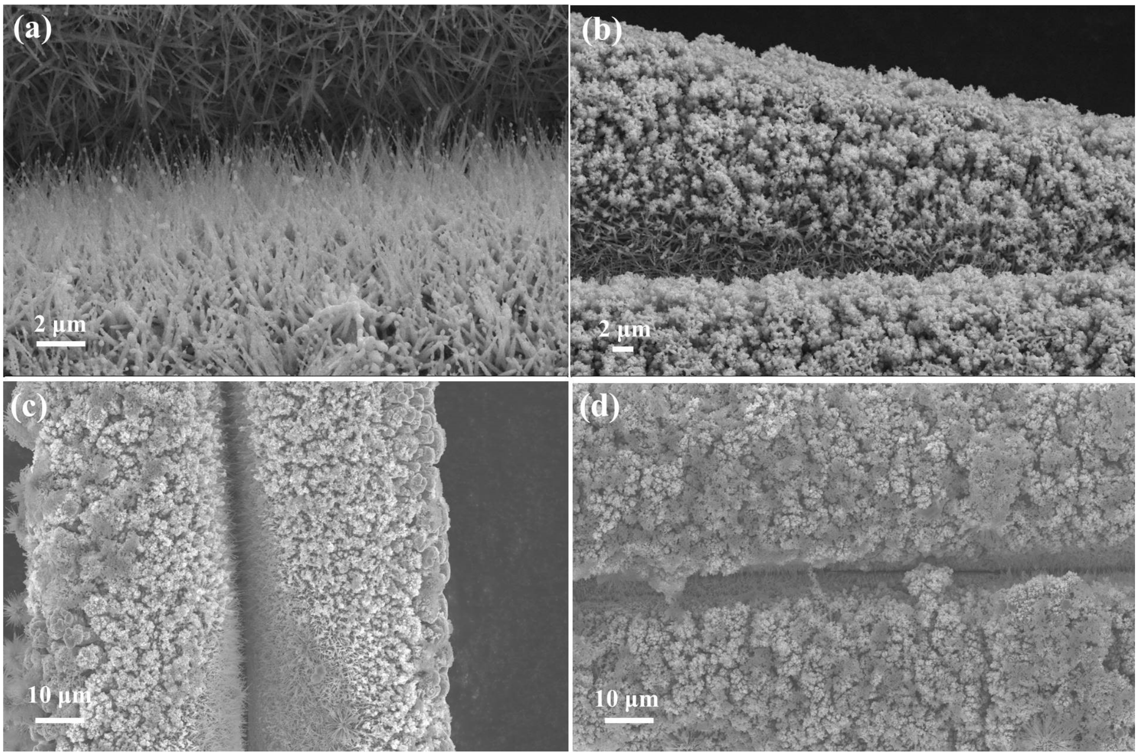


Figure S8. SEM images of NiCoLDH@NiCoSe$_2$ films on stainless steel wires via electrodeposition at -0.8 V under different times: (a) 100 s, (b) 200 s, (c) 300 s and (d) 400 s.

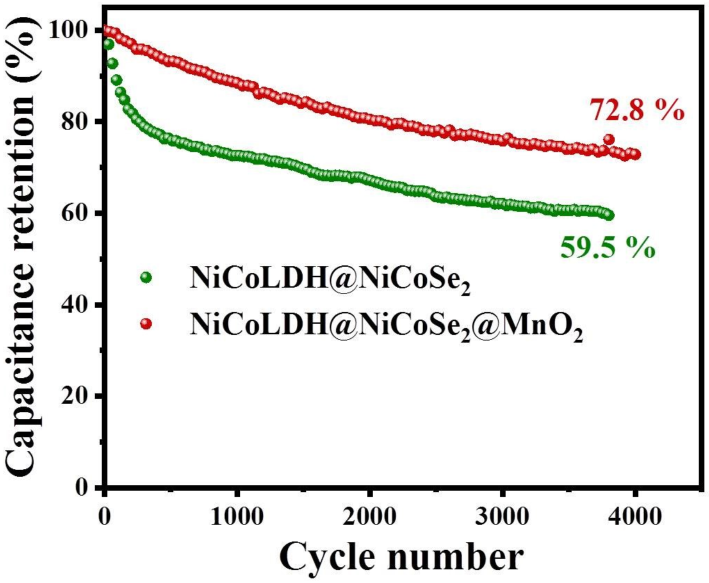


Figure S9. Electrochemically cycling stability of NiCoLDH@NiCoSe$_2$ and NiCoLDH@NiCoSe$_2$@MnO$_2$ films on tainless steel wires.

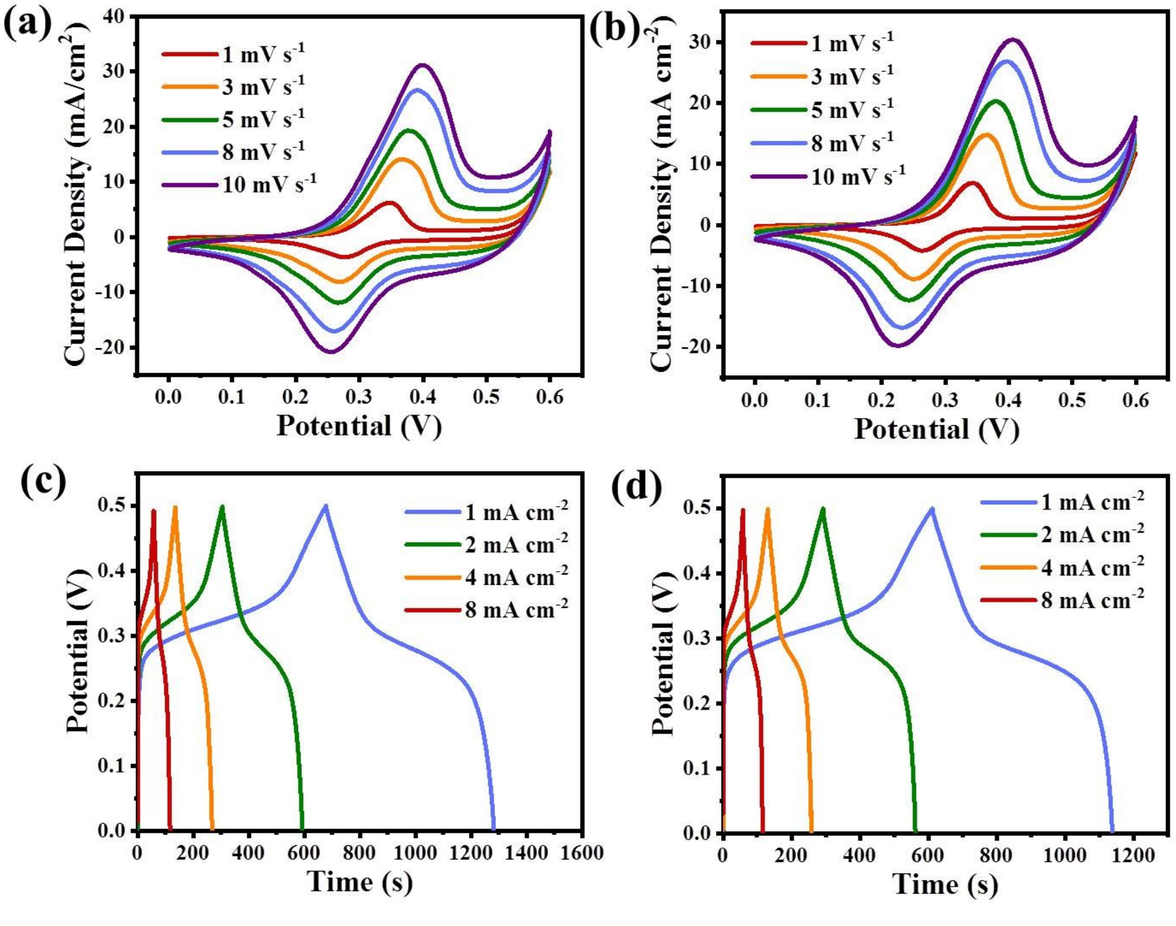


Figure S10. Electrochemical characterizations of NiCoLDH@NiCoSe$_2$@MnO$_2$ electrodes in a three-electrode-system with the KOH electrolyte. (a-b) CV curves and (c-d) GCD curves of different electrodes: (a, c) NiCoLDH@NiCoSe$_2$@MnO$_2$-2, (b, d) NiCoLDH@NiCoSe$_2$@MnO$_2$-3 electrodes.

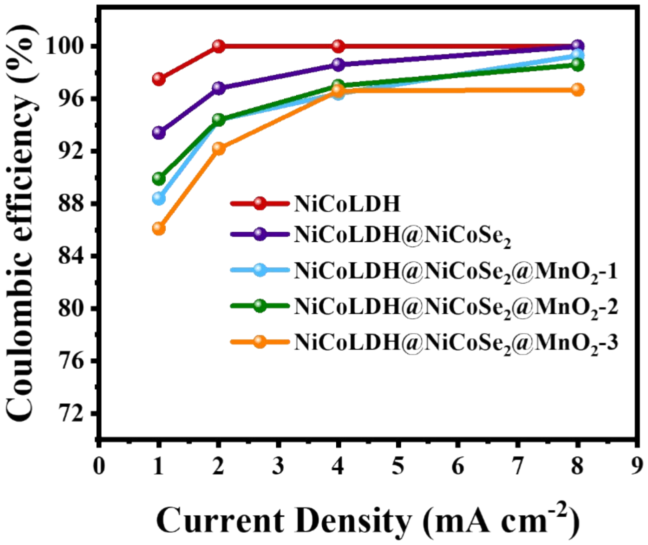


Figure S11. Coulomb efficiencies of five electrodes at different current densities.

References

1. B. Cai, J. Li, L. Wang, X. Li, X. Yang and W. Lu, *Nanotechnology*, 2022, **33**, 295402.
2. Z. B. Feng, L. Wang, D. G. Li, S. B. Gao, Q. Sun, P. Lu, P. F. Xing and M. Z. An, *Nanotechnology*, 2019, **30**, 245602.
3. X. L. Sun, K. Zhao, H. C. Fu, H. W. Guo, J. Shen, F. H. Jin, L. Wang, Z. H. Wang, L. Cui, F. Y. Quan and J. Q. Liu, *J. Energy Storage*, 2023, **63**, 107041.