Balancing High Performance with Synthesis Complexity: One-Step Hydrothermal Growth of Self-Supported $NiCo_2Se_4$ Nanoflowers on Carbon Cloth for Advanced Asymmetric Supercapacitors

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Section S1. Experimental

S1.1 Pretreatment of Carbon Cloth

1. Commercial carbon cloth (WOS1002, CeTech; thickness 0.33 mm) was cut into 2 × 1 cm^2 pieces.
2. The CC substrates were sequentially sonicated in:
    - acetone (20 min)
    - ethanol (20 min)
    - DI water (20 min)

3. Substrates were dried in a vacuum oven at 60 °C for 6 h to remove residual moisture and enhance surface hydrophilicity.

S1.2 One-Step Hydrothermal Synthesis of $NiCo_2Se_4$/CC

1. A precursor solution was prepared by dissolving:
   - 1.0 mmol $Ni(NO_3)_2 \cdot 6H_2O$
   - 2.0 mmol $Co(NO_3)_2 \cdot 6H_2O$
   - 10.0 mmol urea
   - 2.0 mL hydrazine hydrate (85%)
   - 4.0 mmol Se powder

   in 40 mL DI water, followed by magnetic stirring for 30 min.
2. The Ni: Co: Se molar ratio (1:2:4) was selected to promote stoichiometric $NiCo_2Se_4$ formation.
3. A pretreated CC piece was immersed vertically into the precursor solution.
4. The mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave, sealed, and heated at 180 °C for 12 h.
5. After natural cooling, the CC electrode was removed, rinsed repeatedly with DI water and ethanol, and dried in vacuum at 60 °C overnight.
6. The resulting product was used directly as a self-supported working electrode, without binders or additives.
7. The mass loading of $NiCo_2Se_4$ was calculated by weighing the CC substrate before and after synthesis and was typically 2.5 ± 0.2 mg cm^{-2}.

S1.3 Preparation of Control Samples ($NiSe_2$/CC and $CoSe_2$/CC)

1. For monometallic controls, only one metal nitrate was added:

o 3.0 mmol $Ni(NO_3)_2·6H_2O$ *or*

o 3.0 mmol $Co(NO_3)_2·6H_2O$

2. All other reaction parameters—including the amounts of urea, hydrazine hydrate, selenium powder, solvent volume, hydrothermal temperature/time—were kept identical to the procedure in Section S1.2.

3. Products were collected, washed, and dried following the same protocol.

Results and discussion

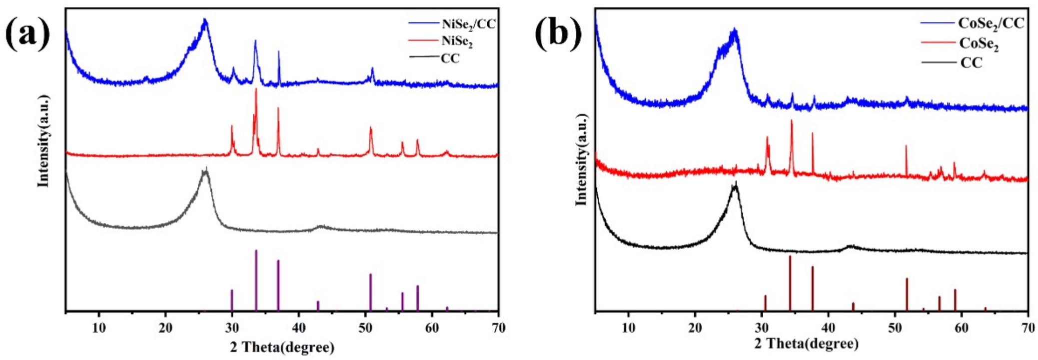

Fig.S1. （a）XRD pattern of CC, $NiSe_2$ and $NiSe_2$/CC composites and （b）XRD pattern of CC, $CoSe_2$ and $CoSe_2$/CC composites

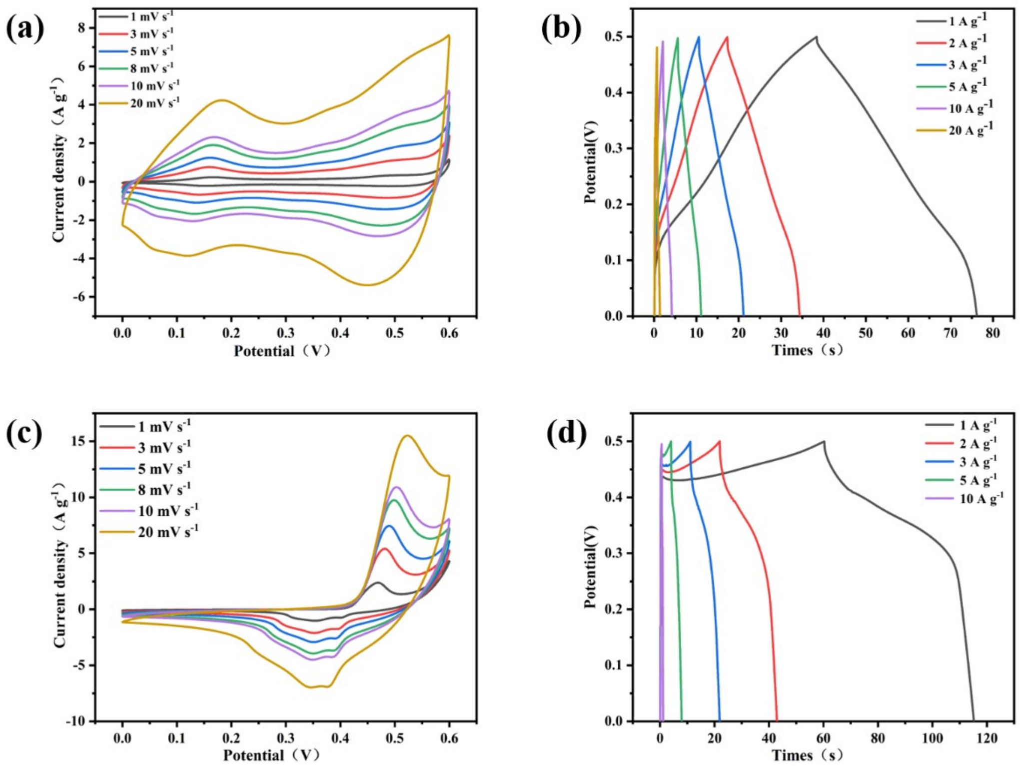

Fig. S2. CV curves at varied scan rate for (a) $CoSe_2$/CC and (c) $NiSe_2$/CC electrodes, GCD curves at varied current densities for (b) $CoSe_2$/CC and (d) $NiSe_2$/CC.

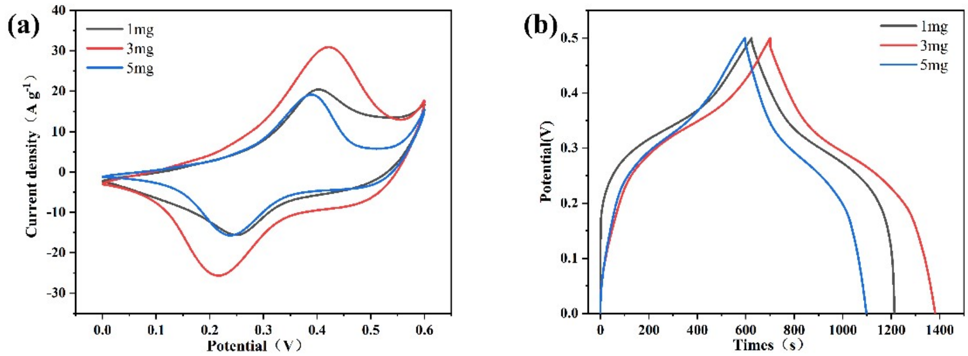

Fig. S3. (a) CV and (b)GCD curves of $NiCo_2Se_4$/CC electrodes with mass loadings of 1, 3, and 5 mg cm^{-2}.

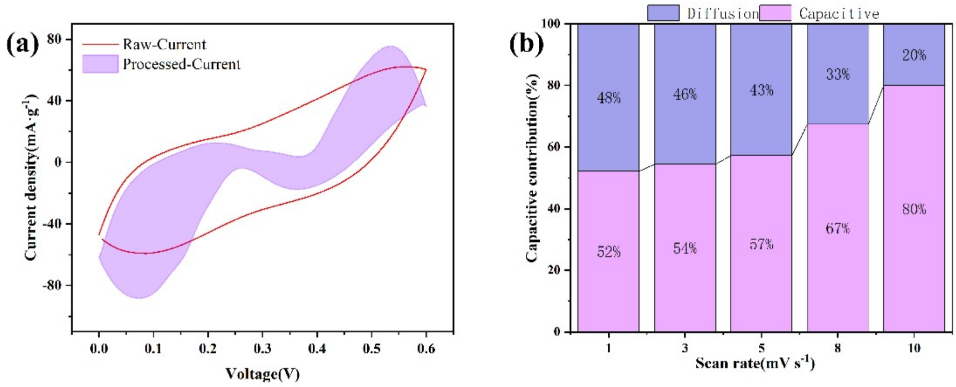

Fig. S4 Capacitive contribution analysis of the $NiCo_2Se_4$/CC electrode based on CV measurements.

(a) Representative separation of the capacitive-controlled current (processed current) and the total current response at a scan rate of 10 mV s^{-1} using the Dunn method ($i(V) = k_1v + k_2v^{1/2}$).

(b) Relative contributions of capacitive-controlled and diffusion-controlled charge storage at different scan rates, where the capacitive contribution gradually increases with increasing scan rate.

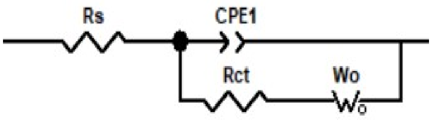

Fig. S5. Equivalent circuit model used to fit the EIS spectrum of the $NiCo_2Se_4$/CC electrode.

Table S1. Equivalent circuit fitting parameters obtained from EIS analysis of the $NiCo_2Se_4$/CC electrode

Parameter	Symbol	Value	Unit	Description
Solution resistance	Rs	0.82	Ω	Electrolyte resistance and intrinsic resistance of current collector
Charge-transfer resistance	Rct	1.95	Ω	Interfacial charge-transfer resistance at electrode/electrolyte interface

Constant phase element	CPE	3.6×10^{-3}	$F \cdot s^{n-1}$	Non-ideal double-layer capacitance
CPE exponent	n	0.86	—	Deviation from ideal capacitive behavior
Warburg coefficient	σ	0.41	$\Omega \cdot s^{-1/2}$	Ion diffusion resistance in porous electrode

Table S2. Relative fractions of surface oxidation states derived from XPS peak fitting

Element	**Oxidation state**	**Relative fraction (%)**
Ni	Ni^{2+}	27.22
Ni	Ni^{3+}	36.40
Co	Co^{2+}	57.62
Co	Co^{3+}	13.51

Table S3. Comparison of synthesis complexity and electrochemical performance of reported Ni–Co selenide–based binder-free electrodes

Electrode material	$NiCo_2Se_4$ nanoflakes	$NiCo_2Se_4$ nanoarrays	Mesoporous $NiCo_2Se_4$ nanotubes	Hollow $NiCo_2Se_4$ nanotube arrays
Substrate	Carbon cloth	Carbon cloth	Carbon cloth	Carbon cloth
Step number	Two-step (growth + selenization)	Two-step	Multi-step	Three-step
Post-thermal treatment	Yes (tube furnace)	No	Yes	Yes

Atmosphere control	Ar	No	Ar	Ar
Template use	No	No	Yes	No
Reaction time	≥24 h	~18 h	≥36 h	≥30 h
Energy consumption	High	Medium	High	High
Hazardous reagents	Se powder	Conventional Se source	Se powder	Se powder
Scalability constraints	High	Medium	High	High
Specific capacitance	~1250 F g^{-1}	1100–1300 F g^{-1}	1000~1400 F g^{-1}	~1379 F g^{-1}
Current density	1 A g^{-1}	1 A g^{-1}	1 A g^{-1}	1 A g^{-1}
Cycling stability	85% / 10,000	88% / 5000	90% / 8000	86% / 6000
Ref	15	16	18	19

Electrode material	$NiCo_2Se_4$ particles	Ni_xCo_ySe_z	NiSe	$CoSe_2$	**$NiCo_2Se_4$ nanoflowers (this work)**
Substrate	Ni foam	Carbon cloth	Carbon cloth	Carbon cloth	**Carbon cloth**
Step number	One-step	One-step	One-step	One-step	**One-step**
Post-thermal treatment	No	No	No	No	No
Atmosphere control	No	No	No	No	No
Template use	No	No	No	No	No
Reaction time	~12 h	~12 h	~12 h	~12 h	~12 h
Energy consumption	Low	Low	Low	Low	**Low**
Hazardous reagents	Conventional Se source	Conventional Se source	Conventional Se source	Conventional Se source	**Hydrazine (low dosage)**
Scalability constraints	Medium	Medium	Low	Low	**Moderate (safety control required)**
Specific capacitance	700–1100 F g^{-1}	~900–1000 F g^{-1}	600–850 F g^{-1}	700–950 F g^{-1}	**1479 F g^{-1}**
Current density	1 A g^{-1}	1 A g^{-1}	1 A g^{-1}	1 A g^{-1}	**5 A g^{-1}**
Cycling	82% / 5000	84% / 6000	83% / 5000	83% / 5000	**87.6% /**

stability					**20,000**
Ref	20	56	57	55	**This work**

Table S4. Performance comparison of $NiCo_2Se_4$/CC//AC devices with recently reported hybrid supercapacitors

Supercapacitor device	Energy density(Wh kg-1)	Power density(W kg-1)	Reference
$CoSe_2$//AC	18.9	387	55
Ni0.85Se-2	18.1	844.5	56
$NiSe_2$//AC	16.9	850	57
Ni3Se_2-24//AC	11.5	750	58
CoSe//AC	18.6	750	59
$MnSe_2$@$NiCo_2Se_4$//AC	69.2	750	60
$NiCo_2Se_4$/NC//AC	63.2	396	19
$NiCo_2Se_4$/CC//AC	**30.389**	**2549.9**	**This work**