

Supporting Information

Ni_{0.9}Co_{1.92}Se₄ Nanostructures: Binder-free Electrode of Coral-like Bimetallic Selenide for supercapacitors

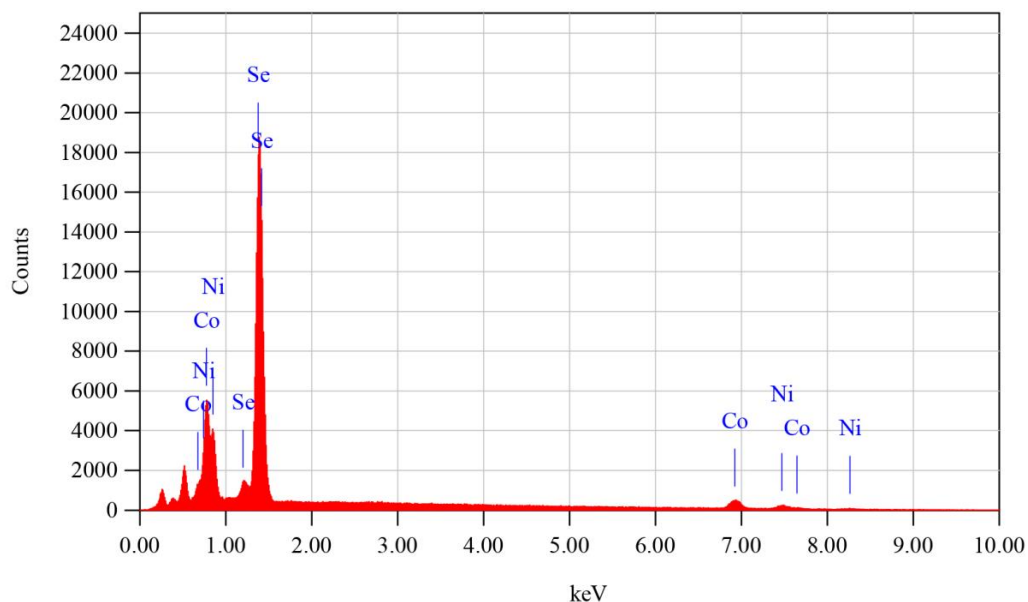
Weidan An, Ling Liu, Yanfang Gao, Yang Liu, Jinrong Liu*

College of Chemical Engineering, Inner Mongolia University of Technology, Hohhot, 010051,
P.R. China.

*E-mail: yf_gao@imut.edu.cn; Fax: +86 471 6503298; Tel: +86 471 6575722

Keywords: nanostructures, bimetallic selenide, binder-free electrode, supercapacitors

The EDX pattern demonstrate that the sample is mainly composed of Ni, Co and Se elements, except a little oxygen signal which may be from moisture and oxygen adsorbed on the surface of sample. The quantitative analyses about the mass and atom percentage is tabulated as follows.



Element	keV	Mass%	Atom%	K
Ni L*	0.851	17.31	20.29	15.6865
Co L*	0.776	25.91	30.24	29.8140
Se L*	1.379	56.78	49.47	54.4995

Figure S1. EDX pattern of the Ni_{0.9}Co_{1.92}Se₄ nanostructures.

The XRD spectra of the Ni-Coprecursor powder shows that the diffraction peaks are well indexed as the $\text{Ni}_3(\text{CO}_3)(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ (JCPDS no.16-0164) and $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ (JCPDS no.48-0083).

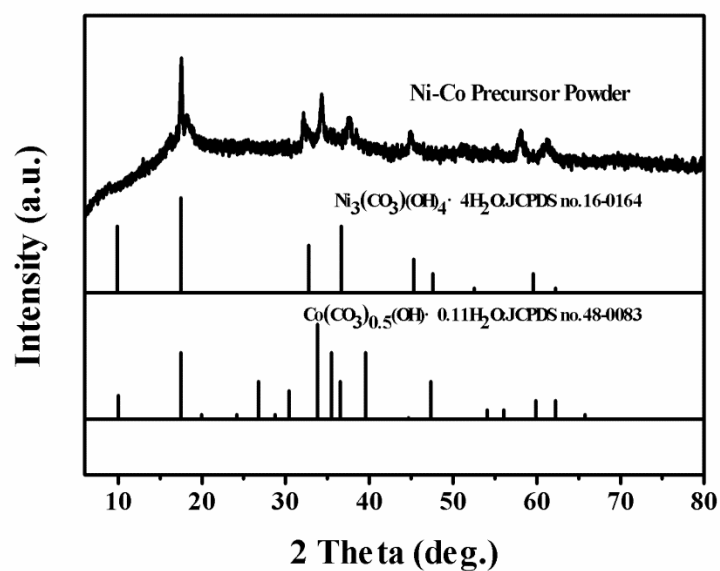


Figure S2. XRD spectra of the Ni-Co precursor powder.

4 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in 80 mL of deionized water to form a homogeneous pink solution, followed by the addition of 12 mmol of NH_4F and 24 mmol of urea, respectively. The solution and the pretreated Ni foam were transferred into a 100 mL Teflon-lined stainlesssteel autoclave, which was sealed and maintained at 120°C for 6h. After the autoclave cooled down to room temperature, the precursor on Ni foam was washed with ethanol and deionized water several times and dried at 80°C for 6h. Then, 200 mg of sodium selenite (Na_2SeO_3) and 10 mL of hydrazine hydrate were added into the 70 mL of absolute ethanol solution with precursor on Ni foam, and the mixture was kept in the autoclave at 140°C for 12h. After the autoclave cooled down to room temperature, washed with ethanol and deionized water several times and dried at 80°C for 6h, we get the black sample of $\text{Co}_{0.85}\text{Se}$ on Ni foam.

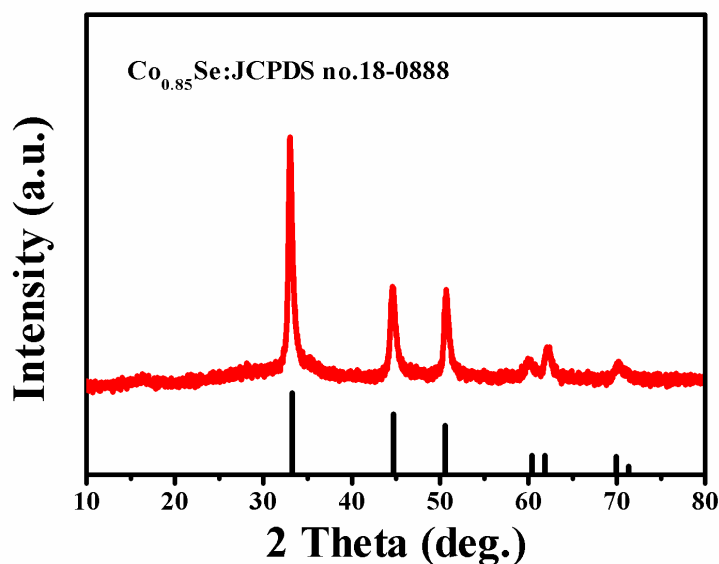


Figure S3. XRD spectra of the $\text{Co}_{0.85}\text{Se}$ powder.

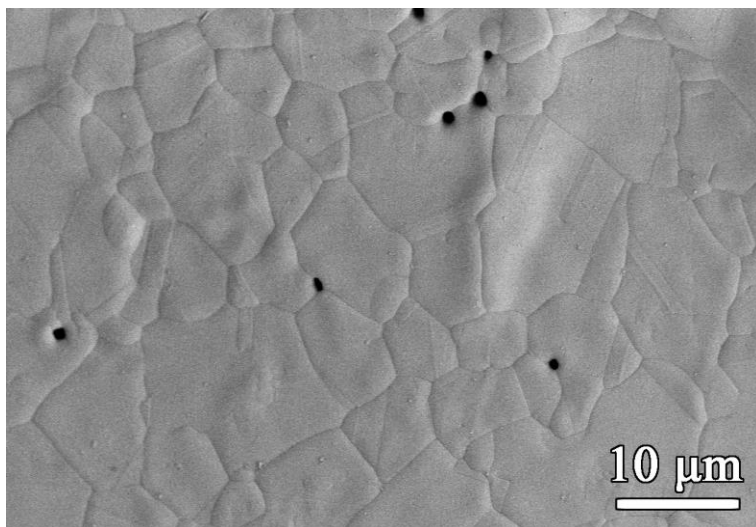


Figure S4. FESEM image of the Ni foam.

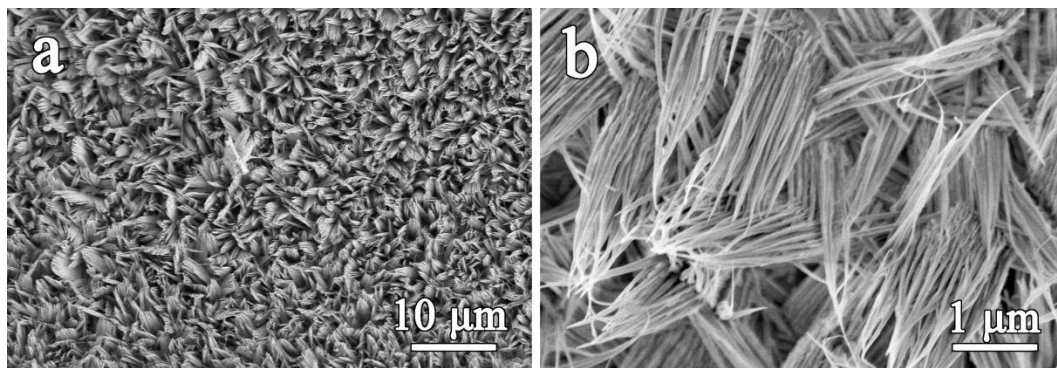


Figure S5. (a) SEM and (b)FESEM images of the $\text{Co}_{0.85}\text{Se}$ precursor on Ni foam at different magnifications.

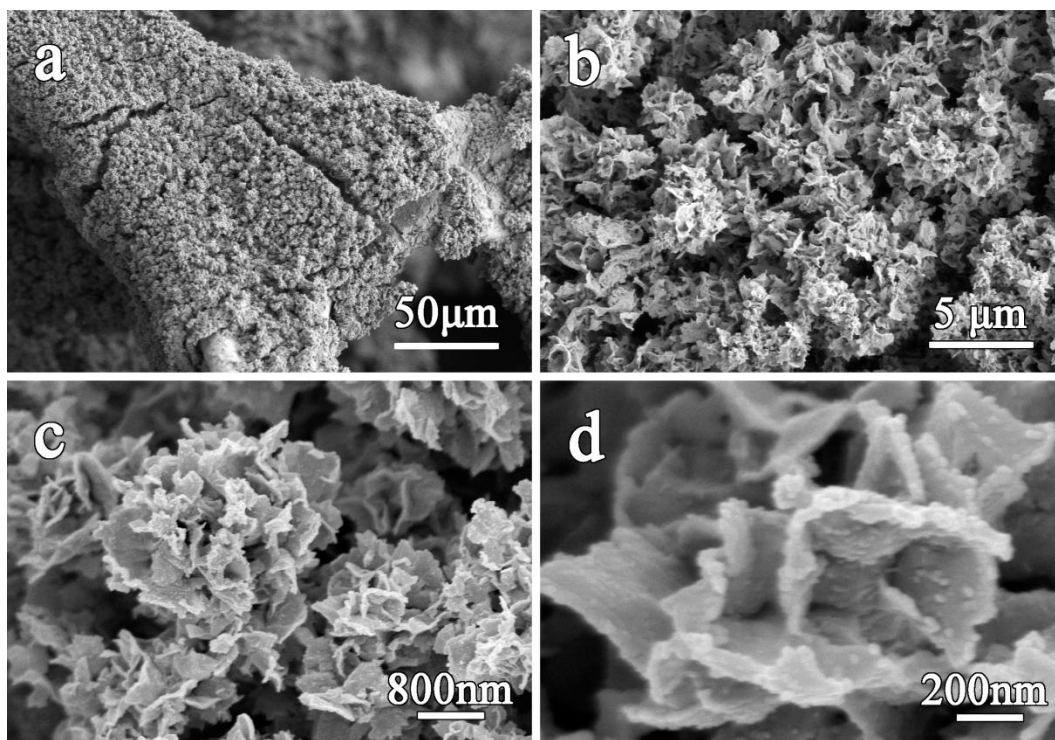


Figure S6. (a,b) SEM and (c,d) FESEM images of the Co_{0.85}Se on Ni foam at different magnifications.

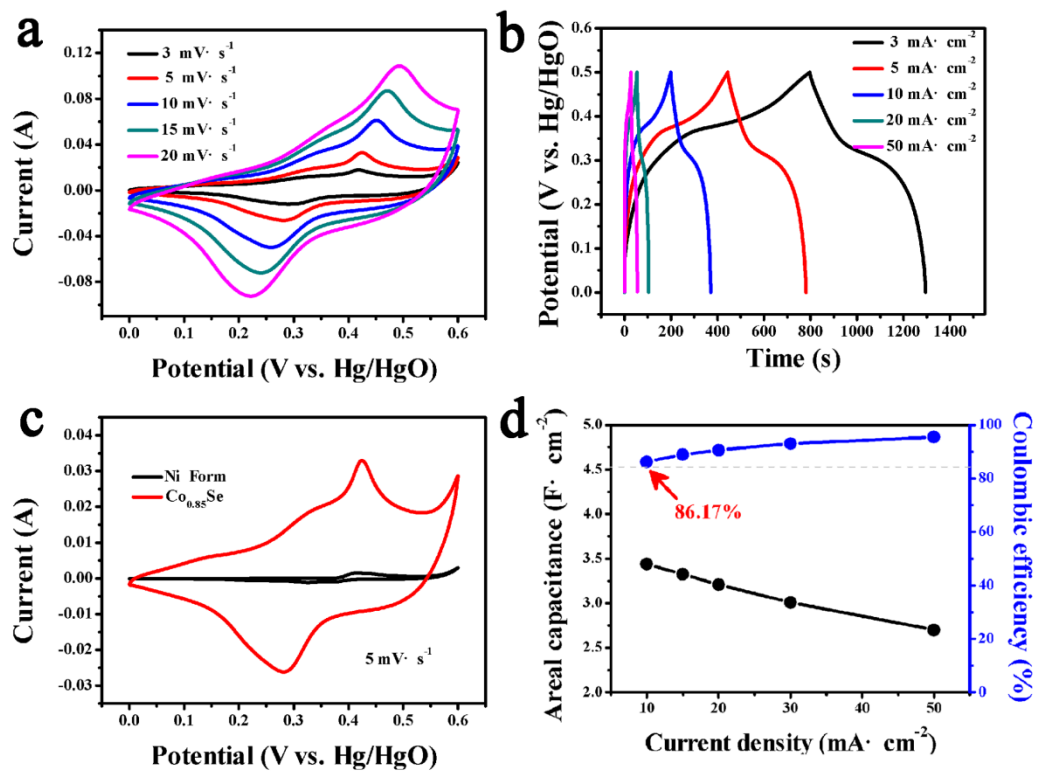


Figure S7. Electrochemical performances of the as-prepared samples: (a) CV curves of Co_{0.85}Se on Ni foam at the scan rates from 3 to 20 mV·s⁻¹; (b) GCD curves of the Co_{0.85}Se on Ni foam at the current densities from 3 to 50 mA·cm⁻²; (c) the CV curves of Ni foam and Co_{0.85}Se on Ni foam at a scan rate of 5 mV·s⁻¹; (d) the areal capacitance and the coulombic efficiency of the Co_{0.85}Se on Ni foam at the current densities from 10 to 50 mA·cm⁻².

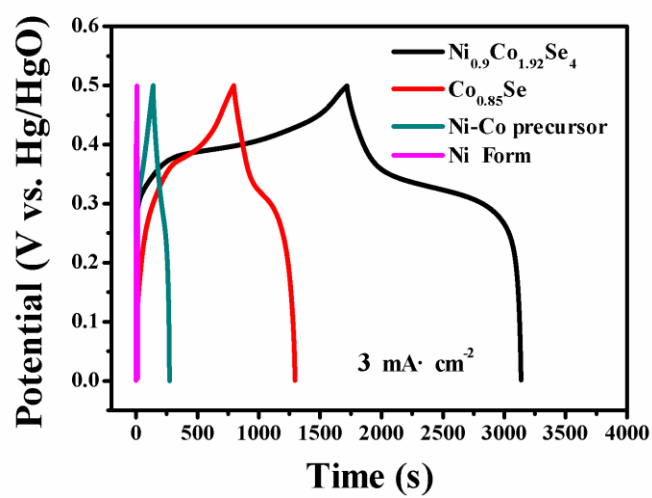


Figure S8. Electrochemical performance comparison of the Ni foam, $\text{Co}_{0.85}\text{Se}$, Ni-Co precursor and $\text{Ni}_{0.9}\text{Co}_{1.92}\text{Se}_4$ nanostructures on Ni foam of GCD curves at the current density of $3 \text{ mA} \cdot \text{cm}^{-2}$.

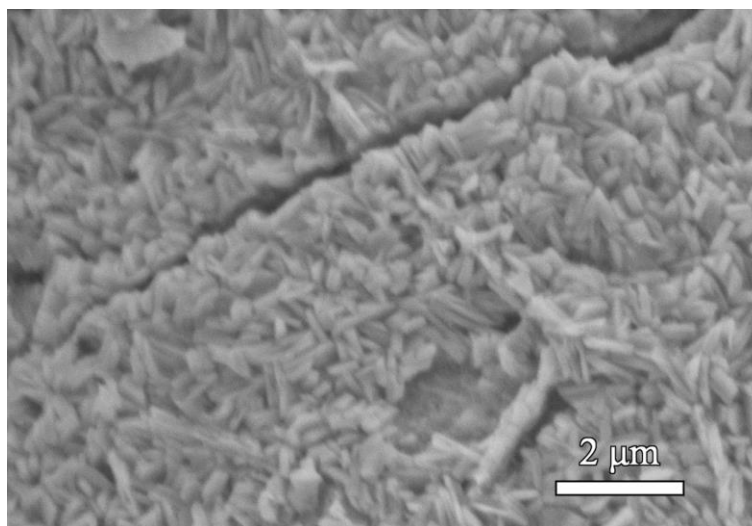


Figure S9. SEM image of the $\text{Ni}_{0.9}\text{Co}_{1.92}\text{Se}_4$ nanostructures on Ni foam after 5000 cycles.

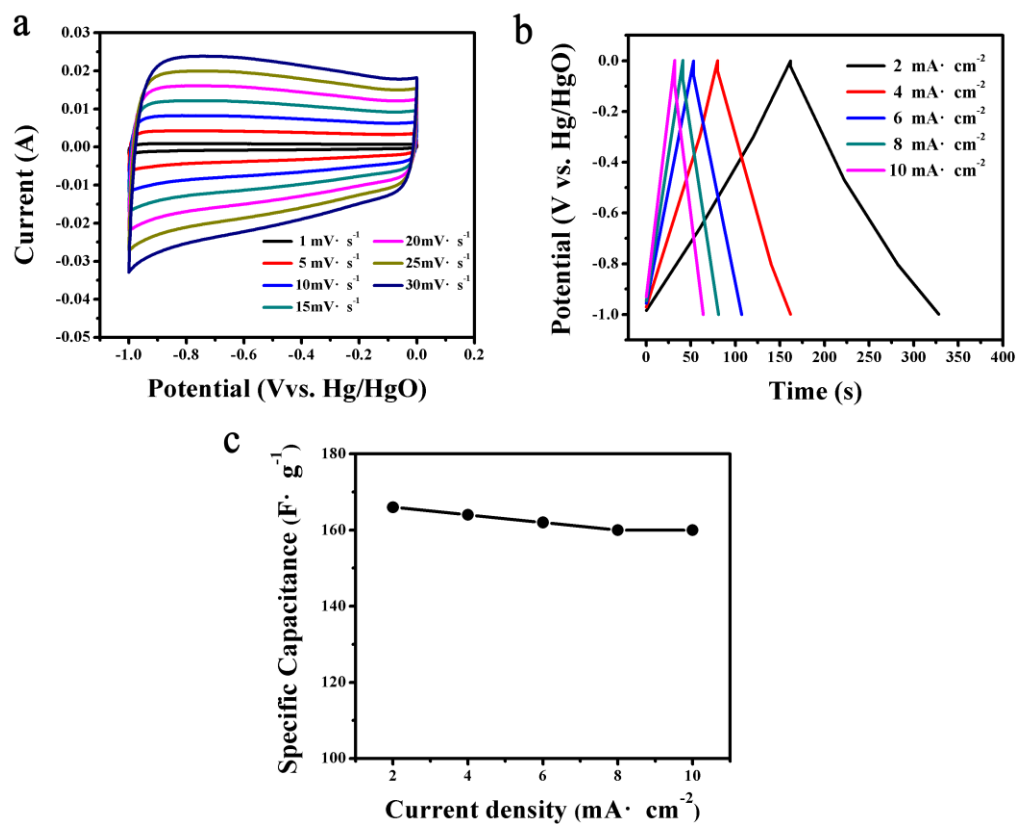


Figure S10. Electrochemical performance of the as-prepared samples: (a) CV curves of AC at the scan rates from 1 to 30 $\text{mV} \cdot \text{s}^{-1}$; (b) GCD curves of AC at the current densities from 2 to 10 $\text{mA} \cdot \text{cm}^{-2}$; (c) the specific capacitance of AC at different current densities.

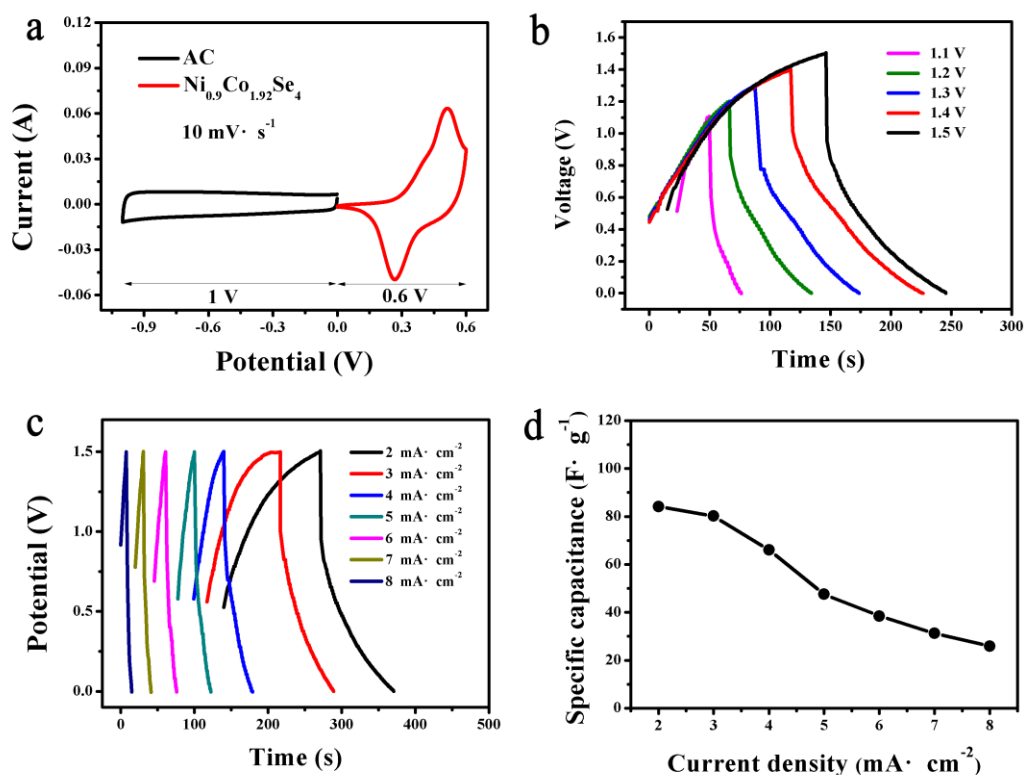


Figure S11. Electrochemical performance of the as-prepared samples: (a) CV curves of the $\text{Ni}_{0.9}\text{Co}_{1.92}\text{Se}_4$ nanostructures and AC with their corresponding potential window at the scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$; GCD curves of the $\text{Ni}_{0.9}\text{Co}_{1.92}\text{Se}_4$ //AC asymmetric supercapacitor: (b) at the different voltages and (c) at the current densities changing from 2 to $8 \text{ mA} \cdot \text{cm}^{-2}$; (d) the specific capacitance of the asymmetric supercapacitor at different current densities.

Table S1. Comparison of Ni_{0.9}Co_{1.92}Se₄ nanostructures and some similar previously reported materials.

Nanostructures	Areal Capacitance	Specific Capacitance	Rate capability	Power density	Capacitance retention	Reference
Hollow Co _{0.85} Se nanowire array on Carbon Fiber Paper	0.93 F·cm ⁻² @ 2 mA·cm ⁻²	674 F·g ⁻¹ @ 2 mA·cm ⁻²	65.9% from 2 to 15 mA·cm ⁻²	10.19 Wh·kg ⁻¹ @ (550 W·kg ⁻¹)	89.00% after 2000 cycles@10mA·cm ⁻²	1
GeSe ₂ Nanostructures	240 μF·cm ⁻² @ 10mA·cm ⁻²	300 F·g ⁻¹ @ 1 A·g ⁻¹	60% from 1 to 10 A·g ⁻¹		77.50% after 2000 cycles@10mA·cm ⁻²	2
CoNi ₂ S ₄ Nanosheet Arrays Supported on Nickel foams	6.39F·cm ⁻² @ 5mA·cm ⁻²	2906 F·g ⁻¹ @ 5 mA·cm ⁻²	78% from 5 to 50 mA·cm ⁻²	33.9 Wh·kg ⁻¹ @ (409 W·kg ⁻¹)	77.96% after 3000 cycles@30mA·cm ⁻²	3
Co _{0.85} Se on Ni foam	3.44 F·cm ⁻² @ 3 mA·cm ⁻²	430.0 F·g ⁻¹ @ 3 mA·cm ⁻²	68% from 3 to 50 mA·cm ⁻²			Additional experiment
Ni-Co precursor	0.80 F·cm ⁻² @ 3 mA·cm ⁻²	145.3 F·g ⁻¹ @ 3 mA·cm ⁻²	5.1% from 3 to 50 mA·cm ⁻²			This work
Ni _{0.9} Co _{1.92} Se ₄ on Ni foam	6.43 F·cm ⁻² @ 2 mA·cm ⁻²	1021.1 F·g ⁻¹ @ 2 mA·cm ⁻²	77% from 2 to 50 mA·cm ⁻²	26.29 Wh·kg ⁻¹ @ (265 W·kg ⁻¹)	88.39% after 5000 cycles@20mA·cm ⁻²	This work

- [1] Banerjee,A.; Bhatnagar,S.; Upadhyay,K.K.; Yadav,P.; Ogale,S.,Hollow Co_{0.85}Se nanowire array on carbon fiber paper for high rate pseudocapacitor.ACS applied materials & interfaces, 2014, 6(21): 18844-18852.
- [2] Wang,X.F.; Liu,B.; Wang,Q.F.; Song,W.F.; Hou,X.J.; Chen,D.; Cheng,Y.B.;Shen,G.Z.,Three-dimensional Hierarchical GeSe₂ Nanostructures for High Performance Flexible All-Solid-State Supercapacitors. Advanced Materials, 2013, 25(10): 1479-1486.
- [3] Hu,W.; Chen,R.Q.; Xie,W.; Zou,L.L.; Qin,N.; Bao.D.H., CoNi₂S₄ Nanosheet Arrays Supported on Nickel Foams with Ultrahigh Capacitance for Aqueous Asymmetric Supercapacitor Applications. ACS applied materials & interfaces, 2014, 6(21): 19318-19326.
- [4] Chen,H.C.; Jiang,J.J.; Zhang,L.; Xia,D.D.; Zhao,Y.D.; Guo,D.Q.; Qi,T.; Wan.H.Z., In situ growth of NiCo₂S₄ nanotube arrays on Ni foam for supercapacitors: maximizing utilization efficiency at high mass loading to achieve ultrahigh areal pseudocapacitance.Journal of Power Sources, 2014, 254: 249-257.