

Supporting Information

Hierarchical “tube-on-fiber” carbon/mixed-metal selenide nanostructures for high-performance hybrid supercapacitors

Li-Ping Lv^{1†}, ChuanweiZhi^{1†}, Yun Gao¹, Xiaojie Yin¹, Yiyang Hu¹, Daniel Crespy², Yong Wang^{1*}

¹*School of Environmental and Chemical Engineering, Shanghai University, 99 Shangda Road, Shanghai, P. R. China, 200444*

²*Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand*

*Corresponding authors: Tel: +86-21-66137723; fax: +86-21-66137725.

Email address: yongwang@shu.edu.cn

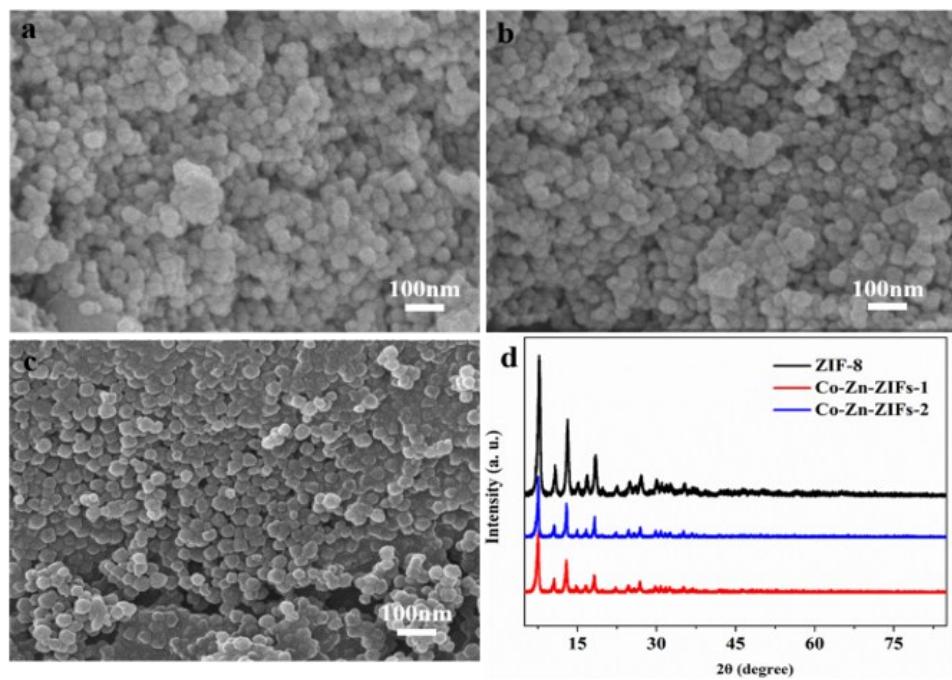


Figure S1. SEM images of (a) ZIF-8, (b) Co-Zn-ZIFs-1, and (c) Co-Zn-ZIFs-2. (d) XRD patterns of ZIF-8, Co-Zn-ZIFs-1, and Co-Zn-ZIFs-2.

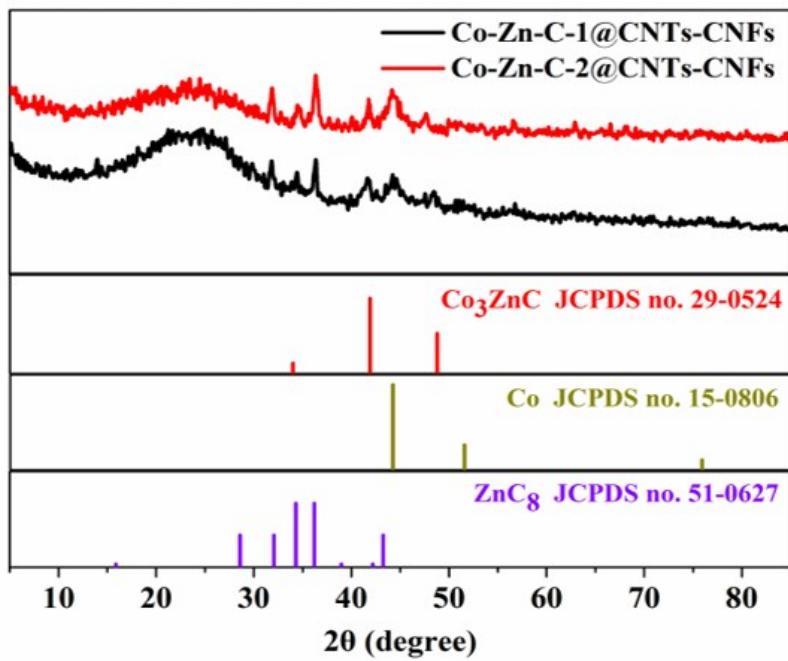


Figure S2. XRD patterns of Co-Zn-C-1@CNTs-CNFs and Co-Zn-C-2@ CNTs-CNFs.

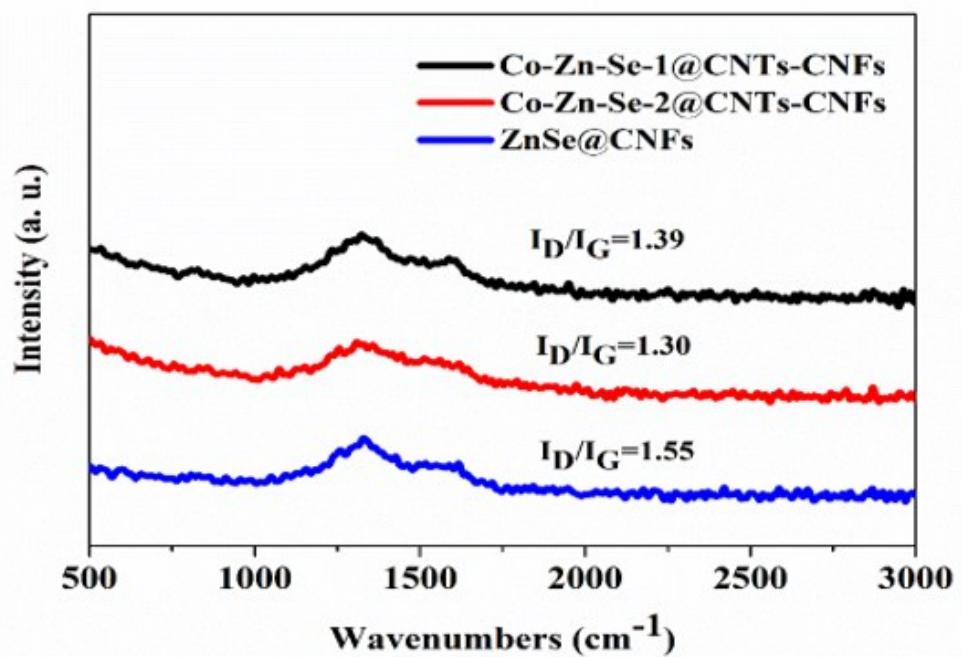


Figure S3. Raman spectra of ZnSe@CNFs, Co-Zn-Se-1@CNTs-CNFs and Co-Zn-Se-2@CNTs-CNFs.

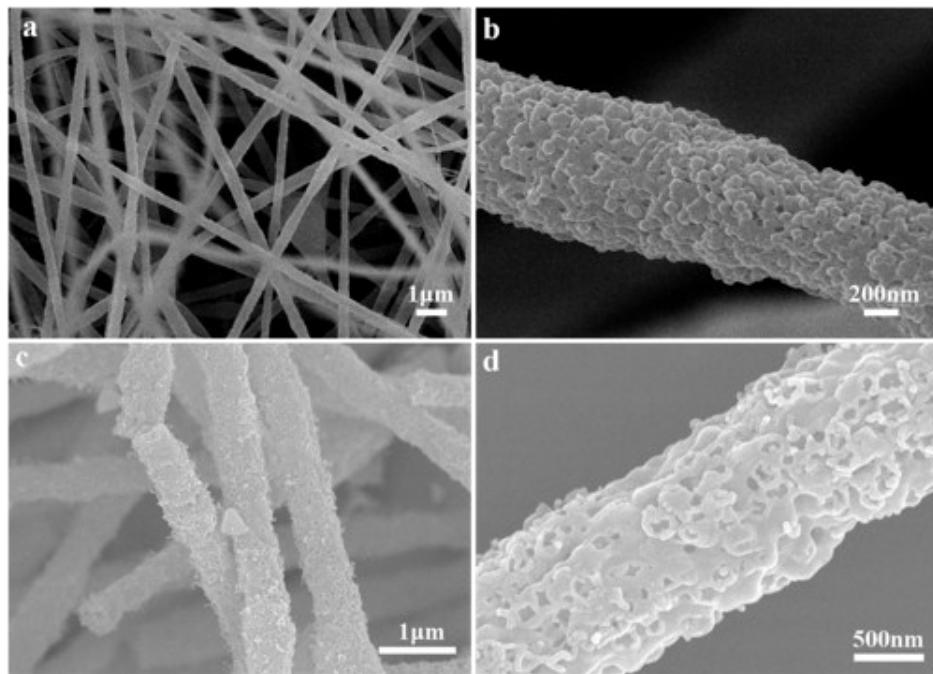


Figure S4. SEM images of (a, b) ZnSe@CNFs and (c, d) Co-Zn-Se-2@CNTs-CNFs.

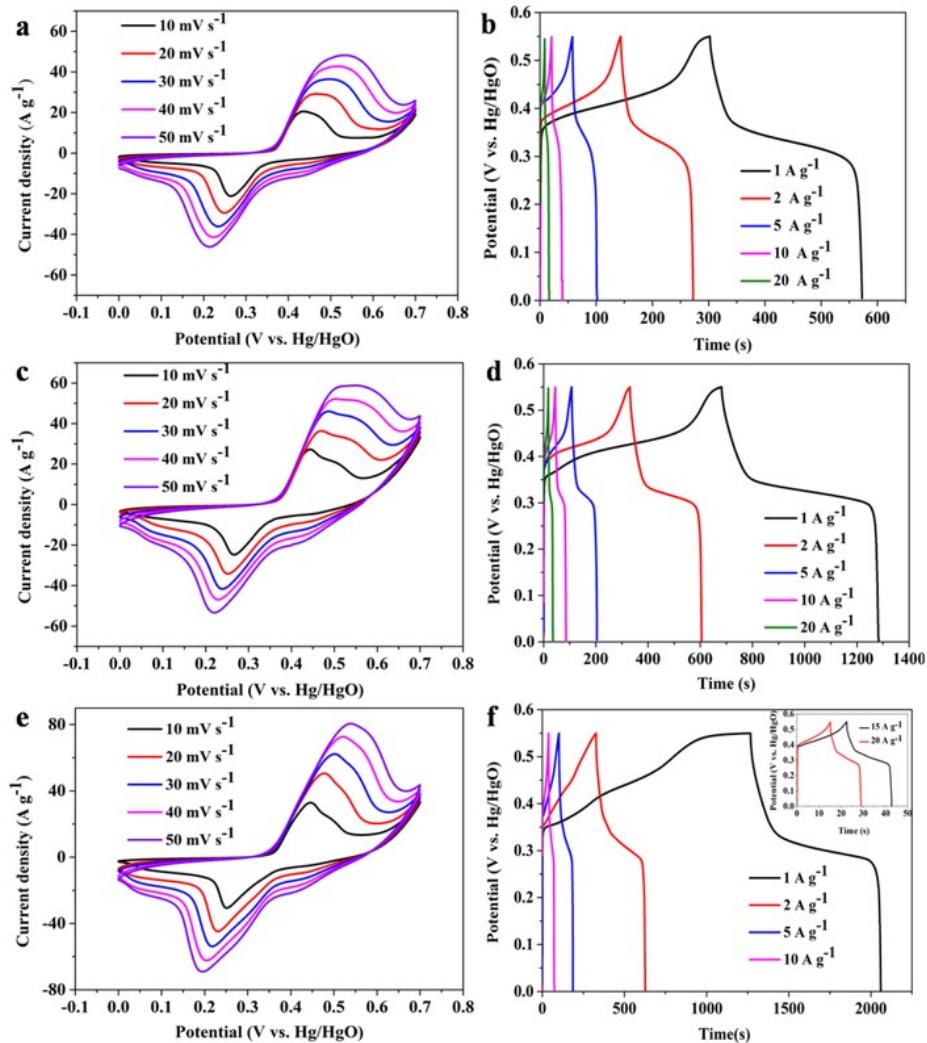


Figure S5. CV curves of (a) ZnSe, (c) ZnSe@CNFs, (e) Co-Zn-Se-2@CNTs-CNFs electrode at various scan rates. GCD curves of (b) ZnSe, (d) ZnSe@CNFs, (f) Co-Zn-Se-2@CNTs-CNFs electrode (1-10 A g⁻¹ and 15-20 A g⁻¹, the inset).

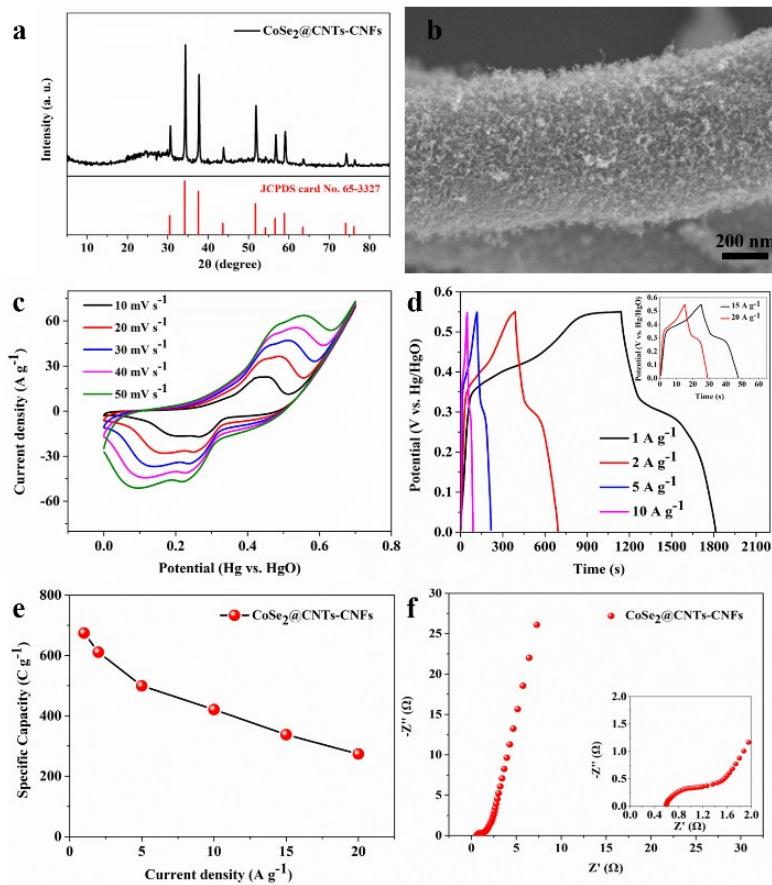


Figure S6 CoSe₂@CNTs-CNFs: (a) XRD patterns; (b) SEM image; (c) CV curves at different scan rates; (d) GCD curves at different current densities; (e) the calculated specific capacities from GCD curves at different current densities; (f) EIS spectra.

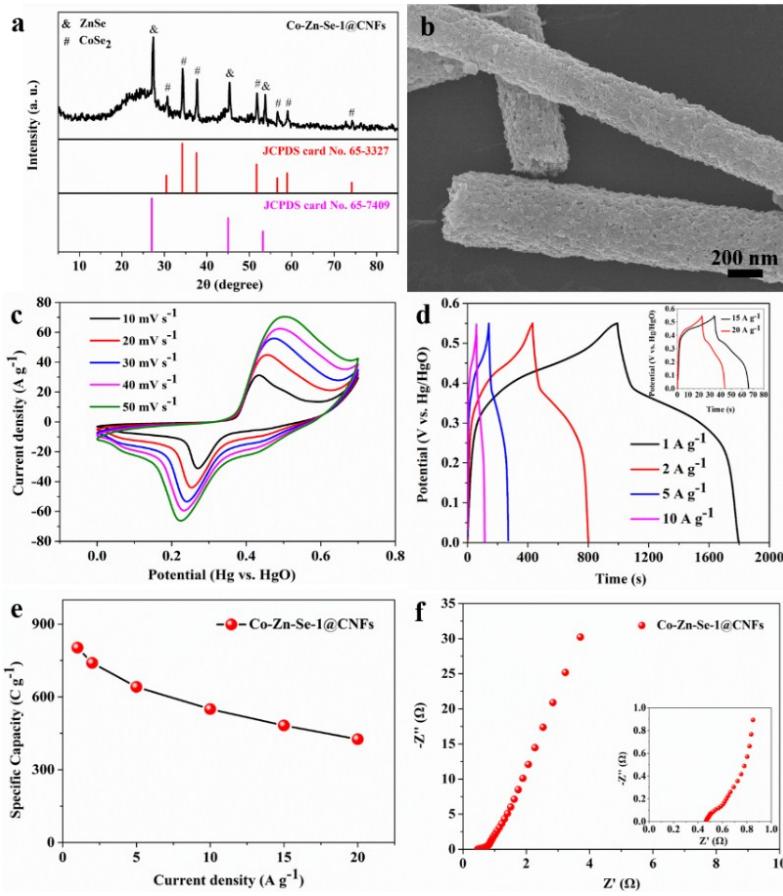


Figure S7 Co-Zn-Se-1@CNFs: (a) XRD patterns; (b) SEM image; (c) CV curves at different scan rates; (d) GCD curves at different current densities; (e) the calculated specific capacities from GCD curves at different current densities; (f) EIS spectra.

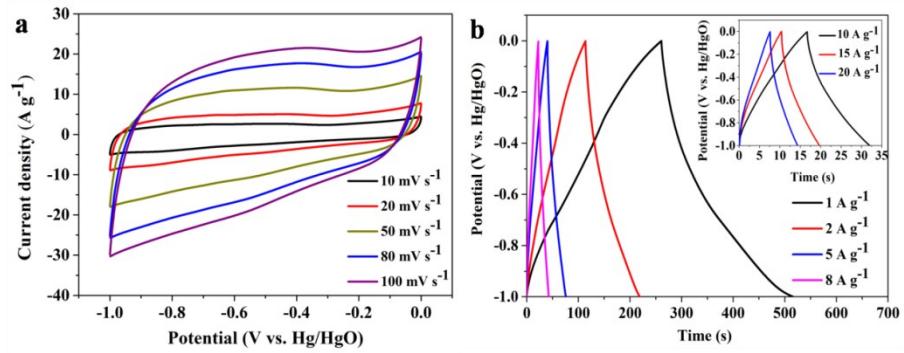


Figure S8. Electrochemical properties of PCNFs: CV curves of PCNFs electrode at various scan rates. (b) GCD curves of PCNFs.

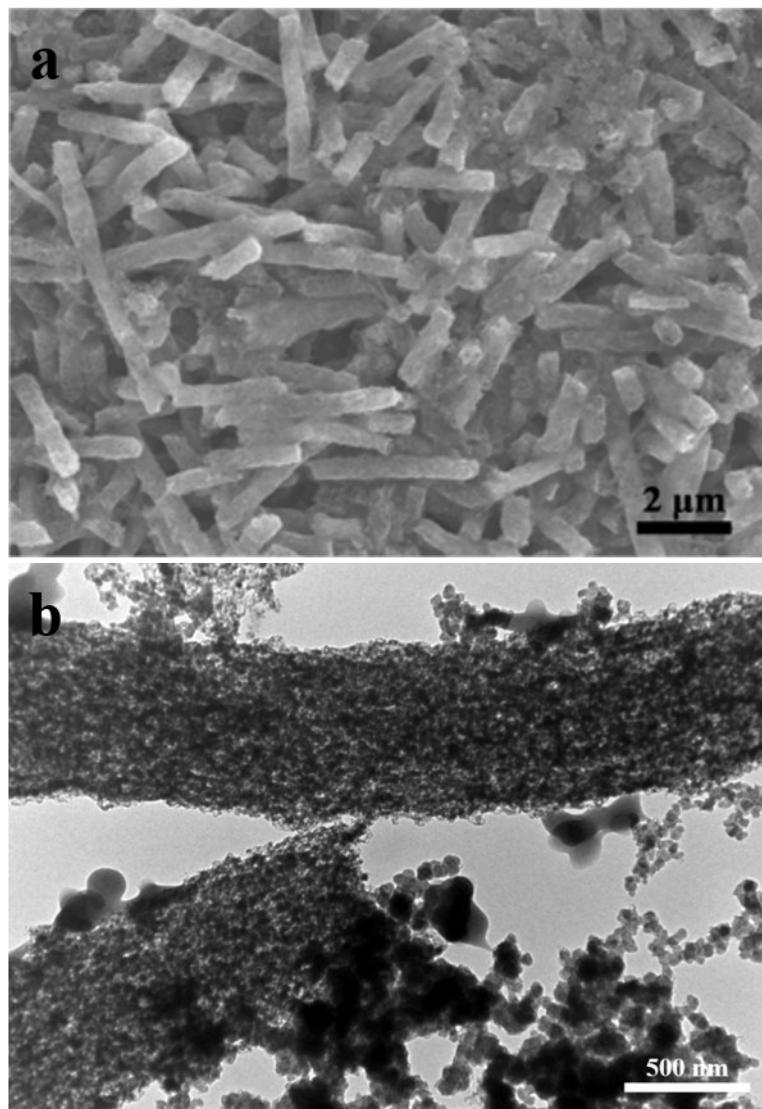


Figure S9. SEM (a) and TEM (b) images of the cathode materials of the Co-Zn-Se-1@CNTs-CNFs//PCNFs HSC device after cycling tests.

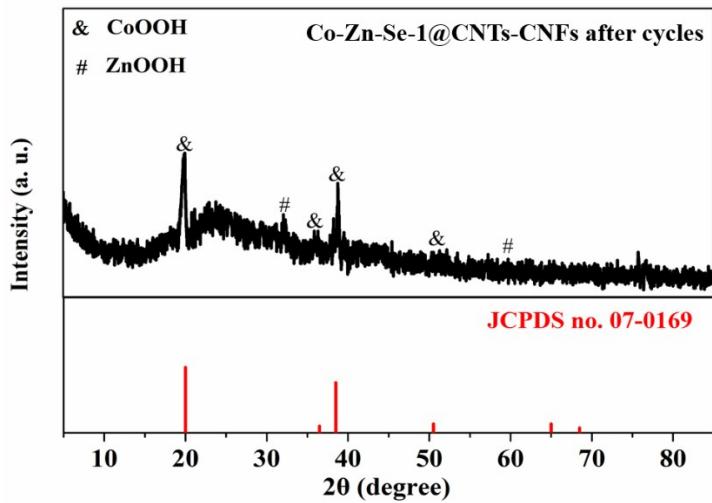


Figure S10 XRD patterns of Co-Zn-Se-1@CNTs-CNFs after 8000 cycles.

Table S1. Parameters of S_{BET} , pore size, and total pore volume of Co-Zn-Se-1@CNTs-CNFs, Co-Zn-Se-2@CNTs-CNFs and ZnSe@CNFs

Entry	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Pore Size [nm]	Pore volume [$\text{cm}^3 \text{ g}^{-1}$]
Co-Zn-Se-1@CNTs-CNFs	324.6	10.8	0.68
Co-Zn-Se-2@CNTs-CNFs	283.1	12.7	0.42
ZnSe@CNFs	307.3	11.0	0.57

Table S2. Results of the elemental content measurements of Co-Zn-Se-1@CNTs-CNFs and Co-Zn-Se-2@CNTs-CNFs.

Samples	Elemental contents (wt%)				
	Zn	Co	Se	C	N
Co-Zn-Se-1@CNTs-CNFs	16.8	2.5	27.5	47.3	5.9
Co-Zn-Se-2@CNTs-CNFs	13.7	5.4	31.8	45.2	3.9

Table S3. Electrochemical performance comparison of metal-selenide based supercapacitor electrodes. (SC: specific capacitance; RP: rate performance; CP: cycling performance.)

Ref.	Composite	SC	RP	CP
This work 1	Co-Zn-Se-1@CNTs-CNFs cube-like NiSe ₂	1040.1 C g ⁻¹ or 1891 F g ⁻¹ (1 A g ⁻¹) 1044 F g ⁻¹ (3 A g ⁻¹)	52.4% (30 A g ⁻¹) 57.5% (30 A g ⁻¹)	97.2% (5000 cycles) 67% (2000 cycles)
2	core-branch CoSe ₂ nanoarray	759 F g ⁻¹ (1 mA cm ⁻²)	78.8% ((15 mA cm ⁻²))	94.5 % (5000 cycles)
3	Co _{0.85} Se nanosheets	1528 F g ⁻¹ (1 A g ⁻¹)	46.7% (20 A g ⁻¹)	92 % (5000 cycles)
4	Ni _{0.85} Se@MoSe ₂ nanosheet	774 F g ⁻¹ (1 A g ⁻¹)	63% (15 A g ⁻¹)	--
5	hollow NiCoSe ₂	750 F g ⁻¹ (3 A g ⁻¹)	44% (30 A g ⁻¹)	92.1 % (5000 cycles)
6	NiSe-G nanohybrids	1280 F g ⁻¹ (1 A g ⁻¹)	80.1%(10 A g ⁻¹)	98 % (2500 cycles)
7	Ni ₃ Se ₂ NSs	251.8 mAh g ⁻¹ (2 A g ⁻¹)	58.5%(20 A g ⁻¹)	101.29% (5000 cycles)
8	Co-Cd-Se	1382 F g ⁻¹ (1 A g ⁻¹)	76% (15 A g ⁻¹)	95.3 % (2000 cycles)
9	hierarchical CFS-CNS	183.4 mAh g ⁻¹ (1 A g ⁻¹)	94%(8A g ⁻¹)	99.2 % (3000 cycles)
10	(Ni _{0.33} Co _{0.67})Se ₂ CHSs	827.9 Fg ⁻¹ (1A g ⁻¹)	78.1% (30 A g ⁻¹)	113% (2000 cycles)

References:

1. S. L. Wang, W. Li, L. P. Xin, M. Wu, Y. Long, H. T. Huang and X. J. Lou, Facile synthesis of truncated cube-like NiSe₂ single crystals for high performance asymmetric supercapacitors, *Chem. Eng. J.*, 2017, 330, 1334-1341.
2. T. Chen, S. Z. Li, J. Wen, P. B. Gui, Y. X. Guo, C. Guan, J. P. Liu and G. J. Fang, Rational Construction of Hollow Core-Branch CoSe₂ Nanoarrays for High-Performance Asymmetric Supercapacitor and Efficient Oxygen Evolution, *Small*, 2017, 1700979.
3. J. Yang, Y. L. Yuan, W. C. Wang, H. C. Tang, Z. Z. Ye and J. G. Lu, Interconnected Co_{0.85}Se nanosheets as cathode materials for asymmetric supercapacitors, *J. Power. Sources*, 2017, 340, 6-13.
4. H. Peng, C. D. Wei, K. Wang, T. Y. Meng, G. F. Ma, Z. Q. Lei and X. Gong, Ni_{0.85}Se@MoSe₂ Nanosheet Arrays as the Electrode for High Performance Supercapacitors, *ACS Appl. Mater. Interfaces*, 2017, 9, 17067-17075.
5. L R. Hou, Y. Y. Shi, C. Wu, Y. R. Zhang, Y. Z. Ma, X. Sun, J. F. Sun, X. G. Zhang and C. Z. Yuan, Monodisperse Metallic NiCoSe₂ Hollow Sub-Microspheres: Formation Process,

- Intrinsic Charge-Storage Mechanism, and Appealing Pseudocapacitance as Highly Conductive Electrode for Electrochemical Supercapacitors, *Adv. Funct. Mater.*, 2018, 1705921.
- 6. B. Kirubasankar, V. Murugadoss, J. Lin, T. Ding, M. Y. Dong, H. Liu, J. X. Zhang, T. X. Li, N. Wang, Z. H. Guo and S. Angaiah, In-situ grown nickel selenide onto graphene nanohybrid electrodes for high energy density asymmetric supercapacitors, *Nanoscale*, 2018.
 - 7. G. Nagaraju, S. M. Cha, S. C. Sekhar, and J. S. Yu, Metallic Layered Polyester Fabric Enabled Nickel Selenide Nanostructures as Highly Conductive and Binderless Electrode with Superior Energy Storage Performance, *Adv. Energy Mater.* 2016, 1601362.
 - 8. Z. B. Zhai, K. J. Huang and X. Wu, Superior mixed Co-Cd selenide nanorods for high performance alkaline battery-supercapacitor hybrid energy storage, *Nano Energy*, 2018, 47, 89-95.
 - 9. C. V. V. M. Gopi, A. E. Reddy and H. J. Kim, Wearable superhigh energy density supercapacitors using a hierarchical ternary metal selenide composite of CoNiSe₂ microspheres decorated with CoFe₂Se₄ nanorods, *J. Mater. Chem. A*, 2018, 6, 7439–7448.
 - 10. L. Quan, T. Q. Liu, M. J. Yi, Q. D. Chen, D.P. Cai and H. B. Zhan, Construction of hierarchical nickel cobalt selenide complex hollow spheres for pseudocapacitors with enhanced performance, *Electrochim. Acta*, 2018, 281, 109-116.