Support information

Yurui Deng[a], Lunlun Gong*[a], Yuelei Pan[a b], Xudong Cheng[a], and Heping Zhang *[a]

* Corresponding authors

a State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, P. R. China

b Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

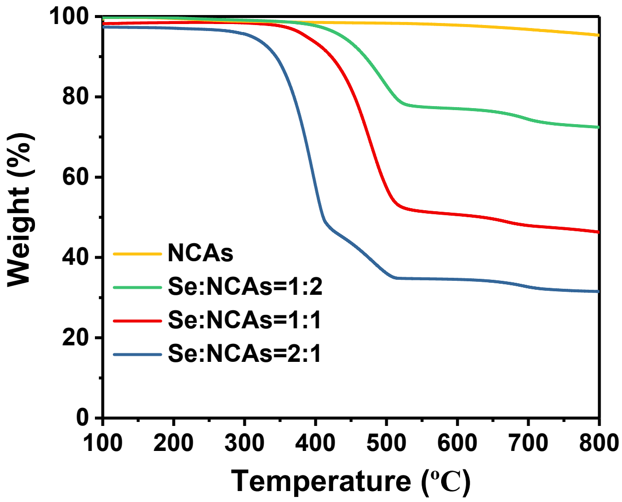

Fig. S1 TG profiles of the obtained composites with various ratios of Se versus NCAs. The content of Se distributed in the porous carbon polyhedrons was determined to be 28.55%, 52.23%, and 68.49%, respectively.

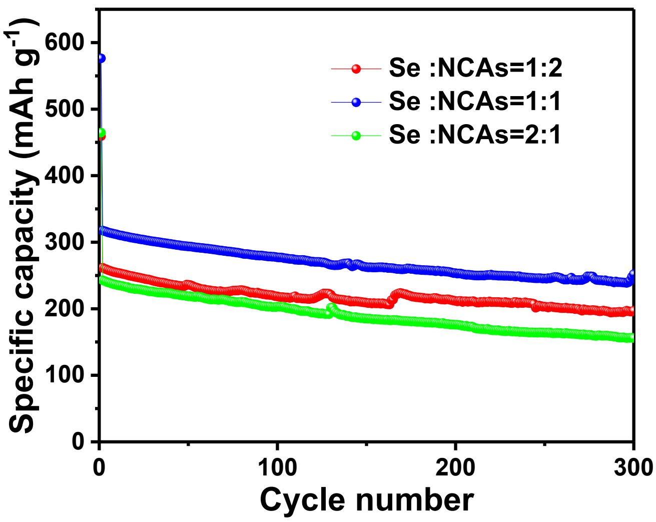

Fig. S2 Cyclic performances of the composites with various ratios of Se versus NCAs at a current density of 0.5A g^{-1} (the specific capacity is based on the Se @ NCAs composite)

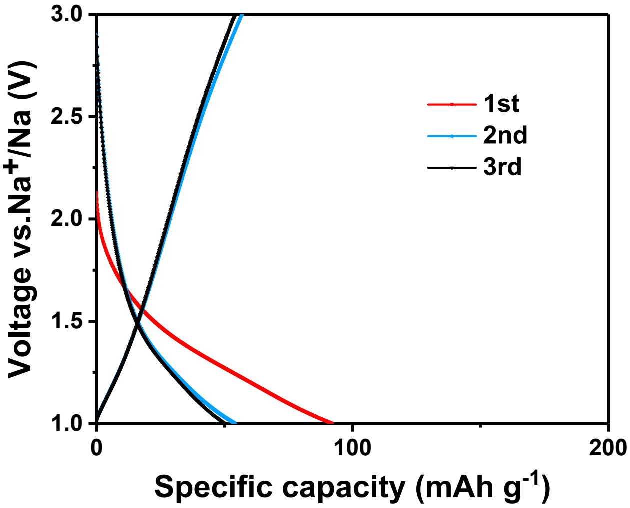

Fig. S3 Galvanostatic charge/discharge profiles of the NCAs at a current density of 0.1 A g^{-1}.

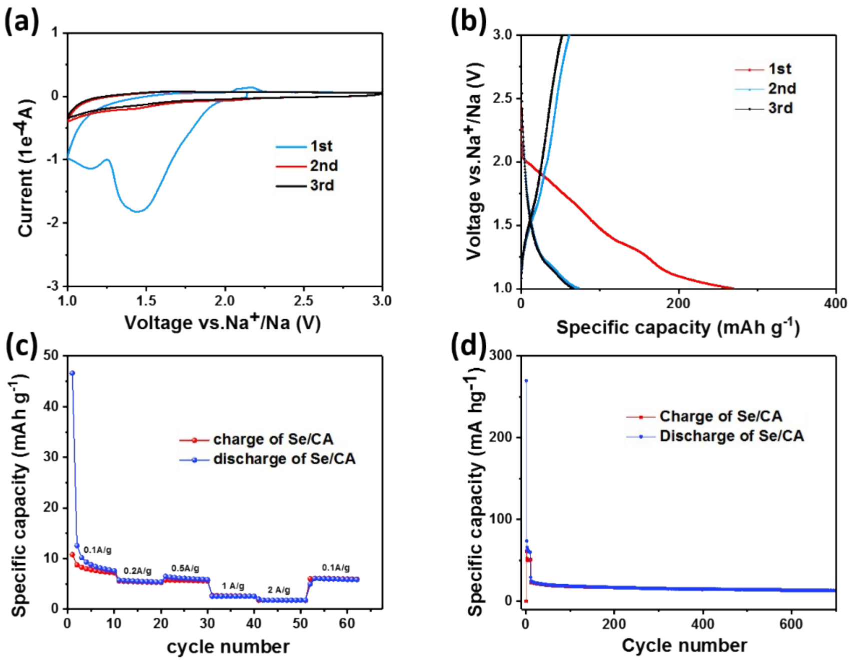

Fig. S4 (a) Cyclic voltammograms of the Se/CAs electrode at a scan rate of 0.1 mV s^{-1} in the voltage window from 1 V to 3 V versus Na+/Na. (b) Galvanostatic charge/discharge profiles of the Se/CAs electrode at a current density of 0.1 A g^{-1} between 1 V and 3 V versus Na^+/Na. (c) Rate capability of the Se/CAs composite at various current densities. (e) A long-term cycling performance of the Se/CAs composite at a current density of 0.5 A g^{-1}.

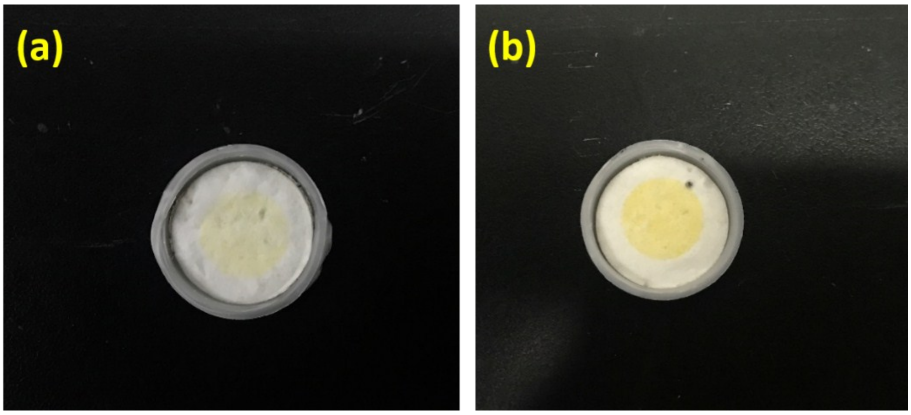

Fig. S5 The color change of electrodes/electrolytes in the Se @ NCAs (a) and Se/CAs (b) cells after cycling.

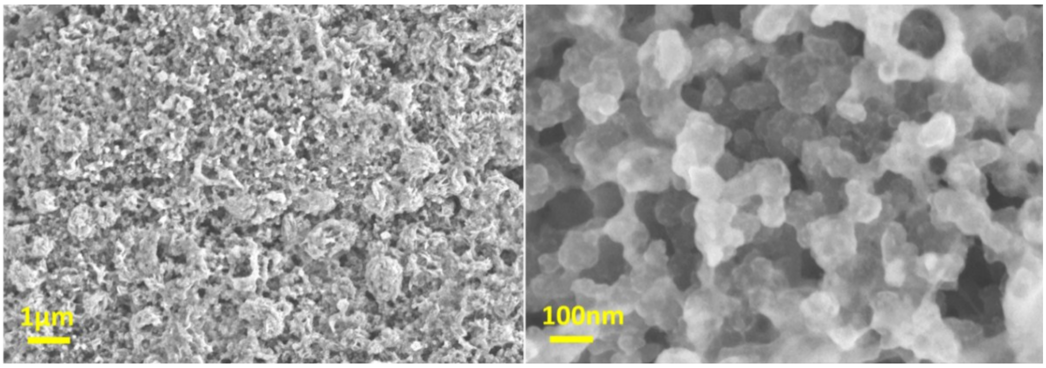

Fig. S6 The SEM image of the cycled Se@NCAs.

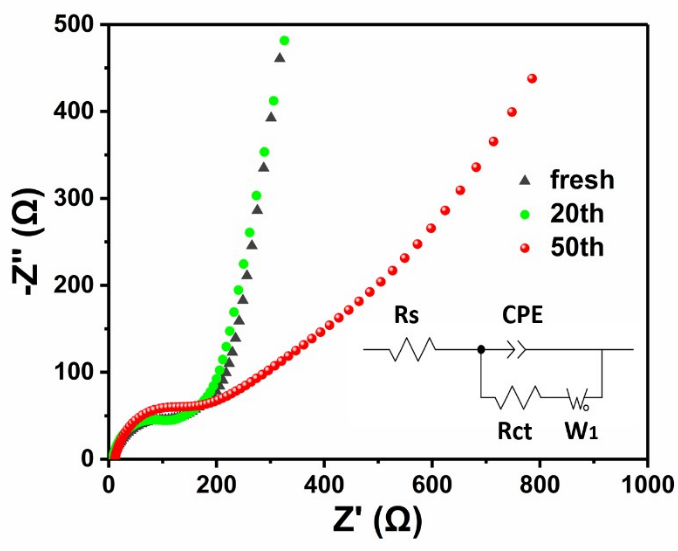

Fig. S7 Nyquist plots of the fresh and cycled Se @ MCNFs cells; the inset exhibits the equivalent circuit to fit the plots.

Table S1 The changes on electrode charge transfer resistance (Rct) and ohmic resistance (Rs) of Se@NCAs cathodes upon cycling

Cycle numer	Fresh cell	10^{th} cycle	20^{th} cycle
Rs (Ω)	6.14	6.941	11.21
Rct (Ω)	120	98.71	96.85

Table S2. The long cycling performance comparison for the published Se-based cathodes for Na–Se batteries.

Materials	Current density ($A\ g^{-1}$)	Reversible capacity ($mA\ h\ g^{-1}$)	references
C/Se	0.1	258 at 50^{th} cycle	[1]
Se/C	0.1695	340 at 380^{th} cycle	[2]
Se/(CNT@MPC)	0.675	440 at 100^{th} cycle	[3]
Se-CCN	0.135	514 at 500^{th} cycle	[4]
Se@CNFs-CNT	0.5	410 at 240^{th} cycle	[5]
CPAN/Se	0.2025	410 at 300^{th} cycle	[6]
Se@MCNFs	0.5	430 at 300th cycle	[7]
Se@NCAs	0.5	407 at 800^{th} cycle	This work

References

1. C. Luo, J. J. Wang, L. M. Suo, J. F. Mao, X. L. Fan and C. S. Wang, *Journal of Materials Chemistry A*, 2015, **3**, 555-561.
2. C. Luo, Y. H. Xu, Y. J. Zhu, Y. H. Liu, S. Y. Zheng, Y. Liu, A. Langrock and C. S. Wang, *Acs Nano*, 2013, **7**, 8003-8010.
3. S. Xin, L. Yu, Y. You, H. P. Cong, Y. X. Yin, X. L. Du, Y. G. Guo, S. H. Yu, Y. Cui and J. B. Goodenough, *Nano Lett*, 2016, **16**, 4560-4568.
4. J. Ding, H. Zhou, H. L. Zhang, T. Stephenson, Z. Li, D. Karpuzov and D. Mitlin, *Energ Environ Sci*, 2017, **10**, 153-165.
5. L. C. Zeng, X. Wei, J. Q. Wang, Y. Jiang, W. H. Li and Y. Yu, *Journal of Power Sources*, 2015, **281**, 461-469.
6. H. Q. Wang, S. Li, Z. X. Chen, H. K. Liu and Z. P. Guo, *Rsc Adv*, 2014, **4**, 61673-61678.
7. B. Yuan, X. Sun, L. Zeng, Y. Yu and Q. Wang, *Small*, 2018, **14**, 1703252.