Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Three-dimensional hierarchical Ni_3Se_2 nanorod array as binder/carbon-free electrode for high-areal-capacity Na storage

Chao-Ying Fan,[ab] *Xiao-Hua Zhang,*[a] *Yan-Hong Shi,*[a] *Hai-Yang Xu,*[b] *Jing-Ping Zhang,*[*a] *Xing-Long Wu,*[*a]

[a]Faculty of Chemistry, National & Local United Engineering Laboratory for Power Batteries, Northeast Normal University, Changchun, 130024, P. R. China.

[b]Key Laboratory for UV Light-Emitting Materials and Technology, Northeast Normal University, Ministry of Education, Changchun, Jilin 130024, P. R. China.

E-mail: xinglong@nenu.edu.cn; jpzhang@nenu.edu.cn.

Experimental Details

The preparation of Ni_3Se_2 electrode with optimal 3DHNA grown on F-Ni: Before using, these F-Ni were cleaned with hydrochloric acid and ethyl alcohol, and then dried in the oven. The hydrazine-Se solution was prepared by adding Se powder (Aladdin, 99.9%, 17.6 mg) and cetyltrimethyl ammonium bromide (Aladdin, 99.0%, 20 mg) into hydrazine hydrate ($N_2H_4 \cdot H_2O$, 15 mL). The solution was stirred at room temperature for 5 h and transferred into 50 mL autoclave. Then, a few pieces of F-Ni that have been cut into circles with diameter of 12 mm were put into the solution and reacted at 150 °C for 12 h. The mass of F-Ni were kept the same. After cooling down to room temperature, the F-Ni were taken out and rinsed with water and ethyl alcohol several times, and then dried at 60 °C to acquire 3DNA electrode. Finally, 3DNA electrode were annealed at 600 °C for 2 h at the N_2 atmosphere to obtain Ni_3Se_2 electrode with optimal 3DHNA. The electrodes obtained by annealing the 3DNA electrode at 500 and 700 °C were also prepared to explore the evolution mechanism of the NA at high temperature. In order to determine the mass of active material on 3DNA electrode, the same experiment process was carried out expect no addition of Se powder (denoted as without Se). As a result, the active material loading of 3DNA can be calculated as following:

$$m_{\text{active material}} = \left(m_{\text{3DNA}} - m_{\text{without Se}}\right) \times 137 \div 78 \qquad (1)$$

Where 137 and 78 stand for the molecular weight of NiSe and Se.

Material characterizations: The XRD patterns of the electrodes before and after annealing were obtained by Rigaku P/max 2200VPC with Cu Kα radiation of λ =1.5406 Å. In order to detect the mass change of the 3DNA electrode during the heat treatment, TGA (Pyris Diamond, PerkinElmer) was carried out in a nitrogen flow with a heating rate of 10 °C min^{-1} until 700 °C. The element composition and chemical state of Ni_3Se_2 electrode with optimal 3DHNA was explored by XPS (ESCALAB 250, Thermo).

SEM (FEI XL 30) and TEM (JEOL JEM-2010F) were employed to characterize the morphology of the electrodes.

Electrochemical measurements: The 2032 coin cell was assembled in the glove box with the water and oxygen value lower than 0.1 ppm. The prepared electrode served as cathode without using carbon and binder while the metal sodium was anode. The active material loading was about 4 mg cm^{-2}. The electrolyte used was the solution of 1 M $NaClO_4$ in a 1:1 volume mixture of ethylene carbonate/propylene carbonate with 5 wt% fluoroethylene carbonate. The electrochemical reaction process was investigated by CV and EIS through the electrochemical station (CHI750E). CV tests were performed at the voltage interval of 0.001-3 V at the scan rate of 0.1 mV s^{-1}. EIS results were acquired in the perturbation amplitude of 5 mV between the frequency of 10^5 Hz and 10 mHz. Galvanostatic tests were conducted through LAND CT2001A battery-testing instrument within the voltage range of 0.001-3 V.

$$NiSe + 2Na^+ + 2e^- = Na_2Se + Ni \quad (2)$$

$$NiSe_2 + 4Na^+ + 4e^- = 2Na_2Se + Ni \quad (3)$$

$$NiSe_{2/3} + 4/3Na^+ + 4/3e^- = 2/3Na_2Se + Ni \quad (4)$$

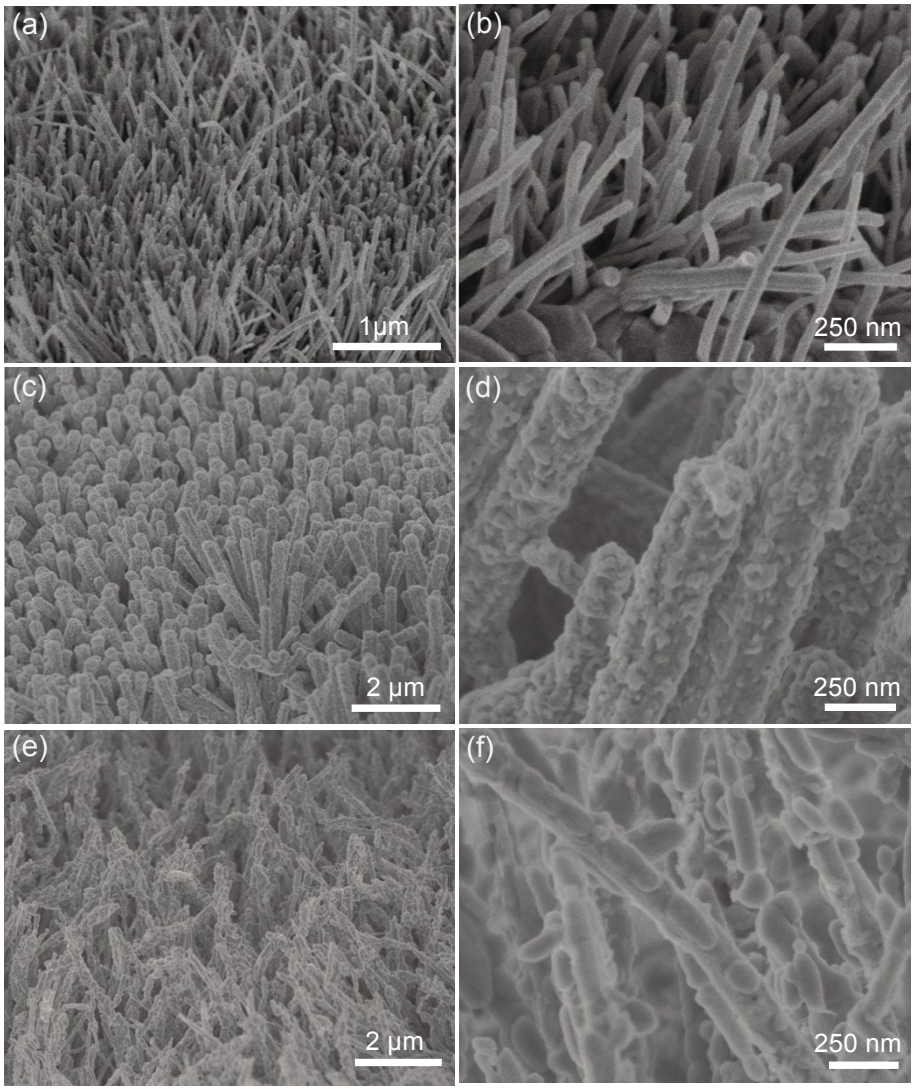

Fig. S1 (a) Low- and (b) high-resolution SEM images of 3DNA electrode. The low- and high-resolution SEM images of the electrodes obtained by annealing the 3DNA at (c, d) 500 °C and (e, f) 700 °C.

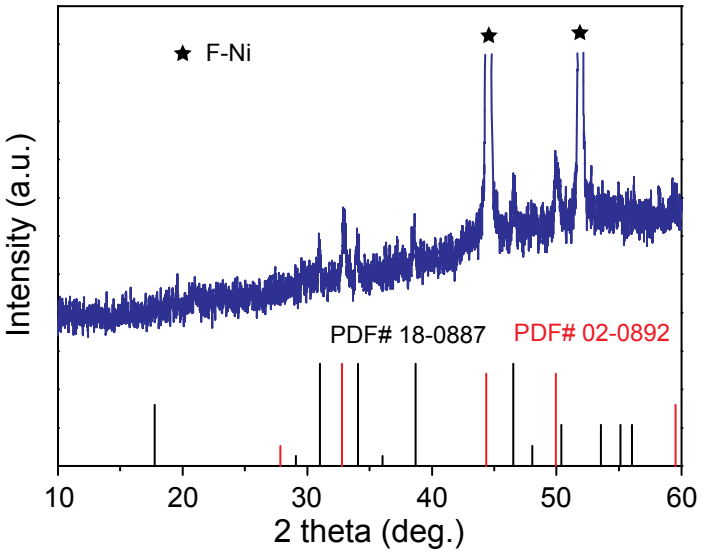

Fig. S2 (a) XRD pattern of the 3DNA electrode.

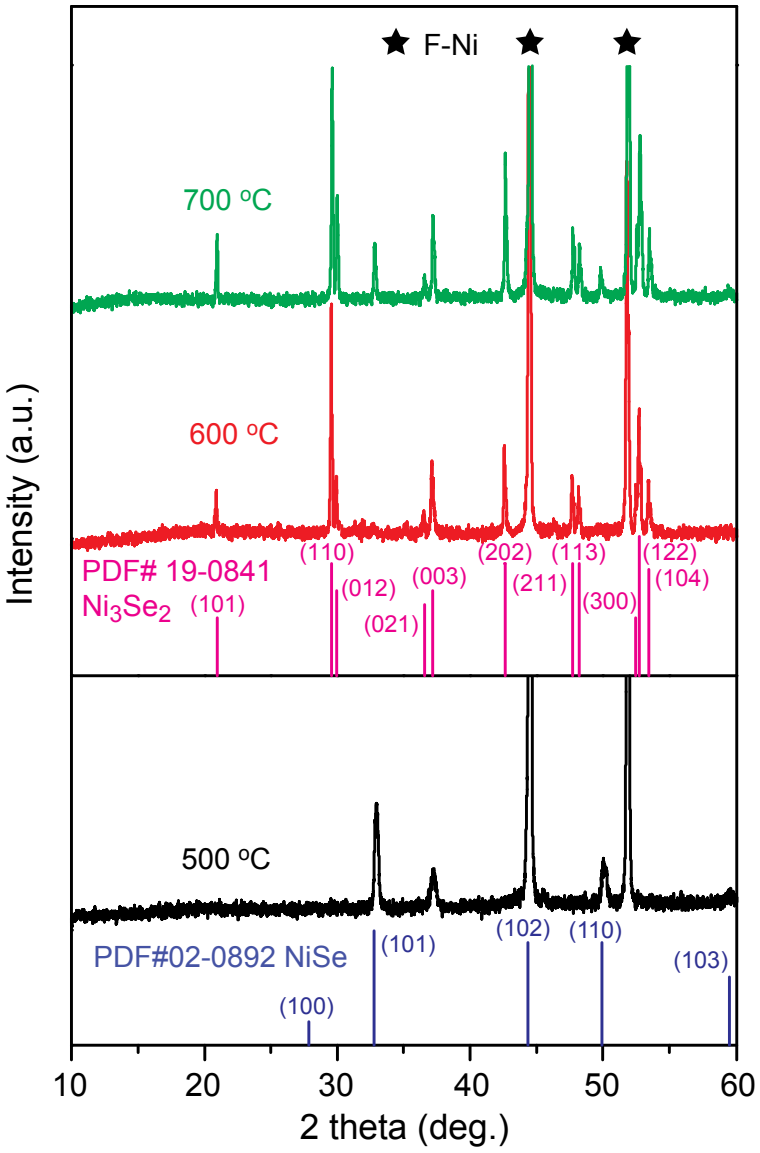

Fig. S3 XRD patterns of the electrodes obtained by annealing the 3DNA electrode at different

temperatures.

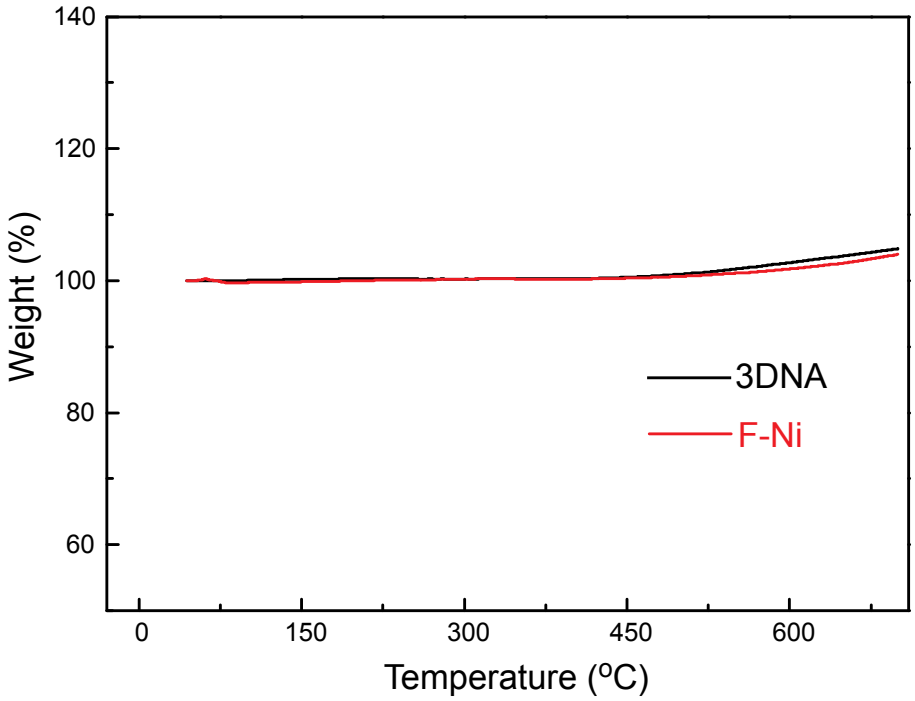

Fig. S4 TGA result of 3DNA and pure F-Ni electrode from room temperature to 700 °C in the N_2 atmosphere with the heating rate of 10 °C min^{-1}.

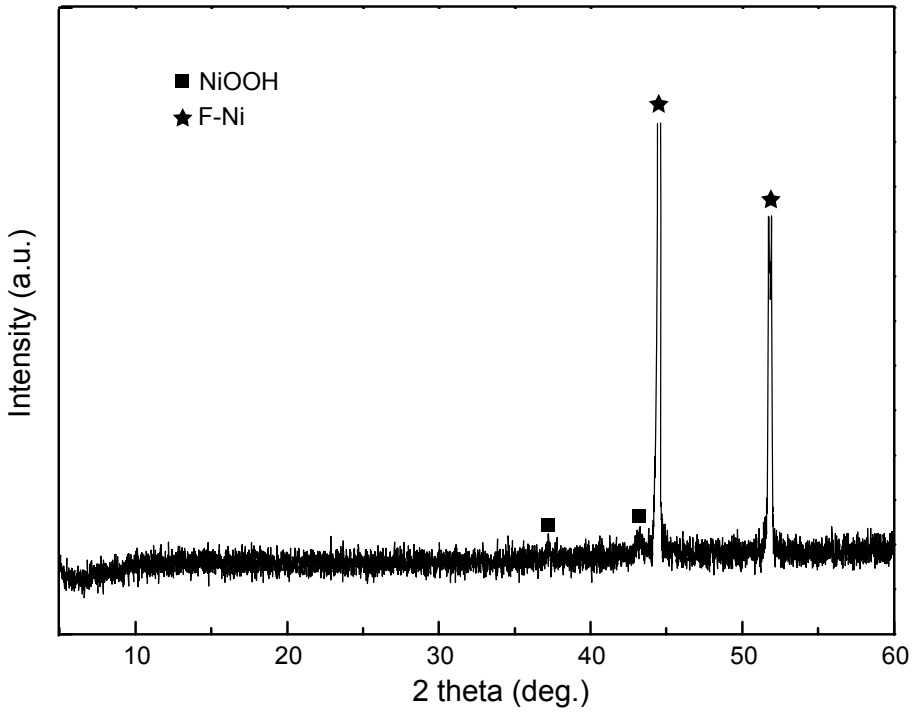

Fig. S5 XRD result of the pure F-Ni after treated at 600 °C.

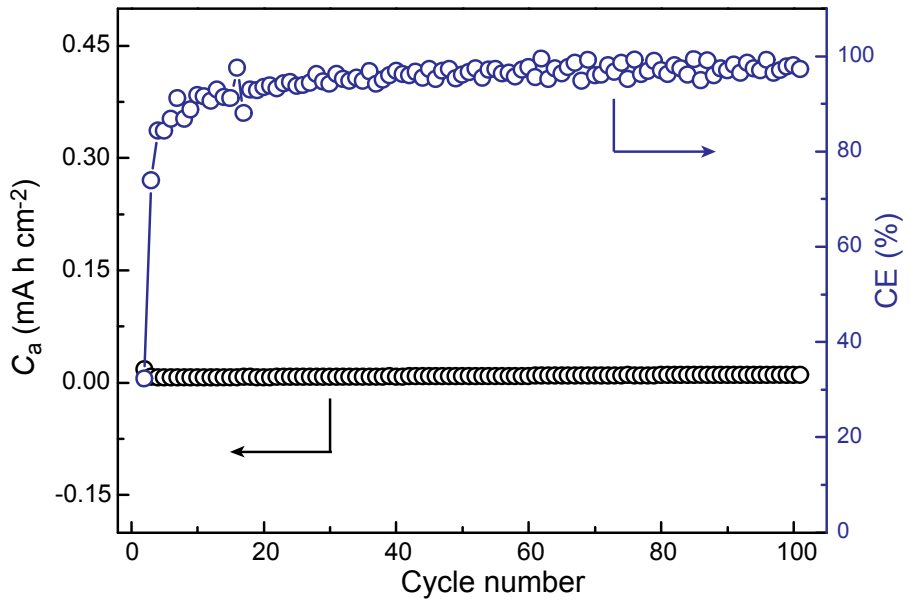

Fig. S6 The cycle performance of the pure F-Ni after treated at 600 °C at 0.2 mA cm^{-2}.

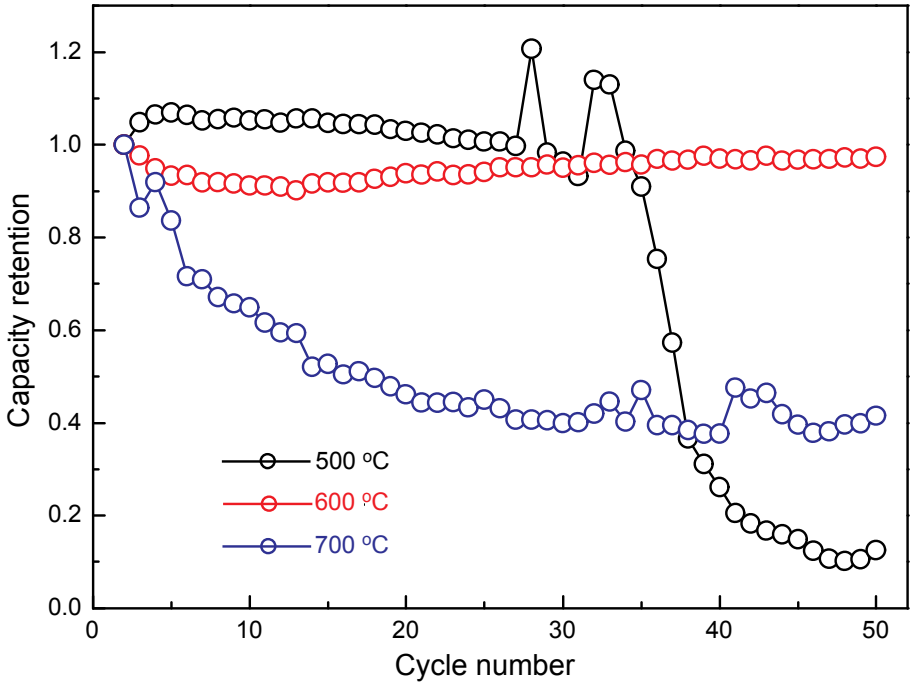

Fig. S7 The comparison of cycle retention for the electrodes obtained by annealing the 3DNA electrode at different temperatures.

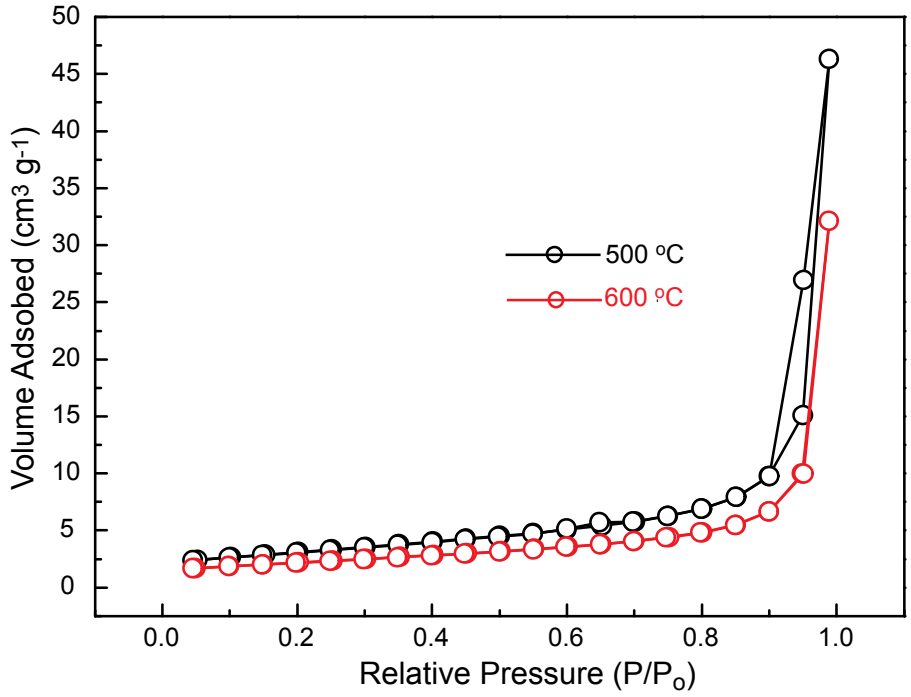

Fig. S8 N_2 adsorption-desorption isothermal of the 3DHNA electrode acquired at 500 °C and 600 °C.

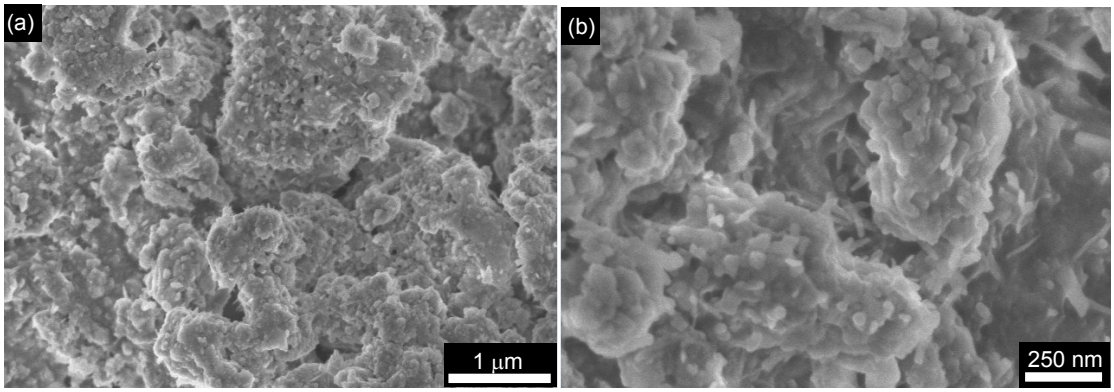

Fig. S9 SEM images after cycles for the electrode obtained by annealing the 3DNA electrode at 500 °C.

Table S1 The elemental composition of Ni_3Se_2 electrode with optimal 3DHNA from the XPS result.

Element	Ni	Se	O
Atom%	15.39%	3.12%	81.49%

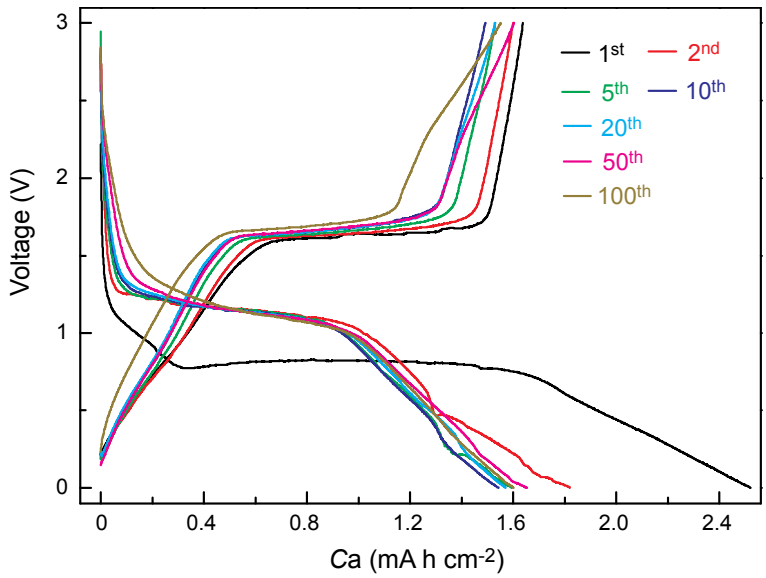

Fig. S10 The charge-discharge curves of the Ni_3Se_2 electrode with optimal 3DHNA for different cycles at 0.2 mA cm^{-2}.

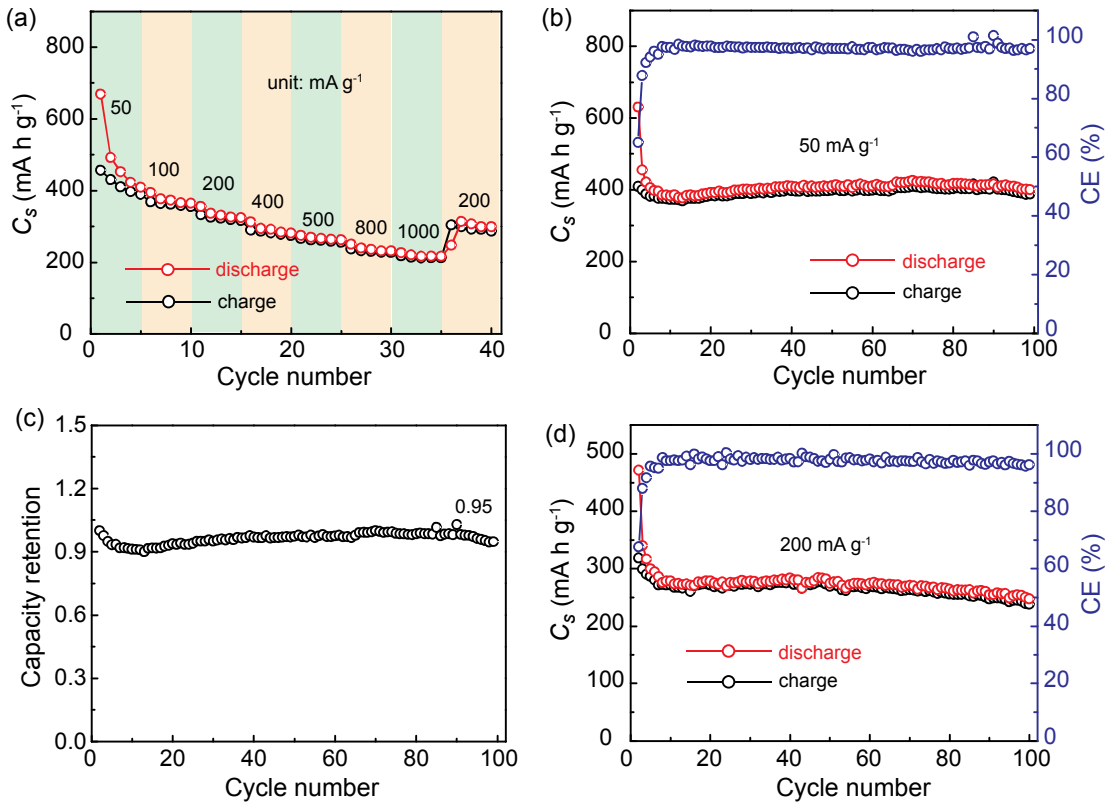

Fig. S11 The electrochemical performance of the Ni_3Se_2 electrode with optimal 3DHNA. (a) C_s at different current densities, (b) cycle performance at 50 mA g^{-1}, (c) capacity retention at 50 mA g^{-1} and (d) cycle performance at 200 mA g^{-1}.

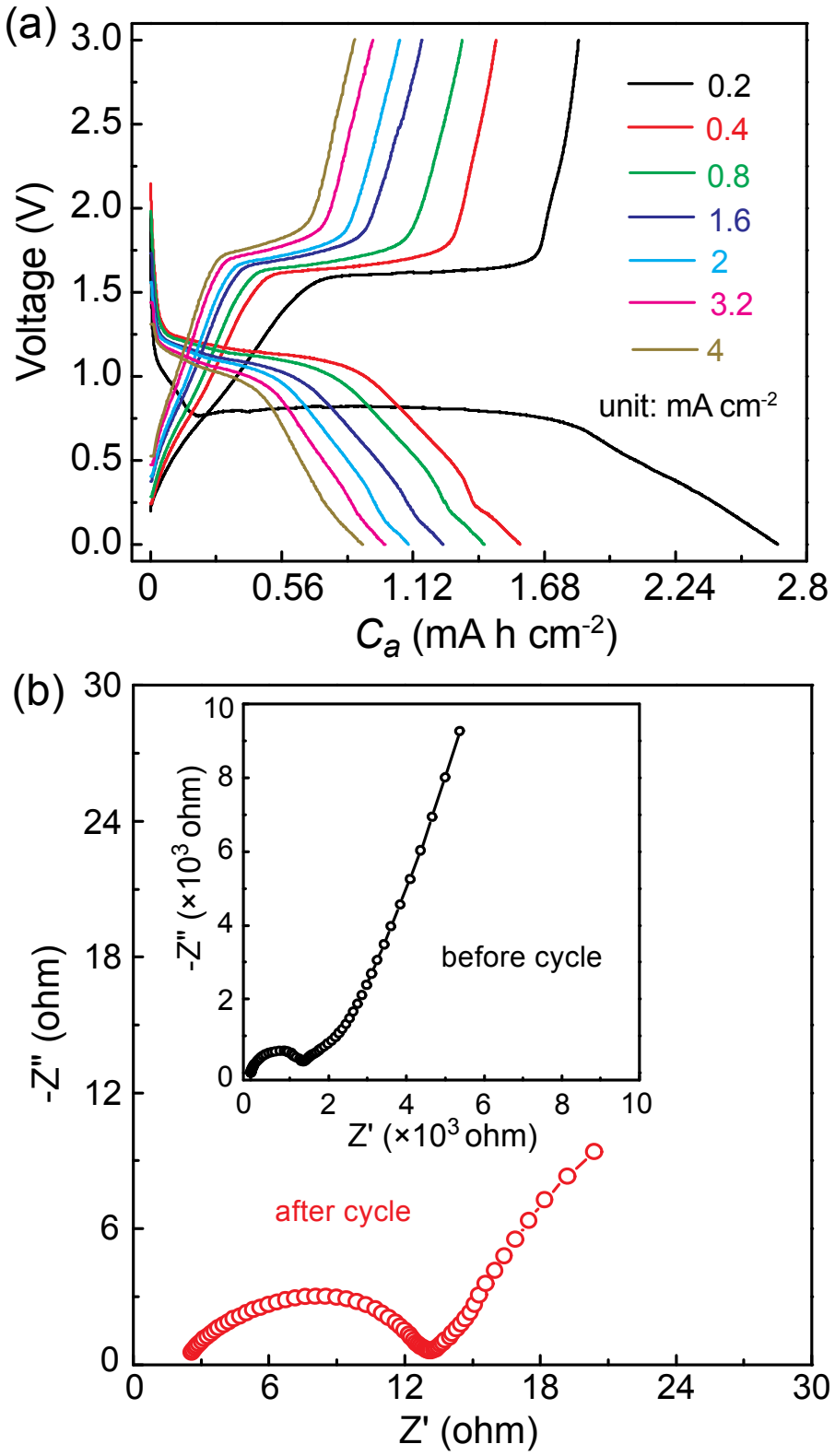

Fig. S12 (a) The charge-discharge curves of the Ni_3Se_2 electrode with optimal 3DHNA at different current densities. (b) EIS results before and after cycle.

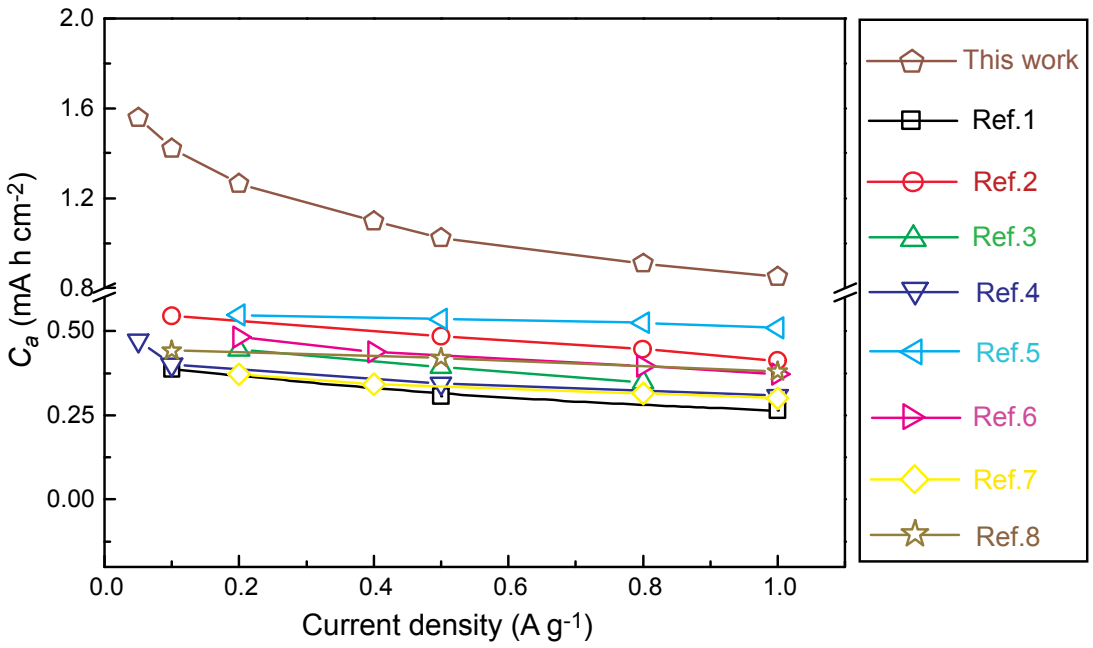

Fig. S13 The comparison of the C_a in this work with other reported metal selenides at different current densities.[1-8]

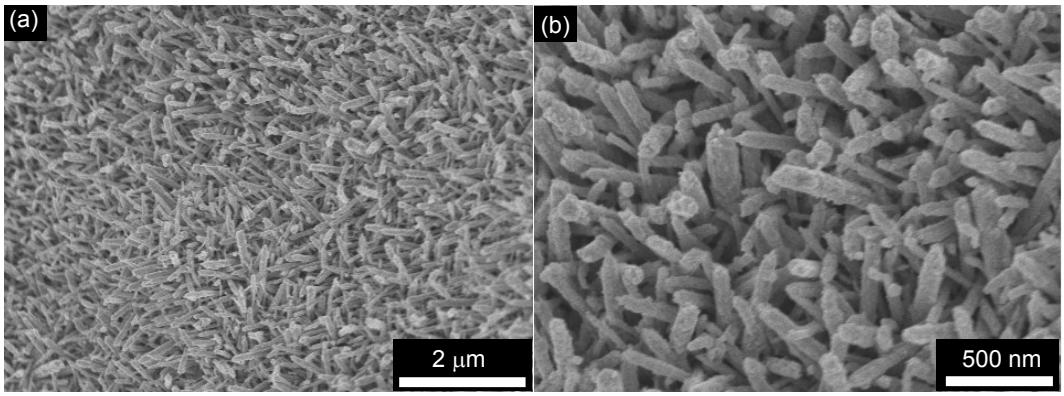

Fig. S14 SEM images of the Ni_3Se_2 electrode with optimal 3DHNA after cycles.

References

1 Z. Xiao, Z. Yang, L. Wang, H. Nie, M. Zhong, Q. Lai, X. Xu, L. Zhang and S. Huang, *Adv. Mater.,* 2015, **27**, 2891.

2 J. S. Cho, S. Y. Lee and Y. C. Kang, *Sci. Rep.,* 2016, **6**, 23338.

3 X. Yang, Z. Zhang, Y. Fu and Q. Li, *Nanoscale,* 2015, **7**, 10198.

4 X. Yang, R. Zhang, N. Chen, X. Meng, P. Yang, C. Wang, Y. Zhang, Y. Wei, G. Chen and F. Du, *Chem.-*

Eur. J., 2016, **22**, 1445.

5 Z. Zhang, X. Yang, Y. Fu and K. Du, *J. Power Sources,* 2015, **296**, 2.

6 G. D. Park, J. H. Lee and Y. C. Kang, *Nanoscale,* 2016, **8**, 11889.

7 G. D. Park and Y. C. Kang, *Chem.-Eur. J.,* 2016, **22**, 4140.

8 J. S. Cho, J. M. Won, J.-K. Lee and Y. C. Kang, *Nano Energy,* 2016, **26**, 466.