

## Supporting Information

### **Ni<sub>3</sub>S<sub>2</sub> nanosheets-anchored carbon submicron tubes arrays as high-performance binder-free anode for Na-ion batteries**

Xueke Xia,<sup>a</sup> Jian Xie,<sup>ab\*</sup> Shichao Zhang,<sup>c</sup> Bin Pan,<sup>d</sup> Gaoshao Cao<sup>b</sup> and Xinbing Zhao<sup>ab</sup>

<sup>a</sup> State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

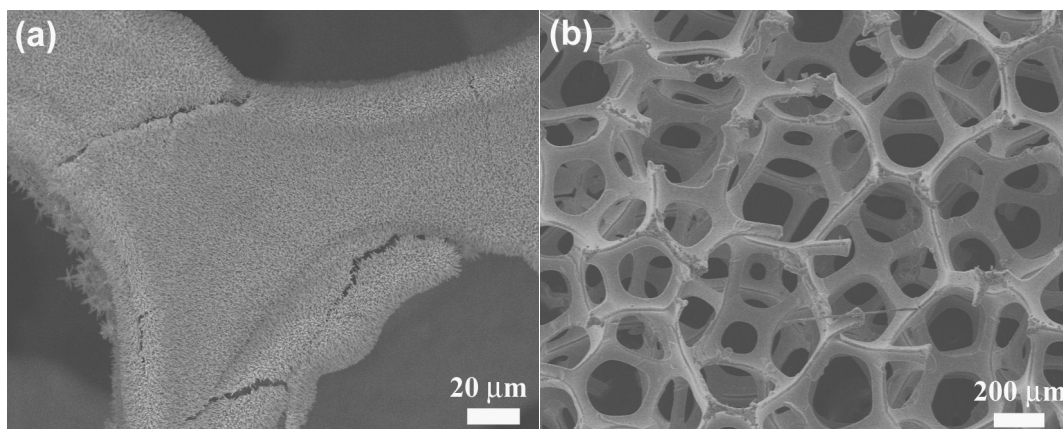
<sup>b</sup> Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Hangzhou 310027, P. R. China

<sup>c</sup> School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100191, P. R. China

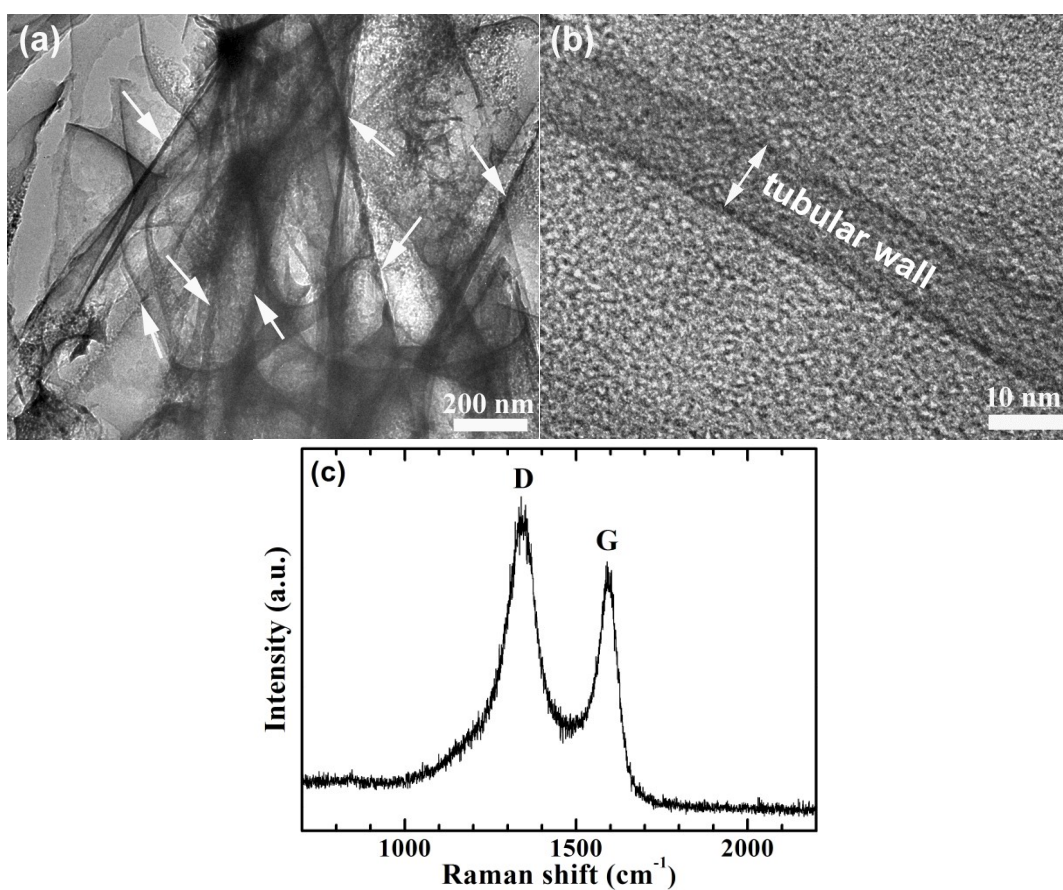
<sup>d</sup> Industrial Technology Research Institute of Zhejiang University, Hangzhou 310058, P. R. China

## **Preparation of Ni-supported CST arrays:**

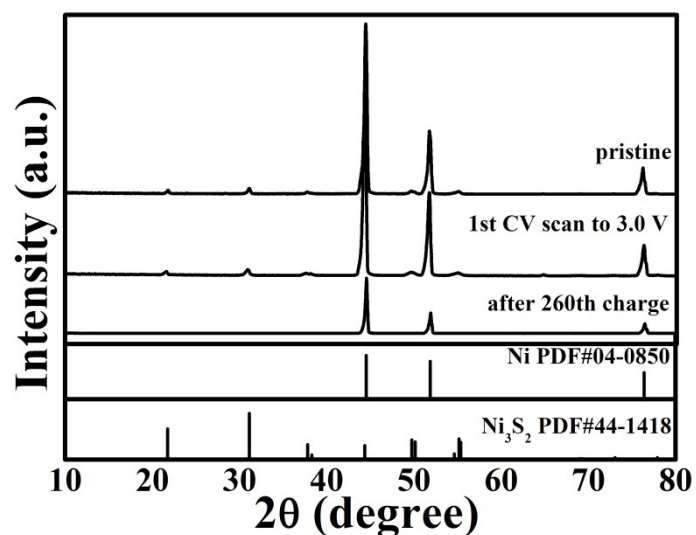
Ni-supported ZnO arrays were synthesized by a hydrothermal route, which were used as the templates to grow Ni-supported CST arrays. First, 0.268 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.127 g of methenamine were mixed in 30 mL of deionized (DI) water under stirring for 15 min to form a homogeneous solution. Second, 2.4 mL of 25 wt% ammonia was added to the above solution under stirring for another 15 min to form a transparent precursor solution. Before ZnO growth, a Ni foam piece (1.6 cm  $\times$  4.8 cm) was soaked in a  $\text{KMnO}_4$  aqueous solution (0.5 mol  $\text{L}^{-1}$ ) for 1 h and washed with DI water repeatedly. The Ni foam piece was then soaked in the above precursor solution overnight. After that, the precursor solution with the Ni foam piece was transferred into a 100 mL Teflon-lined stainless steel autoclave. Hydrothermal reaction was carried out in an electric oven at 90 °C for 24 h to grow ZnO arrays on the Ni substrate. The Ni-supported ZnO arrays were obtained by rinsing the ZnO-loaded Ni foam piece with DI water and absolute ethanol sufficiently followed by heating at 60 °C in air overnight. The proximity of the ZnO arrays was tuned by increasing or decreasing  $\text{Zn}^{2+}$  concentration in the precursor solution so as to increase ( $\sim 1.6 \text{ mg cm}^{-2}$ ) or decrease ( $\sim 0.6 \text{ mg cm}^{-2}$ ) the loading of  $\text{Ni}_3\text{S}_2/\text{CST}$ . Carbon coating on ZnO was performed by soaking the Ni-supported ZnO in a glucose aqueous solution (0.06 M) overnight followed by heating at 500 °C for 3 h under Ar atmosphere. Ni-supported CST was finally obtained by soaking the carbon-coated ZnO in a NaOH aqueous solution (1.5 M) for 48 h to etch ZnO.



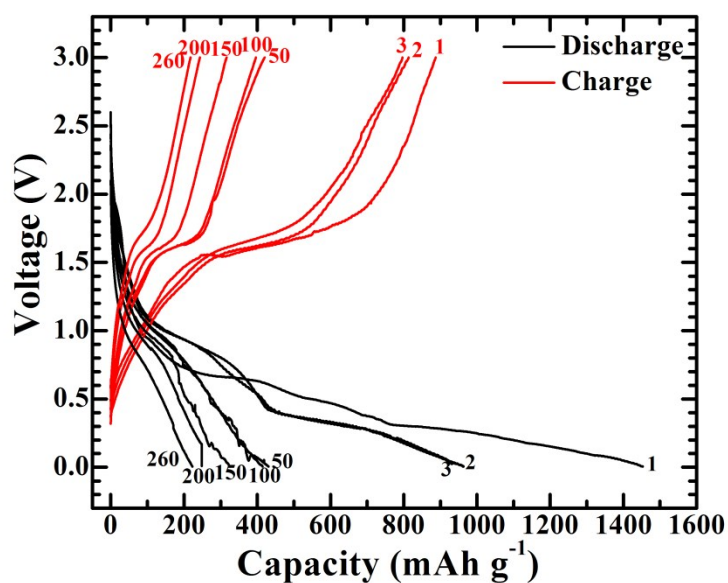
**Fig. S1.** Low-magnification SEM images of (a) Ni-supported ZnO arrays and (b) Ni foam.



**Fig. S2.** (a) TEM image, (b) HRTEM image, and (c) Raman spectrum of CST. The white arrows in Fig. S2a mark the tubular walls of the CST. Fig. S2b shows only the enlarged view of the solid tubular wall of one CST, not including the hollow core of the CST.



**Fig. S3.** XRD patterns of the pristine Ni-supported Ni<sub>3</sub>S<sub>2</sub>/CST electrode, the electrode after CV scanning to 3 V (vs. Na/Na<sup>+</sup>) at 0.1 mV s<sup>-1</sup>, and the electrode after 260 cycles.



**Fig. S4.** Voltage profiles of Ni-supported Ni<sub>3</sub>S<sub>2</sub>/CST at different cycles at 50 mA g<sup>-1</sup>.

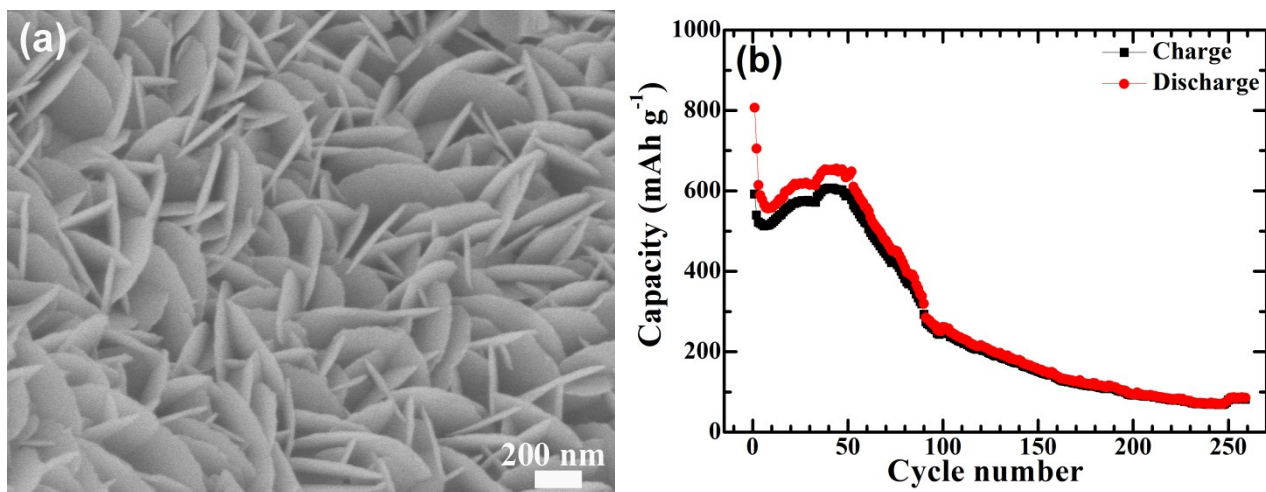


Fig. S5. (a) SEM image and (b) cycling stability of Ni-supported Ni<sub>3</sub>S<sub>2</sub> at 50 mA g<sup>-1</sup>.

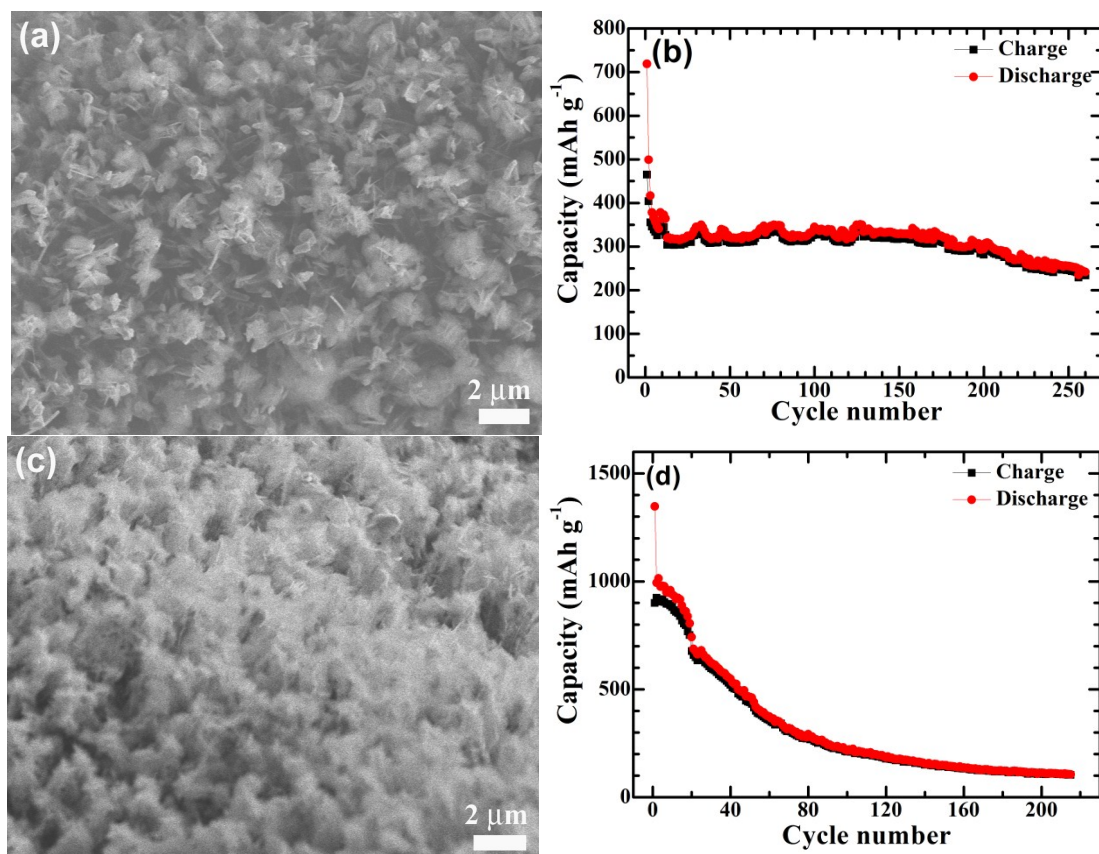
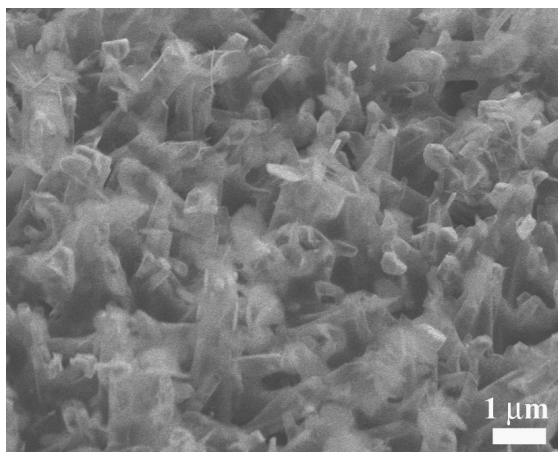


Fig. S6. (a,c) SEM image and (b,d) cycling stability of Ni-supported Ni<sub>3</sub>S<sub>2</sub>/CST with (a,b) lower and higher (c,d) Ni<sub>3</sub>S<sub>2</sub>/CST loading. The current density is 50 mA g<sup>-1</sup>.



**Fig. S7.** SEM image of Ni-supported  $\text{Ni}_3\text{S}_2/\text{CST}$  after 260 cycles.

**Table S1** Cycling stability of some typical sulfides.

Sample	Current density [mA g <sup>-1</sup> ]	Initial capacity [mAh g <sup>-1</sup> ]	Cycle number	Retained Capacity	Reference
Ni <sub>3</sub> S <sub>2</sub> /CST	50	887	100/260	401/212	This work
MnS/G	100	497	125	308	[1]
FeS/C	91	~500	100	365	[2]
Ni <sub>3</sub> S <sub>2</sub> +Ni <sub>7</sub> S <sub>6</sub> /G	100	512.7	50	391.6	[3]
Ni <sub>3</sub> S <sub>2</sub> /PEDOT	600	318.3	30	280	[4]
VS <sub>4</sub> /G	100	450.4	50	237.1	[5]

Note: G is graphene, and PEDOT is Poly(3,4-ethylenedioxythiophene)

- 1 X. J. Xu, S. M. Ji, M. Z. Gu and J. Liu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 20957–20964.
- 2 X. Wei, W. H. Li, J. A. Shi, L. Gu and Y. Yu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 27804–27809.
- 3 W. Qin, T. Q. Chen, T. Lu, D. H. C. Chua and L. K. Pan, *J. Power Sources*, 2016, **302**, 202–209.
- 4 C. Q. Shang, S. M. Dong, S. L. Zhang, P. Hu, C. J. Zhang and G. L. Cui, *Electrochem. Commun.*, 2014, **50**, 24–27.
- 5 R. M. Sun, Q. L. Wei, Q. D. Li, W. Luo, Q. Y. An, J. Z. Sheng, D. Wang, W. Chen and L. Q. Mai, *ACS Appl. Mater. Interfaces*, 2015, **7**, 20902–20908.