Supporting Information

Auto-Generated Iron Chalcogenide Microcapsules Ensured High-Rate and High-Capacity Sodium-Ion Storage

Xusheng Wang, a,b Zhanhai Yang, a Chao Wang, b Luxiang Ma, b Chunsong Zhao, b Jitao Chen, b Xinxiang Zhang b and Mianqi Xue* a

a Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, China.

b Beijing National Laboratory for Molecular Sciences College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

Email: xuemq@iphy.ac.cn
EXPRESSMENTAL SECTION

**Reaction Between the Iron Wires and Selenium/Tellurium Powders.** The iron wires (0.25 mm in diameter and 25 mm in length) were polished before use. Then the iron wires and selenium/tellurium powders were placed at each end of a quartz tube, which was then sealed in the vacuum condition and heated at 500 °C for 150 h to obtain the reaction products.

**Synthesis of the FeSe@FeS, FeS, FeSe, Na$_3$V$_2$(PO$_4$)$_3$ (NVP), LiCoO$_2$, and NCA Materials.** The iron (Alfa Aesar, 99.9%), sulfur (Alfa Aesar, 99.5%), and selenium (Alfa Aesar, 99.999%) powders were mixed uniformly in a mortar at the molar ratio of 1: 0.75 : 0.25. The mixture was transferred into a quartz tube, which was then sealed in the vacuum condition and heated at 400 °C for 50 h to obtain the FeSe@FeS material. The FeS and FeSe materials were synthesized with the same procedure as comparison. The NVP material was synthesized by using a sol-gel method with NaOH, NH$_4$VO$_3$, NH$_4$H$_2$PO$_4$, and citric acid as raw materials. The LiCoO$_2$ and NCA (lithium nickel cobalt aluminum oxide) materials were synthesized by the conventional high-temperature solid-state reaction.

**Synthesis of the Intermediate A, Intermediate B, Fe@FeS, and FeSe/FeS Materials.** The intermediates A and B were selected from the synthesis process in Fig. S5 and taken out of the muffle furnace and cooled to room temperature in a very short time. The Fe@FeS material was prepared with the iron and sulfur powders at a molar ratio of 1 : 0.75 by using the synthesis process in Fig. S5. The FeSe/FeS material was prepared with the Fe@FeS material and Se powders at a molar ratio of 1 (Fe): 0.25 (Se) by using the synthesis process in Fig. S5.

**Material Characterizations.** The crystal structures of FeSe@FeS, Fe@FeS, and FeSe/FeS materials were determined by X-ray diffraction (XRD, PANalytical diffractometer) with Cu Ka
radiation ($\lambda = 1.5416$ Å) (40 kV, 40 mA). The morphological, elemental-mapping, and microstructural characterizations of FeSe@FeS, FeS, Fe@FeS, and FeSe/FeS materials were visualized by scanning electron microscopy (SEM, S4800, Hitachi) and transmission electron microscopy (TEM, JEM-2100F, JEOL). The thermal stability of the FeSe@FeS material was evaluated by differential scanning calorimetry (DSC, Q100DSC, TA) (DCS1 of METTLER TOLEDO for the LiCoO$_2$ and NCA materials).

**Preparation of the FeSe@FeS, FeS, FeSe, NVP, LiCoO$_2$, and NCA Electrodes.** The low mass-loaded FeSe@FeS electrodes were prepared by mixing the FeSe@FeS powders, carbon black, and sodium carboxymethylcellulose (CMC) at a weight ratio of 8 : 1 : 1. The slurry was spread on a copper foil and then dried in an electric thermostatic drying oven at 90 °C. The dried copper foil was cut into disks (11 mm) as the FeSe@FeS electrodes and then dried in an oven at 80 °C for 12 h under vacuum (the loading is 1.6 mg cm$^{-2}$). The FeS and FeSe electrodes were prepared by the same procedure for comparison. The high mass-loaded FeSe@FeS electrodes were prepared by the similar procedure only with the differences of LA133 binder (acrylonitrile copolymer dispersed in water) as the binder and the weight ratio of 85 : 8 : 7. The NVP electrodes were prepared by mixing the NVP powders (90 wt% of pure NVP and 10 wt% of carbon), carbon black, and polyvinylidene fluoride (PVDF) at a weight ratio of 75 : 15 : 10. The slurry was spread on the aluminum foils and then dried in an electric thermostatic drying oven at 90 °C. The dried aluminum foils were cut into disks (11 mm) as the NVP electrodes and then dried in an oven at 120 °C for 12 h under vacuum. The LiCoO$_2$, and NCA electrodes were prepared by the similar procedure only with the difference of the weight ratio of 90 : 5 : 5.

**Electrochemical and Battery Performances of the FeSe@FeS, FeS, FeSe, NVP, LiCoO$_2$, and NCA Electrodes.** The electrochemical and half-cell performances of FeSe@FeS, FeS, and
FeSe electrodes were characterized with sodium metal foils as the counter electrodes, glass fibers as the separators, and 1 mol L$^{-1}$ sodium trifluomethanesulfonate (NaCF$_3$SO$_3$) in diethylene glycol dimethyl ether (DEGDME) as the electrolyte, and then assembled into LIR2032-type coin cells in an argon-filled glove box in which the moisture and oxygen contents were below 0.1 ppm. The half-cell performances of the NVP electrodes were characterized by the similar procedure only with the differences of the sodium metal foils as the anode and 1 mol L$^{-1}$ sodium perchlorate (NaClO$_4$) in propylene carbonate (PC) with 5 vol% fluoroethylene carbonate (FEC) as the electrolyte. The full-cell performances of the FeSe@FeS electrodes were characterized by the similar procedure only with the differences of the NVP as the cathode and 1 mol L$^{-1}$ NaClO$_4$ in DEGDME as the electrolyte. The LiCoO$_2$ and NCA electrodes were assembled in the same procedure only with the differences of lithium metal foils as the counter electrodes, Celgard 2400 as the separators, and 1 mol L$^{-1}$ lithium hexafluorophosphate (LiPF$_6$) in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (v : v : v = 1 : 1 : 1) as the electrolyte. The cycling and rate tests of the assembled batteries were performed on a Land CT2001A battery testing system within the voltage range of 0.25-3.0 V versus Na$^+$/Na (0.01-3.0 V in the Fig. S19c; 2.2-4.0 V for the NVP half cells, and 0.3-2.9 V for the full cells). Cyclic voltammogram (CV) (0.25-3.0 V) and electrochemical impedance spectroscopy (EIS) were measured on an Autolab electrochemical workstation. The cycle number of the cycling performances for the FeSe@FeS half cells in the text starts after several discharge-charge processes, in which a small current density (100-500 mA g$^{-1}$) was used to activate the electrodes to achieve the stable cycling state.
Fig. S1  (a) SEM image of the reaction products between the iron wires and selenium/tellurium powders. It shows a hierarchical structure: inner FeTe, middle FeSe$_{x}$Te$_{1-x}$, and outer FeSe (with gradually reduced Te component). (b) EDX results of the atomic percents of selenium and tellurium at the sites of 1, 2, and 3 in panel (a). The scale bar is 200 μm in panel (a).
**Fig. S2** (a-d) SEM images of the FeSe@FeS material. (e-f) SEM images of the contrastive FeS material. The morphology of FeS is very similar to that of the shell-encapsulation structure of the FeSe@FeS material. The scale bars are severally 20, 10, 2, 2, 1, and 1 μm in panels (a-f).

**Fig. S3** SEM image of the raw iron powders. The scale bar is 50 μm.
Fig. S4 TEM images of the FeSe@FeS material. The layered configuration extends energetically along the planar dimensionality. The scale bars in panels (a) and (b) are 50 and 10 nm, respectively.

![TEM images](image1)

Fig. S5 Synthesis process of the FeSe@FeS material within five steps.

![Synthesis process](image2)

Fig. S6 (a) XRD pattern of the intermediate A in Fig. S5. (b) SEM image of the intermediate A in Fig. S5. The scale bar is 20 μm in panel (b).

![XRD and SEM images](image3)
**Fig. S7** EDX images of the intermediate A in Fig. S5.

![EDX images](image)

**Fig. S8** (a) XRD pattern of the intermediate B in Fig. S5. (b) SEM image of the intermediate B in Fig. S5. The scale bar is 15 μm in panel (b).

![XRD pattern](image)  
![SEM image](image)
**Fig. S9** EDX images of the intermediate B in Fig. S5.

**Fig. 10** XRD pattern of the Fe@FeS product without the introduction of raw Se powders (the initial feeding molar ratio between Fe and S elements is 1 : 0.75).
Fig. 11 SEM and EDX images of the Fe@FeS product without the introduction of raw Se powders (the initial feeding molar ratio between Fe and S elements is 1 : 0.75).

Fig. 12 XRD pattern of the FeSe/FeS product synthesized by the Fe@FeS product and Se powders (the initial feeding molar ratio between Fe element in the Fe@FeS species and added Se element is 1 : 0.25).

Fig. 13 SEM and EDX images of the FeSe/FeS product synthesized by the Fe@FeS product and Se powders (the initial feeding molar ratio between Fe element in the Fe@FeS species and added Se element is 1 : 0.25).
**Fig. S14** CV curves of the first sodiation and desodiation processes for the FeSe@FeS and FeS electrodes. The voltage hysteresis of the FeSe@FeS electrode is smaller than that of the FeS electrode.

**Fig. S15** (a) Galvanostatic discharge-charge curves of the first sodiation and desodiation processes for the FeSe@FeS and FeS electrodes. (b) Change rates of the discharge capacity and charge capacity along with voltage for the FeSe@FeS and FeS electrodes.
**Fig. S16** Voltage drops of the FeSe@FeS electrode during the setting time. For the node of 60 s, the minimum of the voltage drops is 0.466 V for the 600th cycle.

**Fig. S17** (a) EIS patterns of the charged-state FeSe@FeS and FeS electrodes. The inset shows the whole patterns. The simulated values of $R_{ct}$ for the FeSe@FeS and FeS electrodes are severally 20 and 28 Ω. (b) Linear relationship of $Z_{re}$ and $\omega^{-1/2}$ in the low-frequency region. The fitted $\sigma$ (Warburg factor) values for the FeSe@FeS and FeS electrodes are separately 66 and 361.

**Fig. S18** Dependence of peak current on the scan rate for the peak groups a-e in Fig. 3b. The slopes and intercepts could be used to simulate the contribution of the pseudocapacitive behavior.
**Fig. S19** (a) Rate capability of the FeS electrodes. A low discharge capacity of 143 mAh g$^{-1}$ is delivered at 12 A g$^{-1}$ for the FeS electrodes. (b) Cycling performance of the FeS electrodes performed at 0.5 A g$^{-1}$. A discharge capacity of 402 mAh g$^{-1}$ is achieved after 600 cycles. (c) Comparison of the cycling performance within the voltage range of 0.01 and 3.0 V between the FeSe@FeS and FeS electrodes. The FeSe@FeS electrodes exhibit better cycling stability than that of the FeS electrodes.

**Fig. S20** Cycling performance of the FeSe material at 1 A g$^{-1}$. 
**Fig. S21** Comparison of the loadings between the high mass-loaded FeSe@FeS electrodes (8 mg cm\(^{-2}\)) and some long-life (over 500 cycles) SIB anodes. References 1-22 severally represents the 
SnO\(_2\)@C-I, G-NCs, NOC, red P-SWCNT, BPPG, \(\gamma\)-Fe\(_2\)O\(_3\)@C, MoS\(_2\)-G2, SnS\(_2\) NC/EDA-RGO, CoS@rGO, C@SnS/SnO\(_2\)@Gr, GF+V\(_2\)O\(_3\)/CNTs, 3D MoS\(_2\)-graphene, WS\(_2\)@GE, Sb@TiO\(_{2-x}\), H-CoS\(_2\), SbNPs@3D-C, CoSe\(_2\), Sn NDs@PNC, 8-Sn@C, MFO@C, SnS\(_2\)/rGO, and Mo\(_3\)Sb\(_7\)/C materials.\(^{1-22}\)

**Fig. S22** (a) Galvanostatic voltage profiles of the NVP half cell (with the simulated theoretical capacity of 100 mAh g\(^{-1}\)) at 0.1 C between 2.2 and 4.0 V. The initial coulombic efficiency is 97%. (b) Cycling performance of the NVP half cell at 1.0 C between 2.2 and 4.0 V.
Fig. S23 Comparisons of the total exothermic heat (a) and exothermic peak temperature (b) (derived from the DSC data) between the high mass-loaded FeSe@FeS electrodes and some published hard carbons. Letters a-f separately represent the HC (NaClO₄ in EC + PC), C1600 (NaPF₆ in PC), C1600 (NaPF₆ in EC + DMC), PBHMC (NaClO₄ in EC + PC), C1600 (NaClO₄ in PC), C1600 (NaClO₄ in EC + DMC) (descriptions in the brackets are the electrolyte systems). EC: ethylene carbonate; PC: propylene carbonate; DMC: dimethyl carbonate.

REFERENCES


