Supporting information

Chemical Vapor Deposition Growth of Carbon Nanotube Confined Nickel Sulfides from Porous Electrospun Carbon Nanofibers and Their Superior Lithium Storage Properties

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Figure S1. XRD patterns of the intermediates collected at different temperatures during TGA measurement. (a-I) 480 °C; (a-II) 630 °C; (b) 800 °C. Notes: NiS (●), NiO (○), NiSO4 (#).

XRD analysis was performed on the products obtained by stopping the TGA analysis at different temperatures (Figure S1). The product collected at 480 °C is a mixture of NiS and NiO. In the product collected at 630 °C, only NiO and NiSO4 were
detected. The product collected at 800 °C is NiO. Based on the above results, the oxidation of nickel sulfides (Ni$_3$S$_2$) in the CNT@NS@CNF hybrid under the TGA analysis can be proposed as following:

\begin{align*}
2Ni_3S_2 + O_2 &\rightarrow 4NiS + 2NiO \\
NiS + 2O_2 &\rightarrow NiSO_4 \\
2NiSO_4 &\rightarrow 2NiO + 2SO_2 + O_2
\end{align*}

Figure S2. Survey XPS spectrum of CNT@NS@CNFs.

Figure S3. SEM images of the Ni@CNFs obtained by annealing NiAc$_2$/PAN precursor at 800 °C with the absence of thiophene.
To explore the intrinsic factors influencing the morphological and electrochemical characteristics of the CNT@NS@CNFs, a series of controlled experiments were conducted. With an increase of the introduction amount of NiAc$_2$ in the electrospun solution, the nanotubes increase in number and size owing to the increased Ni nanoparticles (Figure S3). However, with increasing the amount of NiAc$_2$ to 2g and 3g in precursor, the as-obtained electrodes even showed worse lithium storage performance, delivering discharge capacities of 411 and 260 mA h/g after 45 cycles at a current density of 100 mA/g, respectively (Figure S3d), which can be attributed to the lower theoretical specific capacity of nickel sulfides. This may also support that the hierarchical CNT-CN architectures contributed a lot capacity owing to the novel structure characteristics.
Figure S5. (a, b) SEM images of (a) CNT@NS@CNF-900 and (b) CNT@NS@CNF-1000. (c) XRD patterns and (d) cycling performances of the CNT@NS@CNFs prepared at different temperatures (the number represents the reaction temperatures).

Temperature-depended experiments were also performed, and the results were shown in Figure S4. When annealing the precursor NiAc$_2$/PAN nanofibers at 900°C and 1000 °C, the nickel sulfide nanoparticles encapsulated inside the tubes changed from ellipsoids to spherical shapes and their size increased with the temperature. As shown in Figure S4c, XRD pattern of CNT@NS@CNFs-800, CNT@NS@CNFs-900 and CNT@NS@CNFs-1000 were compared, revealing the increased crystallinity with increasing annealing temperature. When examined as anode materials for lithium ion batteries, the CNT@NS@CNFs-900, CNT@NS@CNFs-1000 exhibited discharge capacities of 432 mA h/g and 399 mA h/g after 45 cycles at a current density of 100 mA/g. In addition, the reaction time is also an important factor. The CNT@NS@CNFs-1h (obtained by annealing at 800°C for 1h) only showed a discharge capacities of 244 mA h/g after 10 cycles at 100 mA/g. All these products
have a problem of the aggregation of $\text{Ni}_3\text{S}_2$. When the reaction time is double, the $\text{Ni}_3\text{S}_2$ nanoparticles were easier to grow bigger. Higher reaction temperature produced larger $\text{Ni}_3\text{S}_2$ particles inside the carbon fibers owing to the fast nuclear and growth, which caused the inferior mechanical stability and the poorer lithium storage properties.

Figure S6. XRD patterns of iron sulfide and cobalt sulfide obtained using thiophene as sulfur source via CVD method, in which cobalt acetate or iron nitrate were used as Fe or Co sources for the electrospinning.

| Table1. Structures, electrochemical properties and synthesis methods of nickel sulfides as anode materials for lithium ion batteries |
|---------------------------------------------------------------|
| Structure                  | Electrochemical properties          | Synthesis method                                                                 | Ref  |
| NiO/Ni$_3$S$_2$-CNF composites | 519.2 mAh/g after 200 cycles at 0.5 A/g | Ni(NO$_3$)$_2$·6H$_2$O, urea and SDS into distilled water as precursor; hydrothermal reaction at 180°C for 12 h; annealing at 500°C in N$_2$ atmosphere for 2 h | 1   |
| kiwano-like hollow structure NiS$_2$ electrode | 681 mA h/g after 100 cycles at 50 mA/g | NiCl$_2$·6H$_2$O, N$_2$H$_4$·H$_2$O and NaOH dissolved into ethylene glycol as precursor; hydrothermal reaction at 120°C for 2 h, the product is mixed with sulfur and maintained at 170°C for 10h. | 2   |
| NS@CNT electrode | 644 mA h/g after 100 cycles at 0.3 A/g | Nickel chloride hexahydrate and thiourea as electrodeposition solution, a piece of CNT placed | 3   |
| Material                          | Capacity (mAh/g) | Cycles | Preparation Details                                                                                                                                                                                                 | References |
|----------------------------------|------------------|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| CMK-3-Ni$_3$S$_2$ composites     | ~520 mAh/g       | 100    | Sucrose, SBA-15[Ni(NO$_3$)$_2$·6H$_2$O and H$_2$SO$_4$ dissolved in deionized water as precursor solution; annealing at 700$^\circ$C for 3 h in N$_2$ atmosphere and wash by NaOH solution | This work  |
| CNTs@C@NiS electrodes            | 649 mAh/g        | 100    | CNTs and glucose heated at 180$^\circ$C for 6 h in Teflon-lined autoclave, the product mixed with NiCl$_2$·6H$_2$O, thiourea and glucose for hydrothermal reaction at 180$^\circ$C for 12 h | 5          |
| Ni$_3$S$_2$ nanosheet array       | 660.9 mAh/g      | 60     | Na$_2$S$_2$O$_3$·5H$_2$O and Na$_2$SO$_4$ solution, Ni foam for hydrothermal reaction at 130$^\circ$C for 2 h                                                                                                                                  | 6          |
| CNT@NS@CNFs                      | 630 mAh/g        | 200    | PAN/NiAc$_2$ nanofibers annealing at 800$^\circ$C for 30 min in thiophene atmosphere                                                                                                                                     |            |

References.
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