Supporting Information for

Facile Preparation of Ultrathin Sulfur-Wrapped Polyaniline Nanofiber Double Layer Composite as High Performance Cathode Material of Lithium-Sulfur Battery

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Detailed Methods

Materials
Aniline was distilled under reduced pressure. Deionized (DI) water was used throughout the experiments. All the other reagents were used as received without further treatment.

Preparation of water dispersible PANI nanofibers
In a typical procedure, 2 ml aniline was dispersed in 200 ml DI water. Subsequently, 11.1 ml concentrated sulfuric acid and 83.9 mg p-phenylenediamine was added into the suspension under vigorous stirring. Meanwhile, 4.564 g ammonium peroxydisulfate (APS) was dissolved in 100 ml of 1 M sulfuric acid aqueous solution. Both of the aniline suspension and APS solution were stirred in an ice bath (0-5 °C) for 20 min. After that, the APS solution was quickly poured into the aniline suspension with violent stirring for 30 s. The reaction vessel was left still for 24 h at room temperature. The products were harvested by filtration and washed with DI water several times until the pH value of the filtrates approached 7. Then as-obtained PANI nonofibers were dedoped into EB nanofibers by dispersing the filter cake in a 0.5 M solution of ammonium hydroxide for 24 h. EB nanofibers were obtained by filtration, washed with DI water until the filtrates approached neutral. Water dispersible PANI nanofibers were prepared according to our previous report. The acidic phosphate ester bearing one ethylene glycol segment and EB nanofibers were added to a conic flask with 200 ml DI water under violent stirring. After stirring 24 h, water dispersible PANI nanofibers were washed with DI water till pH value of filtrate approached 7. Finally, the product obtained was dried in vacuum at 60 °C till constant weight.

Preparation of S-PANI nanofibers
29.93 g sodium thiosulfate and 12.45 g concentrated sulfuric acid were dissolved in 50 ml DI water respectively. Then add them to 200 ml of 8.27 g L⁻¹ PANI nanofibers water dispersion dropwise at a speed of 50 drops per minute under violent stirring. The dispersion was filtered after 24 h, and then S-PANI nanofibers filter cake was washed with DI water several times till the pH value of filtrate approached 7. Finally, the product obtained was dried in vacuum at 45 °C till constant weight.

Preparation of S-C composite
Super-Li was used as the carbon matrix. It was mixed together with sulfur (mass ratio S/C=65:35). Then, the mixture grinded in ball mill for 3 h and thermally treated under Ar at 180 °C for 12 h.
Material characterization

The morphologies of the S-PANI composites were observed using a FEI XL30 ESEM field emission scanning electron microscope (SEM) with an operating voltage of 15 kV with chromium coating and the composition was analyzed by energy-dispersive X-ray spectroscopy (EDS). Samples for TEM observation were prepared by dropping a diluted suspension of the sample powders onto a standard carbon-coated formvar film on a copper grid. The interior structure of S-PANI nanofiber was examined by a JEOL JEM-2010 transmission electron microscope (TEM) at an acceleration voltage of 200 kV equipped with energy dispersive spectroscopy (EDS).

Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere with a heating rate of 10 °C per min from room temperature to 900°C. Wide-angle X-ray diffraction (XRD) experiments were performed using a D8 ADVANCE X-ray generator with a Cu anode (λ= 1.54 Å). The nitrogen absorption and desorption isotherms of PANI-S were obtained at 77.3 K with a Quantachrome ASiQwin surface area pore size analyzer. X-ray photoelectron spectroscopy (XPS) studies were conducted on a VG ESCALAB Mk II spectrometer with an Al Ka X-ray source. Malvern Zetasizer Nano ZS90 was used to test Zeta potentials in this work.

Electrochemical measurements

The S-PANI composites were mixed with conductive carbon black (super-P Li) and polytetrafluoroethylene (PTFE) binder (60 wt. %) at a weight ratio of 70 : 20 : 10 in water solution to form a slurry. Similarly, the S-C composites were mixed with PTFE at a weight ratio of 90: 10 to form slurry. The resultant slurries were uniformly spread onto a carbon-coated aluminum foil. The mass loading of cathodes was about 1.5–2.5 mg per cm². The electrolyte was 1.0 M lithium bis(trifluoromethane)sulfonylimide (LiTFSI) in 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1: 1 by volume). CR2016-type coin cells were fabricated by sandwiching a porous polypropylene separator (Celgard 2500) between the S-PANI electrode and Li metal foil (Materials Technology Co., LTD., China) in a high-purity Ar-filled glove box.

The cells were discharged and charged from 1.5–3.0 V at various C rates by using a LAND electrochemical station (Wuhan) to test their electrochemical performances. The cyclic voltammetry (CV) of the composite cathode was conducted on an electrochemical interface (Solartron SI1287) workstation at room temperature.

Diagram of S-PANI Composite
Green: PANI, yellow: sulfur

The thickness of the sulfur layer could be derived as follows:

\[
S_{\%} = \frac{w_s}{w_{\text{PANI}} + w_s}
\]

\[
\frac{S_{\%}}{1 - S_{\%}} = \frac{w_s}{w_{\text{PANI}} + w_s} = \frac{\rho_s \pi (R^2 - r^2)}{\rho_{\text{PANI}} \pi r^2}
\]

\[
\frac{w_s \rho_{\text{PANI}}}{w_{\text{PANI}} \gamma \rho_s} = \frac{R^2}{r^2} - 1
\]

\[
\frac{R}{r} = \frac{r + ts}{r} = \sqrt{\frac{w_s \rho_{\text{PANI}}}{w_{\text{PANI}} \gamma \rho_s} + 1}
\]

\[
ts = r \left( \sqrt{\frac{w_s \rho_{\text{PANI}}}{w_{\text{PANI}} \gamma \rho_s} + 1} - 1 \right) = r \left( \sqrt{\frac{S_{\%} \rho_{\text{PANI}}}{1 - S_{\%} \gamma \rho_s}} + 1 - 1 \right)
\]

\[
ts = r \left\{ \left[ \frac{S_{\%}}{1 - S_{\%}} + \gamma \rho_s \right] \rho_{\text{PANI}} \right\}^{1/2} - 1 \}
Figure S1. SEM images of water dispersible PANI nanofibers
Figure S2. Original TEM images of S/PANI nanocomposite
Figure S3. Zeta potential of de-doped PANI

Figure S4. Zeta potential of PANI doped by H\textsubscript{2}SO\textsubscript{4}

Figure S5. Zeta potential of PANI doped by acidic phosphate ester
As shown in Figure S5, $\text{SO}_4^{2-}$ replaced the initial dopant phosphate ester as the presence $\text{H}_2\text{SO}_4$ in the process of generating sulfur.

As shown in Figure S7, both of the EIS spectra comprised a depressed semicircle at the high-frequency region and an inclined tail in the low-frequency region. The intercept at the real axis $Z'$ of the EIS spectra corresponded to the combined resistance $R_e$, which was closely related to the resistance of the composite, the ionic resistance of the electrolyte, and the contact resistance at the
interface between composite and current collector. The $R_e$ for the S/PANI composite was 3.2 $\Omega$ and 7.8 $\Omega$ for the S/C composite. The semicircle in the high-frequency region was related to the interface charge transport process of the composite cathode, and the diameter of this semicircle corresponded to the charge transport resistance $R_{ct}$. The $R_{ct}$ simulated from the equivalent circuit were 125.1 $\Omega$ for S/PANI composite and 81.2 $\Omega$ for S/C composite, respectively. The larger resistance of the S/PANI composite, including $R_e$ and $R_{ct}$, indicated that the interfacial charge transport and Li ion diffusion processes were not as convenient as S/C composite, namely, more energy degradation (maybe the heat energy or internal energy) during each cycling and a worse Coulombic efficiency. Certainly, a definite answer to this question needs a more detailed and systematical investigation.