Supporting Information

One-Step Synthesis of Urchin-Like Sulfur/Polyaniline Nano-Composite as Promising Cathode Material for High-Capacity Rechargeable Lithium-Sulfur Battery

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1. Experimental detail

a. The preparation of S/PANI nano-composite

The aniline monomer (Sigma-Aldrich) was distilled twice under reduced pressure. Other reagents and solvents were purchased from commercial suppliers and used without further purification.

**Urchin-like Sulfur/Polyaniline Composite:** 1.422 g \( \text{Na}_2\text{S}_2\text{O}_3 \) was dissolved in 45 mL de-ionized water to form even solution A. 0.559 g aniline was dissolved in 55 mL of 1M hydrochloric acid to form even solution B. Then, both of solution A and B were added into 40 mL CHCl\(_3\) with 12.09 g Fe(NO\(_3\))\(_3\) and 5.7 g (NH\(_4\))\(_2\)S\(_2\)O\(_4\) at a rate of 5 mL/min at room temperature via two dropping funnels under vigorous stirring. After addition, the mixture was allowed to react for 3 days at room temperature with a continuous stirring. As described in the manuscript, two reactions occurred simultaneously in the system: (1) the heterogeneous S nucleation reaction of \( \text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \rightarrow \text{S}_↓ + \text{H}_2\text{O} + 2\text{NaCl} + \text{SO}_2↑ \), and (2) the polymerization of monomer aniline initiated by Fe(NO\(_3\))\(_3\) and (NH\(_4\))\(_2\)S\(_2\)O\(_4\). The sulfur/polyaniline (S/PANI) composite was filtered and washed with ethanol and de-ionized water for three times to remove the survival reactants. Finally, the product was dried in vacuum at 60 °C for 24 hours to get 0.639 g the light green urchin-like S/PANI nano-composite.

**Characterization of Product:** X-ray diffraction patterns of the samples were recorded using Cu Ka (\( \lambda = 1.5406\text{Å} \)) radiation at 40 kV and 40 mA with D8 Advance X-ray Reflector. Scanning electron microscope morphologies of the samples were carried out on FEI KL30 ESEM field emission scanning electron microscope with operating voltage of 20 kV. Fourier transform infrared spectra were recorded on a Bruker TENSOR-27 spectrophotometer at a resolution of 4 cm\(^{-1}\). X-ray photoelectron spectroscopy measurements were recorded on a VG Scientific ES-CALAB 250 spectrometer with Al Ka X-ray source (1486.5 eV) using a pass energy of 20 eV at takeoff angles of 90°. The Brunauer-Emmett-Teller (BET) surface area was measured on a fully automated ASAP 2020 accelerated surface area and porosimetry analyzer (Micromeritics Co., Norcross, GA). All the electrochemical tests were recorded on Solartron SI 1287 electrochemical interface. The current densities at different charge-discharge rates are: 1.69 mA/cm\(^2\) (1C), 0.84 mA/cm\(^2\) (0.5C), 0.34 mA/cm\(^2\) (0.2C) and 0.17 mA/cm\(^2\) (0.1C).

**Preparation of Electrode and Battery:** The electrodes for electrochemical tests or assembly as the cathode of the lithium-sulfur (Li-S) batteries were prepared by mixing 180 mg urchin-like S/PANI composite, 20 mg cation aqueous polyurethane resin adhesion agent and 2 g deionized water together to make a relatively homogeneous mixture at room temperature. Next, this mixture
was coated and pressed on a $15 \times 20$ cm aluminum foil by the MTI AFA-III automatic coater and then dried at $60^\circ C$ for 36 hours in vacuum oven. Then, this aluminum foil was cut into the discs with diameter of 1.6 cm, and the average mass loading of cathode material on each disc was approximate $2 \text{ mg/cm}^2$.

The 2032-type coin cell was used for the electrochemical testing with an excess lithium film as the anode. The solution of 1.435 g lithium bis(trifluoromethanesulfonyl) imide and 0.276 g LiNO$_3$ dissolved in 2.5 mL 1,2-dimethoxyethane and 2.5 mL 1,3-dioxolane was chosen as the electrolyte. The Whatman GF/D glass microfiber filter paper was used as the separator, its high intensity could avoid the battery short circuit caused by the forming of lithium dendrite. All assemble process of the Li-S battery was operated in an inert atmosphere.

b. The preparation of deposition S

1.422 g Na$_2$S$_2$O$_3$ was dissolved in 45 mL de-ionized water to form an even solution, then, 55 mL of 1M hydrochloric acid was added into it. After stirring for 30 minutes, the deposition S was filtered and washed with de-ionized water for three times to remove the survival reactants. Finally, the product was freeze-dried to get 0.279 g the light yellow S powder.

c. The preparation of PANI nano-rods

0.559 g aniline was dissolved in 55 mL of 1M hydrochloric acid to form even solution, then, it was added into 40 mL CHCl$_3$ with 16.22 g FeCl$_3$ at a rate of 1 mL/min at room temperature via a dropping funnel under vigorous stirring. After addition, the mixture was allowed to react for 1 day at room temperature with a continuous stirring. The PANI was filtered and washed with amount of ethanol and de-ionized water for three times to remove the survival reactants. Finally, the product was dried in vacuum at $60^\circ C$ for 24 hours to get 0.518 g the light green PANI nano-rod powder.
2. The BET data of PANI nano-rods and S/PANI nano-composite

Figure S1. The BET surface area data of the PANI nano-rods (a) and the urchin-like S/PANI nano-composite (b).