

Supporting Information

Yolk-Shell Structure of Polyaniline Coated Sulfur for Lithium-Sulfur Batteries

Weidong Zhou,^{*,†} Yingchao Yu,[†] Hao Chen,[†] Francis J. DiSalvo[†] & Héctor D. Abruña^{†,*}

[†] Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

* Corresponding author: weidong.zhou@cornell.edu, hda1@cornell.edu

Methods

Materials Synthesis. Na₂S₂O₃ (2.37 g) in 50 ml water was slowly added into a dilute sulfuric acid solution (500ml, 3mM) containing 1% (weight ratio) of polyvinylpyrrolidone (PVP, Mw~40,000). After stirring for 2 hours at room temperature, the sulfur particles were collected by centrifugation and re-dispersed into 300ml aqueous solution of PVP (1%). 200mg aniline and 10ml sulfuric acid (1M) were added into the above emulsion. 0.5g ammonium persulphate in 30ml water was then added dropwise under a nitrogen flow at 0⁰C. After stirring at 0⁰C for 24hours, the polyaniline coated sulfur particles were collected by centrifugation and dried under vacuum overnight. To prepare the sulfur-polyaniline yolk-shell structures, the powder of the core-shell particles was sealed into a glass tube filled with argon and heated to 180⁰C for 12hours.

Electrochemical Measurements. To prepare the cathodes, sulfur based materials were first mixed with carbon black and water soluble binder sodium alginate (80:15:5 by weight) through ground in a mortar. The mixture was then spread evenly on the aluminum foil and roll-pressed to produce electrode films with an average sulfur loading of 2mg cm⁻², which were heated at 50⁰C

for 12 hours under vacuum before using to fabricate the coin cells. 2032 type coin cells were fabricated in an argon filled glove box using lithium foil as the anode and TFSI (1M in DOL/DME) containing LiNO_3 (1 wt%) as the electrolyte. The sulfur contents of S-Pani core-shell and yolk-shell in the cathode films were calculated to be 65.6% and 46.4%, respectively.

Material Characterization. Electron microscopy imaging was carried out using a Schottky-field-emission-gun Tecnai F20 scanning transmission electron microscope (STEM) operated at 200 keV. The energy dispersive x-ray (EDX) analysis was performed in the F20 using an Oxford detector, at a beam current of about 1 nA. An EDX resolution of 1-5 nm is routinely achieved on this setup. Sulfur was not found to sublime into vacuum within the electron microscope under the testing conditions, likely due to the core-shell or yolk-shell structure, which protects sulfur against sublimation.

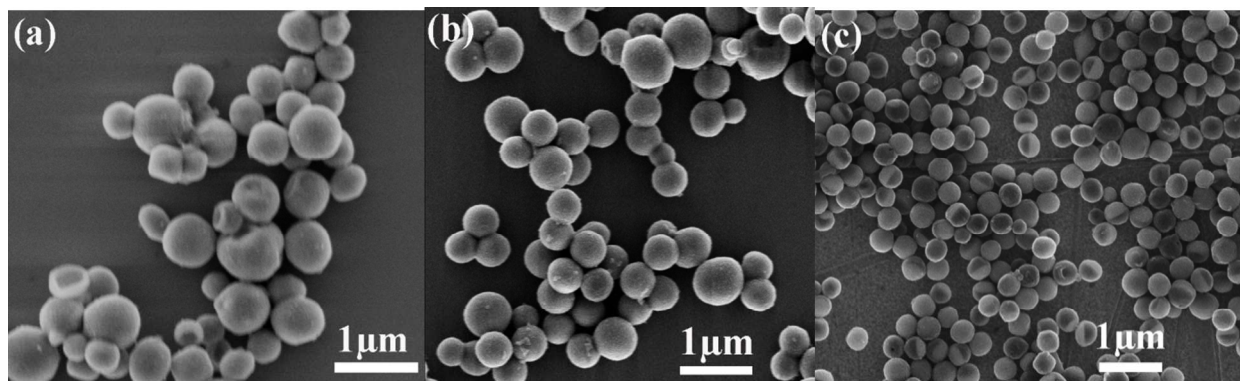


Figure S1. SEM images of S-Polyaniline core-shell structures prepared using HCl(a), HCOOH(b) and H_2SO_4 (c) as the acid sources.

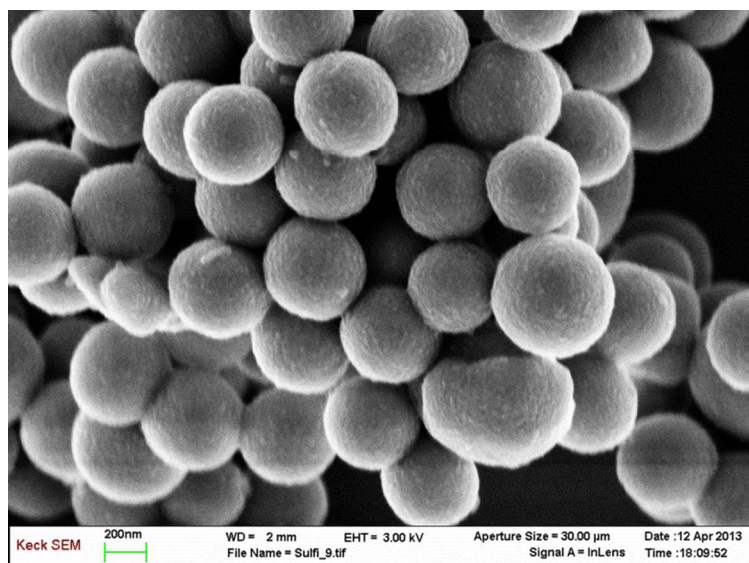


Figure S2 The magnified SEM image of the S-Pani core-shell structure.

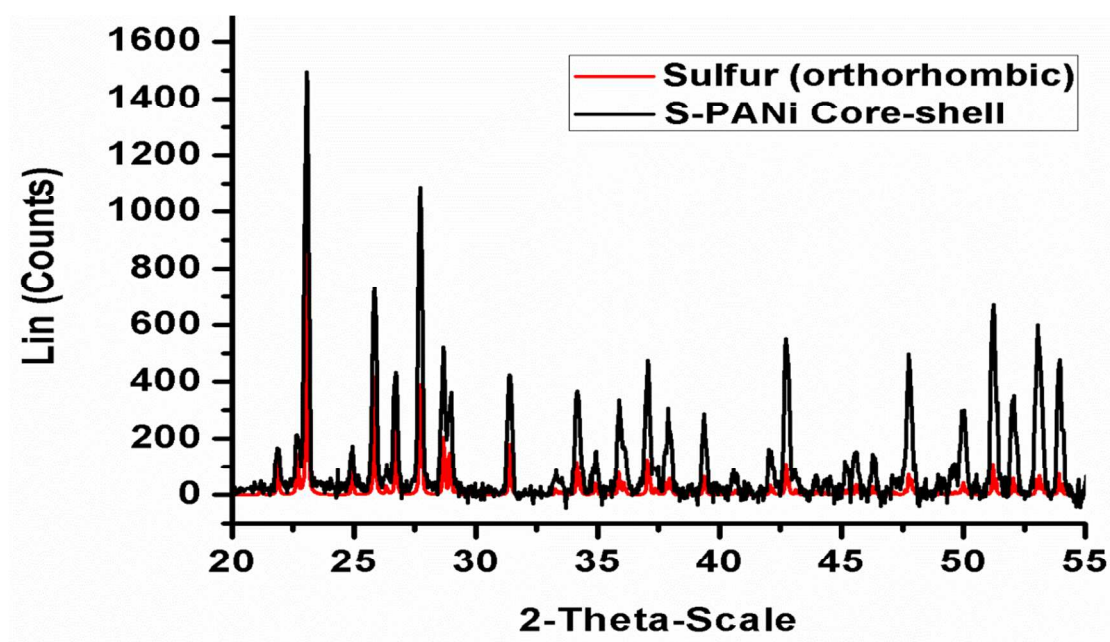


Figure S3 X-ray diffraction (XRD) of S-Pani composite shows it matches PDF card of pure sulfur(orthorhombic) since polyaniline (PAN) is amorphous. X-Ray Diffraction (XRD) data were collected using the D8-Advance DaVinci system with the Bragg-Brentano geometry and Cu K α radiation (40kV and 40mA). The samples were prepared conservatively on quartz discs. Scans range from 10°-90° with fixed sample illumination and a 0.04°/s step size and 1s/step rate with variable rotation at 15rpm.

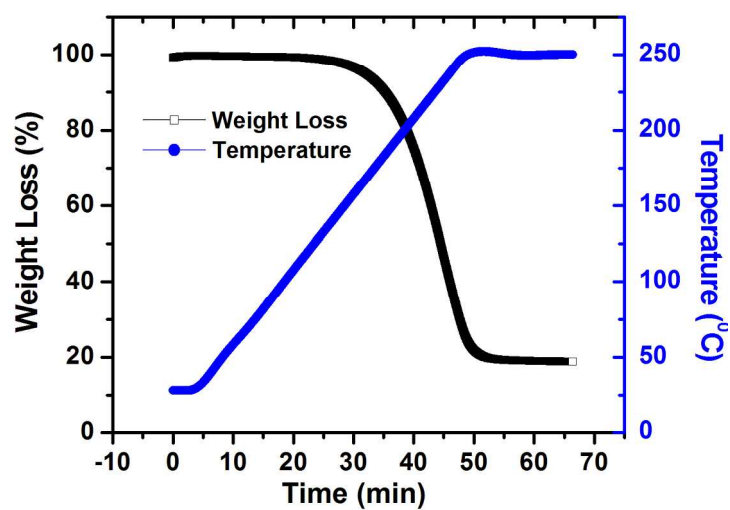


Figure S4 The thermal gravimetric analysis (TGA) of the S-Pani core-shell composite in argon flow.



Figure S5 The image of S-Pani core-shell(left) and heat treated yolk-shell(right) composite.

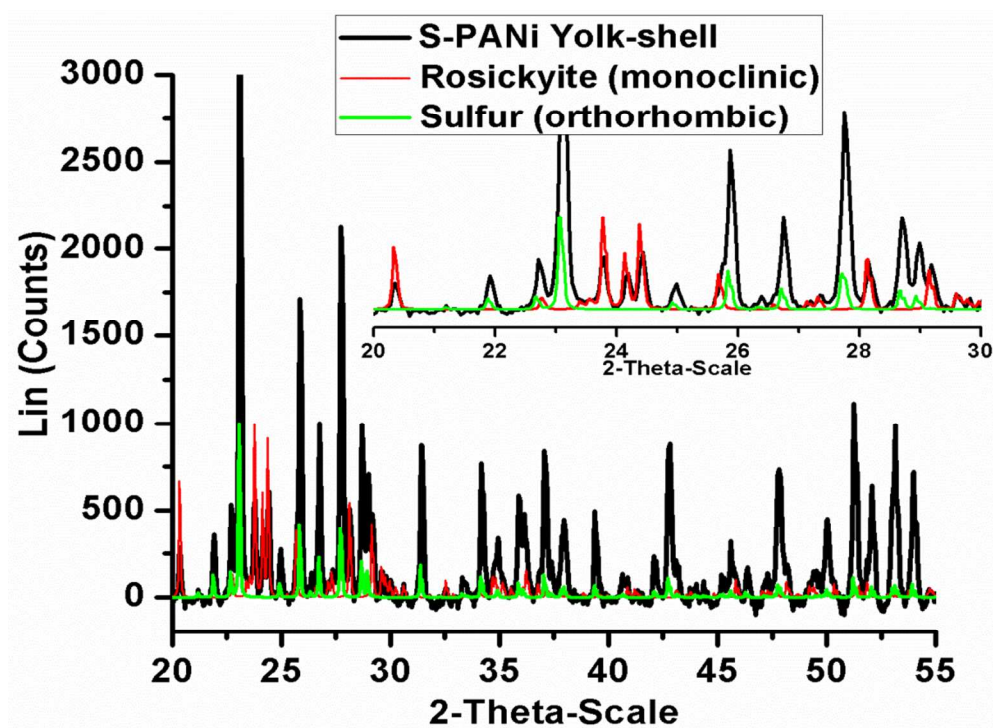


Figure S6 XRD of S-Pani yolk-shell composite shows it matches the combine of the pure sulfur(orthorhombic) with PDF card of 04-012-7311 and Rosickyite(monoclinic) with PDF card of 04-007-2069. Compared with the XRD spectra of S-Pani core-shell composite, the S-Pani yolk-shell composite gave obvious peaks at 20.36, 23.78, 24.13, 24.37, 28.13, 29.11, which are typical signals from Rosickyite(monoclinic).

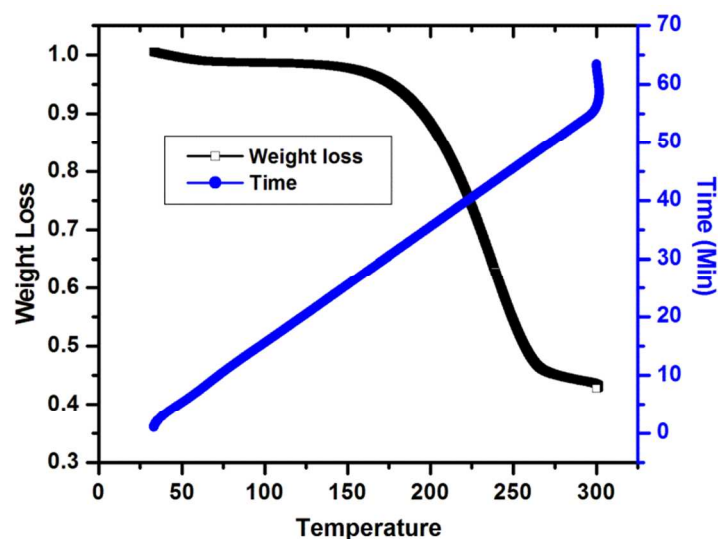


Figure S7 The thermal gravimetric analysis (TGA) of the S-Pani yolk-shell composite in argon flow.