Electronic Supplementary Information for

An Organometallic Approach for Ultrathin $SnO_xFe_yS_z$ Plates and their Graphene Composites as Stable Anode Materials for High Performance Lithium Ion Batteries

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Experimental General

Transmission electron microscopy (TEM), high resolution TEM and energy dispersive X-ray spectroscopy (EDS) were taken using a JEOL 2100F unit operated at 200kV. Samples for TEM were prepared on copper grid by drop-casting methylene chloride solution of the nanomaterials. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku MAX-2200 and filtered Cu-K α radiation. Elementary analysis was performed on a CE EA1110 elementary analysis instrument. X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo VG and Monochromatic Al- $K\alpha$ radiation.

Preparation of organometallic precursor

Bis(ferrocene-1,1'-dithiolato)tin (FT)

The used organometallic precursor, bis(ferrocene-1,1'-dithiolato)tin (FT) was prepared by a slightly modified method of literature.(ref. 9 in text) First, for preparation of 1,2,3-trithia-[3]-ferrocenophane, in a flame-dried 100 mL Schlenk flask, 2.0 g (11 mmol) ferrocene and 1.6 mL (11 mmol) tetramethylethylenediamine (TMEDA) were added to freshly-distilled ether (30 mL) under argon. To the mixture, 16 mL of 1.2 M n-BuLi (26 mmol) was added dropwise at 0 °C. The reaction mixture was stirred overnight at room temperature. Then, 1.3 g sulfur (41 mmol) was added and the reaction mixture was stirred overnight. The product was extracted using ether and 15% aqueous NaOH solution. After evaporating the solvent in organic layer, the 1,2,3-trithia-[3]-ferrocenophane was purified by column chromatography using hexane as the eluent. Single-crystalline 1,2,3-trithia-[3]ferrocenophane was obtained by recrystallization from hexane in the refrigerator. Second, for preparation of ferrocene-1,1'-dithiol, 1,2,3-trithia-[3]-ferrocenophane (3.6 g, 0.13 mol) was treated with LiAlH₄ (1.2 g, 0.031 mole) in freshly distilled diethyl ether (200 ml) at room temperature. LiAlH₄ should be added very slowly. The reaction mixture was refluxed at 50 °C for 2 hours and then, poured into 300 ml water with ice bath. The degassed water with nitrogen bubbling should be used to improve the isolated yield. The addition of potassium hydroxide (5.0 g) resulted in water soluble potassium salts. The aqueous was extracted with diethyl ether four times to remove the ether-soluble impurities. Then, gradual acidification with concentrated HCl resulted in ether-soluble ferrocene-1,1'-dithiol. The evaporation of solvent gave bright yellow solid. Because the ferrocene1,1'-dithiol is relatively unstable under air, the prepared compound should be used as soon as possible. Third, for preparation of **FT**, 1.9 g (7.5 mmol) of ferrocene-1,1'-dithiol was reacted with 1.7 g (7.5 mmol) $SnCl_2 \cdot 2H_2O$ in anhydrous ethanol (130 mL) in 100 mL Schlenk flask. This solution was heated at 50 °C for 30 min. After evaporating the solvent, the remaining yellow solid was extracted with hot benzene. Then, the volume of solution was reduced to 20 ml by evaporating. Finally, the single crystalline red crystals of the organometallic precursor, **FT** were obtained by cooling the solution to room temperature. The elemental analysis for the obtained **FT** ($C_{20}H_{16}S_4SnFe_2$) showed 39.06 w% C, 2.80 w% H and 21.1 w% S with theoretical values of 39.09 w% C, 2.62 w% H and 20.9 w% S respectively.

Preparation of SOFS plates: The organometallic precursor (**FT**, 50 mg, 0.081 mmol) was dissolved in well-dried oleylamine (3 mL) under argon in flame-dried 10 mL vial. Trioctylphosphine (2 mL) was added to precursor solution. The resultant orange-colored solution was hot-injected into oleylamine (4 mL) at 240 °C under argon. After injection, the color of solution turned to black. After aging at this temperature for additional 1 hour, the reaction mixture was cooled into room temperature. The addition of excess methanol resulted in the formation of precipitates which were retrieved by centrifugation. After being washed with methanol two times, the precipitates were dried under vacuum.

Preparation of graphene-SOFS composites: The **SOFS** plates (20 mg) and graphene oxide flakes (20 mg) prepared from graphite by the Hummers method¹⁰ were well-dispersed in 5 mL of THF/H₂O (1:1) mixture respectively. Then, two solutions were combined and hydrazine monohydrate (0.40 mL) was added. The black precipitates were gradually formed and retrieved by centrifugation, washed with water and acetone and dried under vacuum.

Fabrication of coin cells: For electrochemical studies, The **SOFS**-graphene composites (80 mg), Super P carbon black (10 mg) and polyvinylidene fluoride binder (10 mg) were mixed in N-methylpyrrolidone (NMP). After coating the copper foil with this mixture, the electrode was dried under vacuum at 120 °C overnight and heat-treated at 300 °C for 5 hours under argon. The diameter of copper electrode was 14 mm. The average loading amount of electrode materials was 1.0 mg/cm². Cell tests were conducted using coin-type half cells (CR2016 type) with Li metal as the counter electrode and 1M LiPF₆ in ethylene carbonate/diethyl carbonate (1:1 v/v) as the electrolyte. The discharge/charge cycle tests were performed using WBCS3000 automatic battery cycler system.

Figure S1. Additional TEM images of the of SOFS plates.

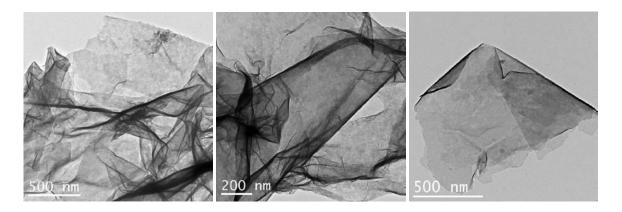


Figure S2. TEM images of the materials prepared at various reaction temperatures.

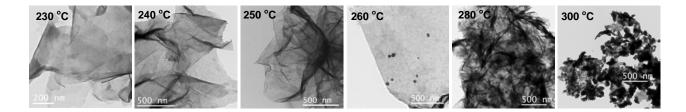


Figure S3. PXRD patterns of materials prepared at various reaction temperatures.

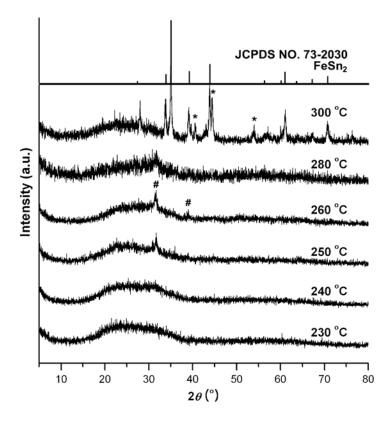


Figure S4. HR-TEM images of the SOFS plates.

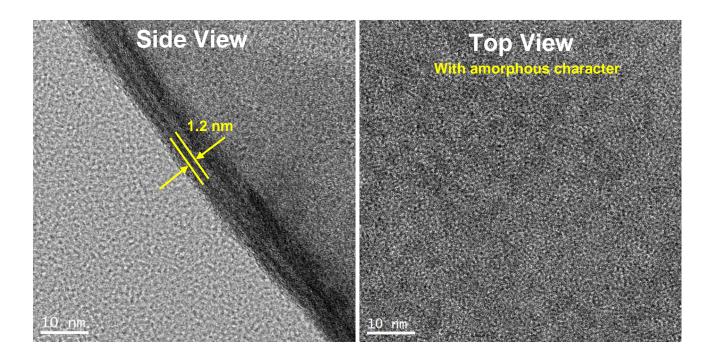


Figure S5. XPS spectra of the SOFS plates.

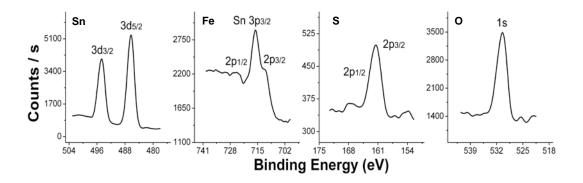


Figure S6. The PXRD pattern of the **SOFS** plates heated a 500 °C for 3 hours under argon.

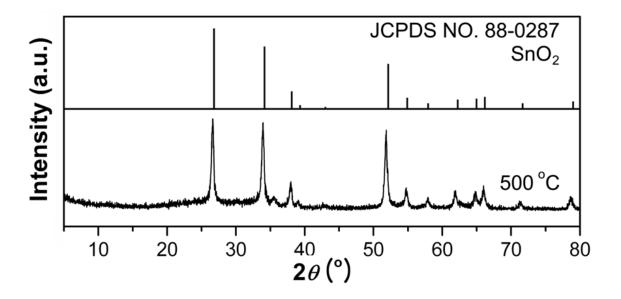


Figure S7. The comparison of EDS spectra of plates after exposure to air for 1h (a) and 1day (b).

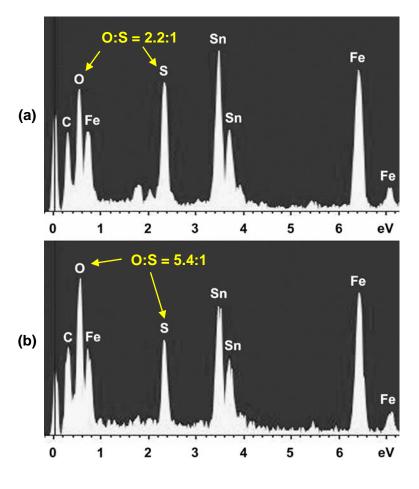
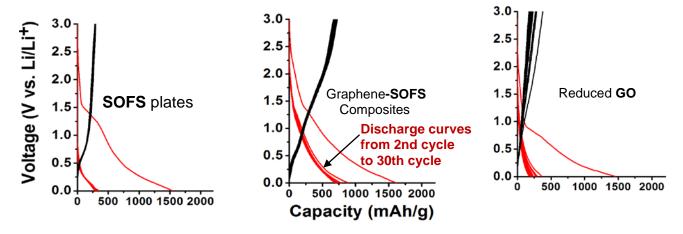
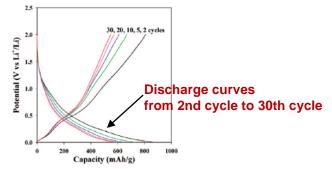


Figure S8. Charge (black)-discharge (red) curves of the **SOFS** plates, the graphene-**SOFS** composites and reduced **GO**.

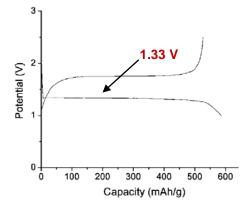


$$SnO_2 + 4 Li^+ + 4e^- \rightarrow Sn + 2Li_2O$$
 irreversible $Sn + 4.4Li^+ + 4.4e^- \leftrightarrow Li_{4.4}Sn$ reversible



Cf. Charge/discharge curves of SnO₂-graphene composites in ref. 11a in text (*Nano Lett.* 2009, **9**, 72)

$$FeS + 2Li^+ + 2e^- \leftrightarrow Fe + Li_2S$$
 reversible



Cf. Charge/discharge curves of FeS materials in ref. 12b in text (*J. Phys. Chem.* 2008, **112**, 15060)

Figure S9. Comparison of columbic efficiencies of the graphene-**SOFS** composites, **SOFS** plates and graphene without use of **SOFS** materials.

