Supporting Information

Three-dimensional nanostructured composite lithium soap fibers for constructing high-performance lithium metal anode interfacial layers

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EXPERIMENTAL SECTION

Preparation of Composite Lithium Soap Fibers

Lithium hydroxide hydrate (Lithium hydroxide hydrate, AR, Energy Chemical) was dissolved in deionized water and heated to 80°C to ensure complete dissolution. 1,2-Hydroxystearic acid (12-Hydroxyoctadecanoic acid, $C_{18}H_{36}O_3$, Energy Chemical) was also heated to dissolve in deionized water. Three organic acids were used as chelating agents: Azelaic acid (AA, $C_9H_{16}O_4$, 99%, MACKLIN), Sebacic acid (SA, $C_{10}H_{18}O_4$, 99%, MACKLIN), and Dodecanedioic acid (DA, $C_{12}H_{22}O_4$, 99%, MACKLIN). These chelating agents were dispersed in a mixed solvent of ethanol and deionized water. Both solutions were heated to 100°C and then mixed uniformly. The mixed solution was further heated to 120°C, and lithium hydroxide hydrate dissolved in warm water at 80°C was slowly added at a rate of 30 drops per minute while continuously stirring. After complete addition, the solution was kept at temperature with continuous stirring for 2 hours and then cooled slowly. In this experiment, the molar ratio of 1,2-hydroxystearic acid, chelating agent, and lithium hydroxide hydrate was maintained at 1:1:3. After the reaction mixture was completely cooled, it was transferred to a forced-air oven and dried at 60°C for 12 hours, followed by drying in a vacuum oven at 60°C for 6 hours. The three types of synthesized lithium composite soap fibers were named AA, SA, and DA, respectively, based on the different chelating agents used.

Preparation of Li@DA

The preparation of Li@DA was carried out in a glove box ($H_2O<0.01$ ppm, $O_2<0.01$ ppm) and a temperature of 25 ℃. The three types of synthesized lithium composite soap fibers were dissolved in mineral oil (Mo, Aladdin) and stirred at room temperature for 24 hours to achieve maximum solubility. The supernatant was taken, and the mineral oil containing lithium composite soap fibers was coated onto a rolling mill. Through mechanical physicochemical rolling, the initial lithium foil (150 μm, 99.9%, China Energy Lithium Co., Ltd, Tianjin) was continuously rolled down to a thickness of 100 μm, resulting in the composite lithium anode material.

Preparation of Cathode

Using N-methyl-2-pyrrolidone（NMP, Aladdin）as the solvent, $LiFePO_4$ (LFP) powder, carbon black, and polyvinylidene fluoride (PVDF) were mixed uniformly in a mass ratio of 8:1:1 and coated onto C@Al foil to fabricate the LFP cathode. After drying in a forced-air oven at 80°C for 10 hours, the coated foil was transferred to a vacuum drying chamber and dried further at 110°C for 8 hours. The $LiFePO_4$ cathode had an active material loading of 12.0 mg/cm^2 (single side).

Material Characterization

The surface chemical composition of the Li foil were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha$^+$), which equipped with a vacuum transfer accessory were conducted at KW-ST Lab. Surface functional group information of bare lithium and Li@DA was obtained using Fourier-transform infrared spectroscopy (FTIR, Nicolet IS50, Thermo Fisher Scientific). The morphology and elemental distribution of the samples (initial lithium foil and lithium foil after certain cycles) were characterized by scanning electron microscopy (SEM, JEOL JSM-7610FPlus equipped with Oxford ULTIM MAX 40 energy-dispersive spectrometer). The contact angle of liquid electrolyte (~10 μL droplet) on the surfaces of bare lithium and Li@DA was measured at room temperature (25°C) using the contact angle system OCA 20 (Dataphysics, Germany) in a dry chamber. Using a self-made in-situ optical microscope (DMM 900 c, Caikon), the deposition process of bare Li and Li@DA at a current density of 2 mA/cm^2 was characterized in-situ. The electrolyte used was LS009. The nitrogen adsorption-desorption test was conducted on Composite Lithium Soap Fibers at 77.3 K to analyze their pore size distribution and other structural information (BET, Micromeritics, ASAP 2460 3.01) .

Electrochemical Measurements

The discharge/charge testing were conducted on a Neware Battery system. All coin cells were assembled in a glovebox filled with Ar (H_2O < 0.01 ppm, O_2 < 0.01 ppm), using Celgard®2400 as the separator. The electrolyte for symmetric cells was 1.0 M LiTFSI in DME:DOL = 1:1 vol% with 2.0% $LiNO_3$ (LS009). The electrolyte for $LiFePO_4$ full cells was 1.0 M $LiPF_6$ in EC:EMC:FEC = 3:7:1 vol% (LB515). To ensure standardized testing, 75 μL of electrolyte was used in each coin cell. The LFP full cells were initially activated for two cycles at 0.1C and then tested for charge/discharge between 2.5 and 4.2 V at 2C (1C = 170 mA/g). Tafel curves and EIS spectra (10^{-1} to 10^{5} Hz) were obtained using an electrochemical workstation (Ivium, Netherlands).

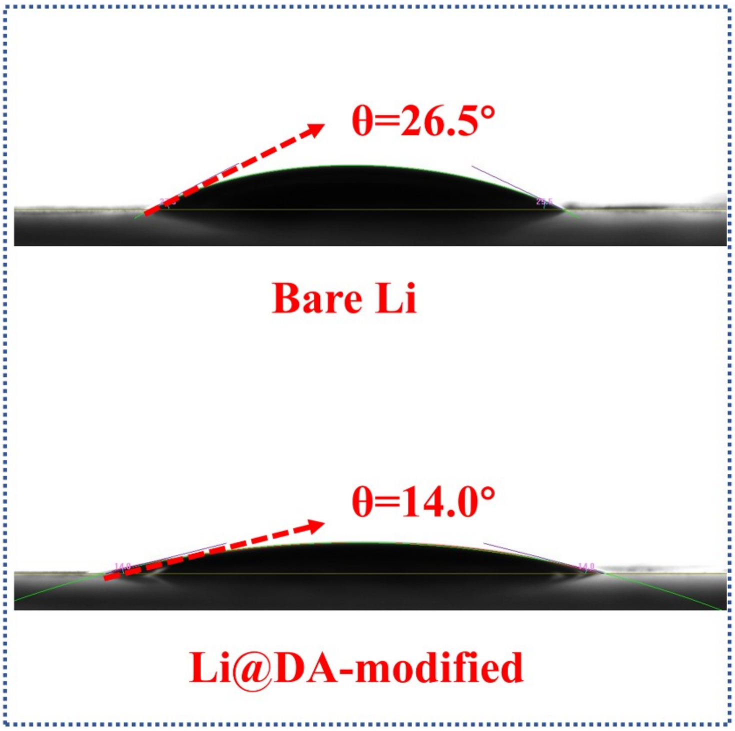

Figure S1. Contact angle tests of LS009 electrolyte drop with bare Li and Li@DA.

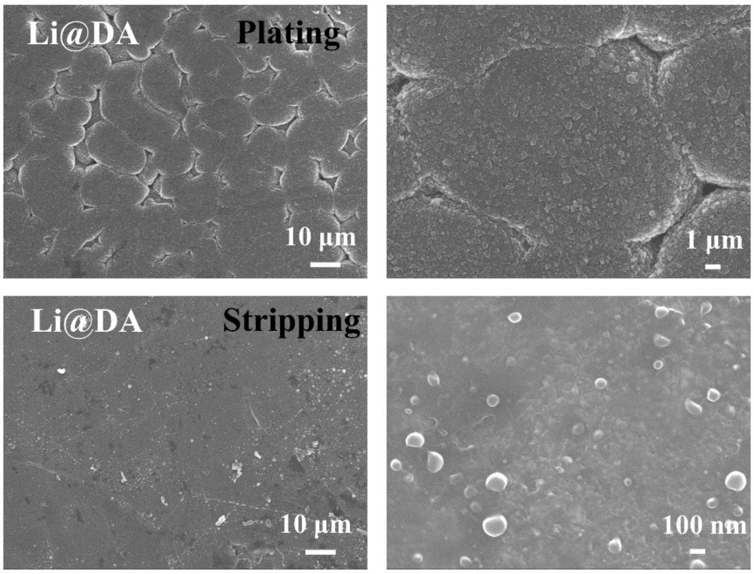

Figure S2. SEM images of the plating and stripping of the Li@DA symmetric cells after delithiation for 6 hours and subsequent relithiation for 6 hours at 0.25 mA/cm^2.

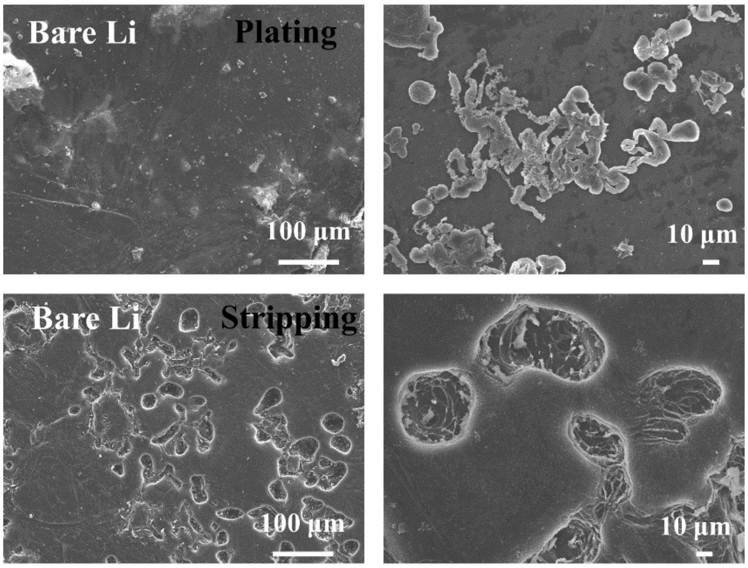

Figure S3. SEM images of the plating and stripping of the bare Li symmetric cells after delithiation for 6 hours and subsequent relithiation for 6 hours at 0.25 mA/cm².

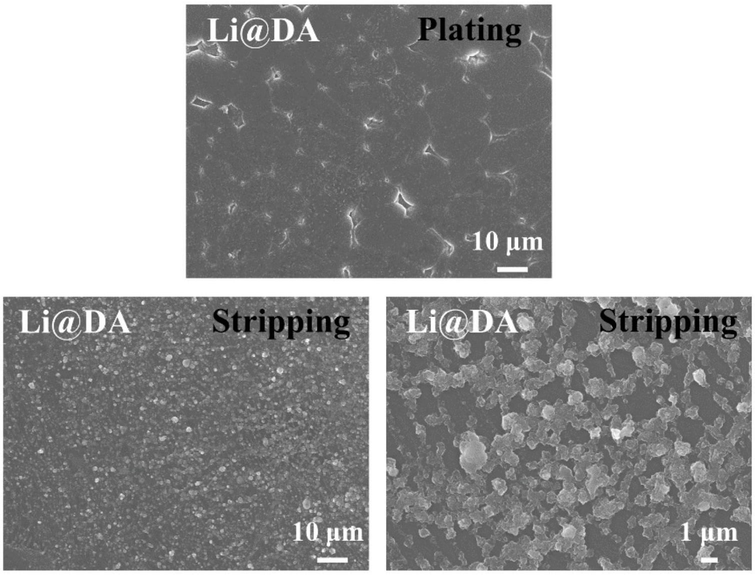

Figure S4. SEM images of the plating and stripping of the Li@DA symmetric cells after delithiation for 6 hours and subsequent relithiation for 10 hours at 0.25 mA/cm².

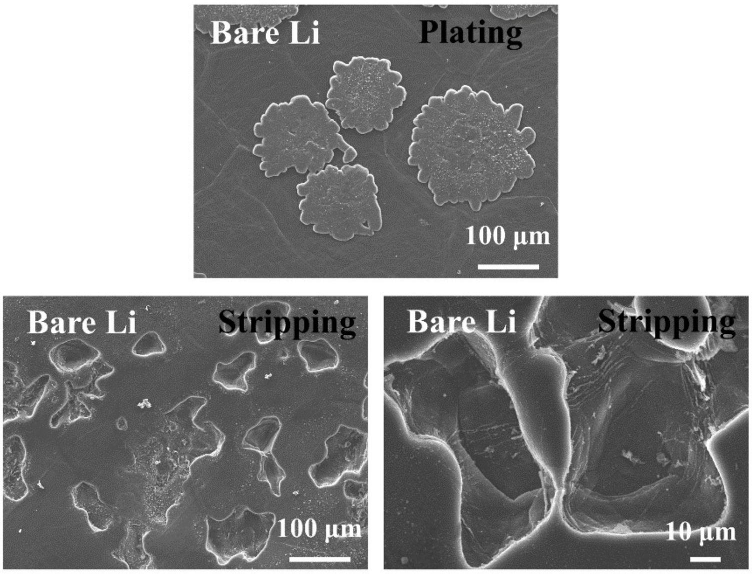

Figure S5. SEM images of the plating and stripping of the bare Li symmetric cells after delithiation for 6 hours and subsequent relithiation for 10 hours at 0.25 mA/cm².

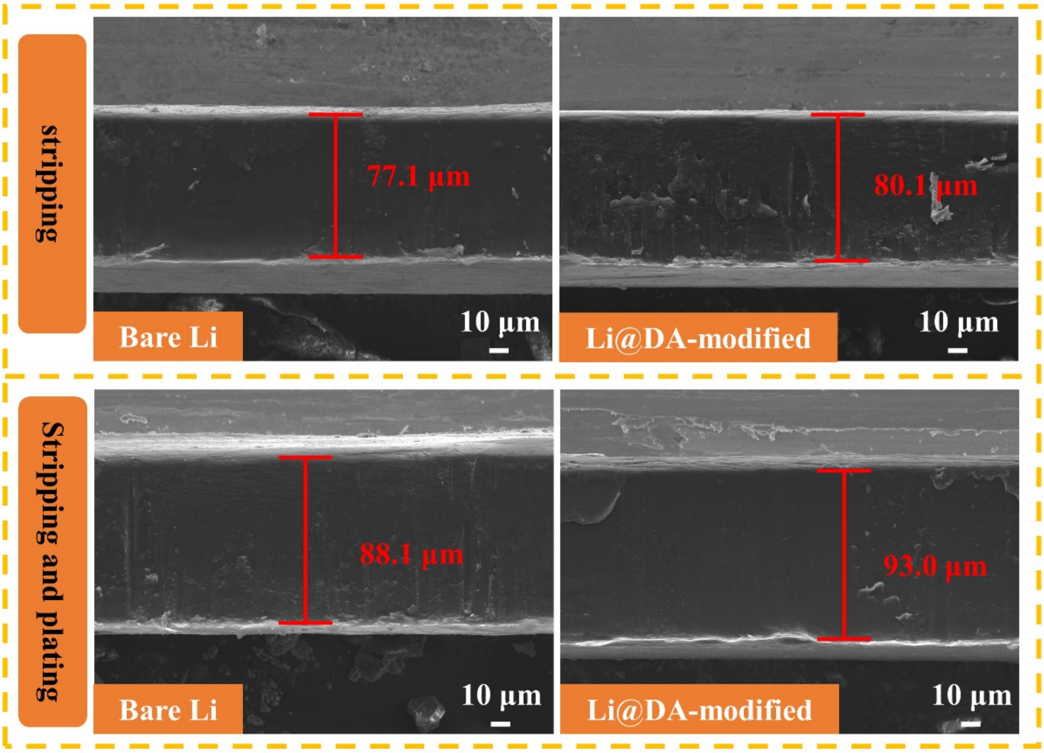

Figure S6. SEM images of the cross-sections of the anodes of the bare Li symmetric cells and Li@DA symmetric cells.

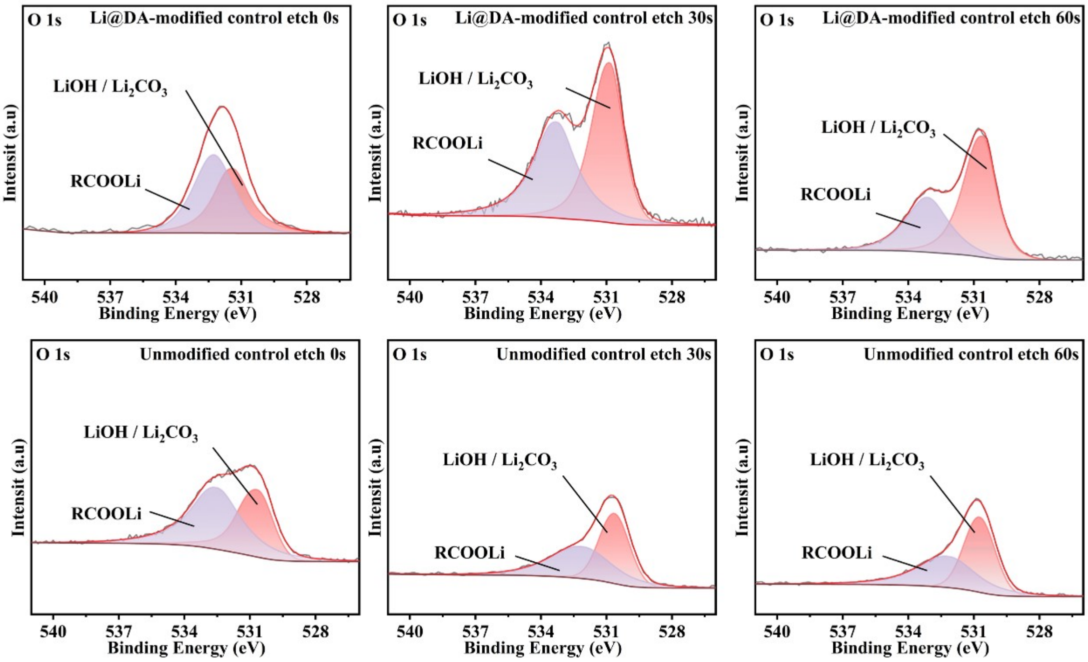

Figure S7. The O 1s X-ray photoelectron spectroscopy (XPS) spectra.

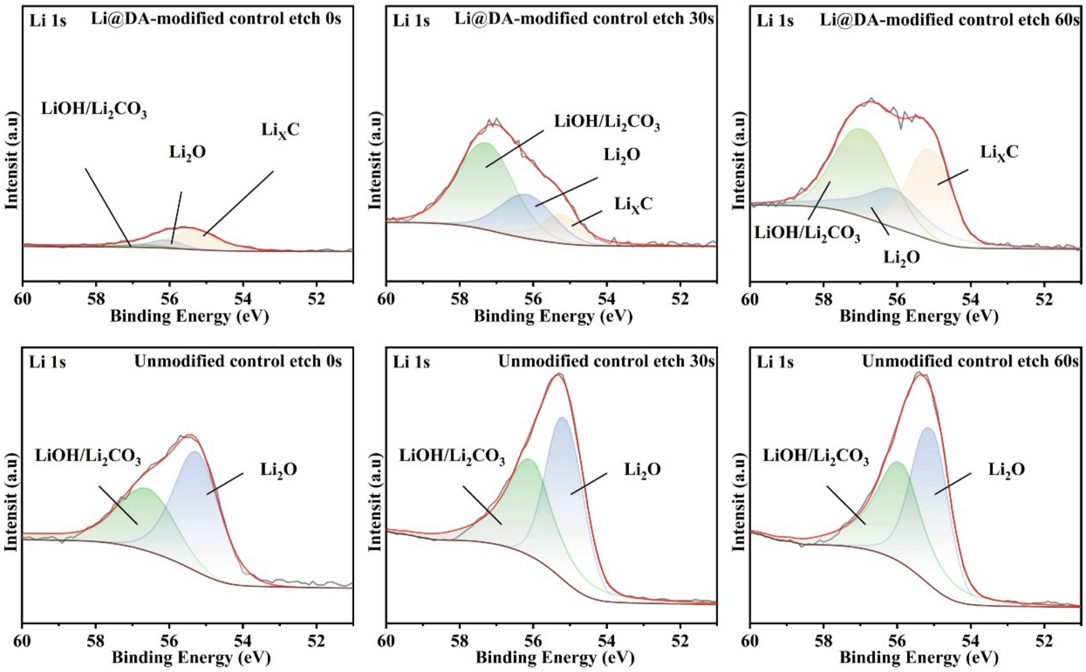

Figure S8. The Li 1s X-ray photoelectron spectroscopy (XPS) spectra.