

Electronic Supplementary Information

Synthesis of sulfur/activated carbon aerogels composite with a novel homogeneous precipitation method as cathode materials for lithium-sulfur batteries

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Experimental

1.1 Synthesis of sulfur/activated carbon aerogels composite

The carbon aerogels (TianJin, Deruifengkai, China), which were prepared by a sol–gel process, drying technique and carbonization^{1,2}, were etched by KOH at 800 °C for 120 min using 4:1 KOH:C ratio under argon atmosphere to obtain ACAs.

The synthesis process for the S-ACAs composite is illustrated in Fig. 1.

First, 0.4 g sublimate sulfur (AR, Aladdin, China) was completely dissolved in 10 g of 17% mass fraction of ammonium sulfide solution (AR, ShangHai Shiyi, China) by stirring. Then, 0.2 g of ACAs was suspended in the above solution by adding a small amount of TX-100 (Polyethylene Glycol Octylphenol Ether, (C₂H₄O)_nC₁₄H₂₂O, Fisher scientific) under ultrasonic vibrations. By heating to 95 °C, sulfur precipitated onto the surface and into the interspaces of the nano-sized ACAs. During the homogeneous precipitation processing, the sulfur particles grew to a thermodynamically favored size. Simultaneously, the carbon nanoparticles in the composite became interconnected with each other through self-assembling and finally wrapped the sulfur. After allowing the reaction mixture to stir for 2 h, the product was filtered and washed several times with deionized water, ethanol and acetone. The S-ACAs composite thus collected was dried in an air-oven at 50°C for 24 h. The sulfur content in the composite was determined by thermogravimetric analyzer (TGA, SDTQ600) at a heating rate of 5 °C /min from 20 to 500 °C with flowing air as showing in Fig. S1. The S-ACAs composites with 64.5 wt.% sulfur as confirmed by the TGA data were employed for further experiments.

1.2. Material characterization

Field emission scanning electron microscopy (FESEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, Tecnai G2 20ST) were applied to characterize the materials. X-ray diffraction (XRD, Rigaku3014) measurements were made with Cu K α radiation. Thermogravimetric analysis (TGA, SDTQ600) was conducted in determining the sulfur content in the composites. N₂ adsorption/ desorption measurements were performed by using Quantachrome instrument (Quabrorb SI-3MP) at 77 K.

1.3. Cell assembly

The composite cathode slurry was made by mixing 70 wt.% S-ACAs composite material, 20 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP) solvent. Then, the slurry was spread onto aluminum foil (20 μ m), and dried at 60 °C under vacuum overnight. The sulfur contents in the S-ACAs composite cathode were about 64.5 wt.%, so the composite cathode contained 45 wt.% active materials. The pristine sulfur cathode containing 45wt.% sublimate sulfur, 45 wt.% carbon black, and 10 wt.% PVDF binder was prepared in the same way for comparison. The pristine sulfur used for comparison is the purchased sublimate sulfur (AR, Aladdin, China) which was sieved between 1~10 μ m. Coin-type (CR2025) cells were assembled in an argon-filled glove box (Universal 2440/750) in which oxygen and water contents were less than 1 ppm. The electrolyte used was 1 M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI, Sigma Aldrich) in a solvent mixture of 1,3-dioxolane and 1,2-dimethoxyethane (1:1, v/v) (Acros Organics) including 0.1 M LiNO₃. Lithium metal was used as counter electrode and reference electrode and Celgard 2400 was used as separator.

1.4. Electrochemical characterizations

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted using PARSTAT 2273 electrochemical measurement system. CV tests were performed at a scan rate of 0.1 mV s⁻¹ in the voltage range of 1.5 to 3.0 V. EIS measurements were carried out at open-circuit potential in the frequency range between 100 kHz and 10 mHz with a perturbation amplitude of 5 mV. Galvanostatic charge/discharge tests were performed in the potential range of 1.5 to 3.0 V at 25 °C by using a LAND CT2001A battery-testing instrument.

[1] N P Liu, J Shen, D Liu, *Electrochimica Acta*, 2013,**97**,271-277.

[2] Z. Z Benabithe, F C Marin. Okushi, C M Castilla, *J. Power Sources*, 2012, **219**, 80-88.

Supporting figure

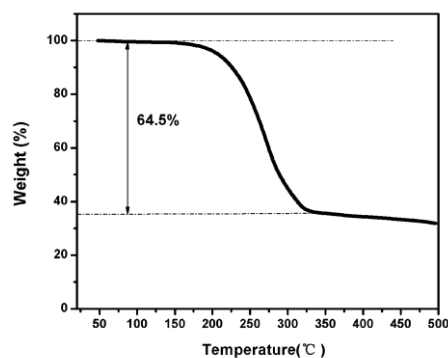


Fig. S1 TGA curve of S-ACAs composite recorded in air.

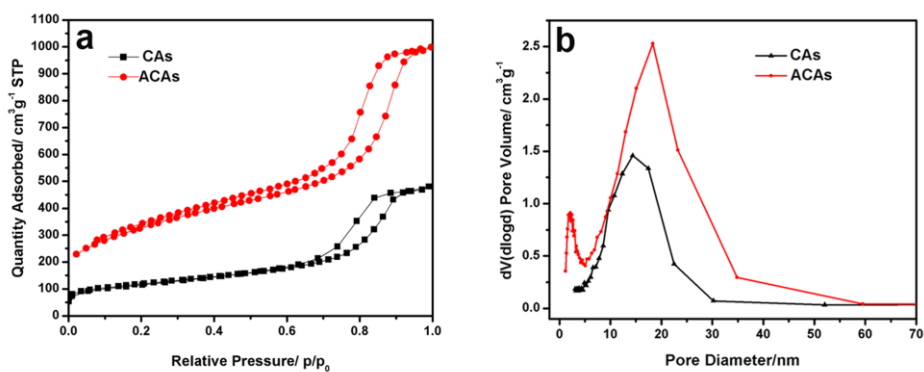


Fig. S2 N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of CAs and ACAs.

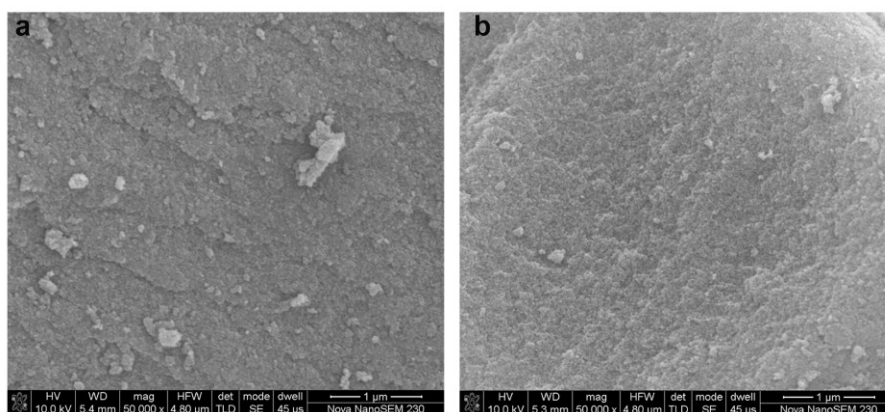


Figure. S3 High-magnification SEM images of the carbon aerogels (a) and activated carbon aerogels (b).

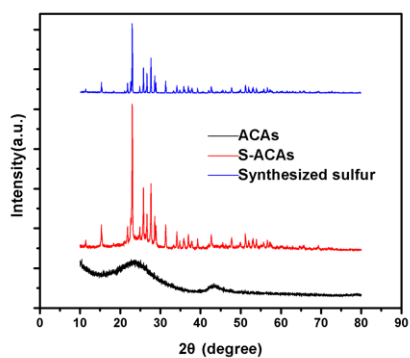


Fig. S4 XRD patterns of as-synthesized sulfur, ACAs and S-ACAs composites.

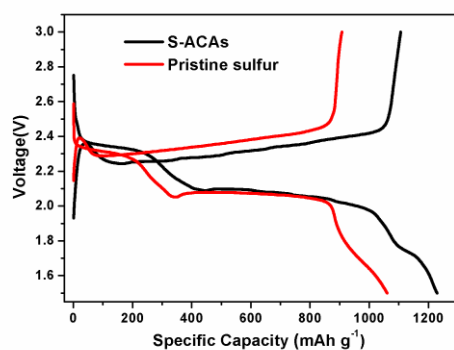


Fig. S5 The initial discharge/charge voltage profiles of Li/S cells with the pristine sulfur cathode, S-ACAs composite cathode at 335 mA g⁻¹.

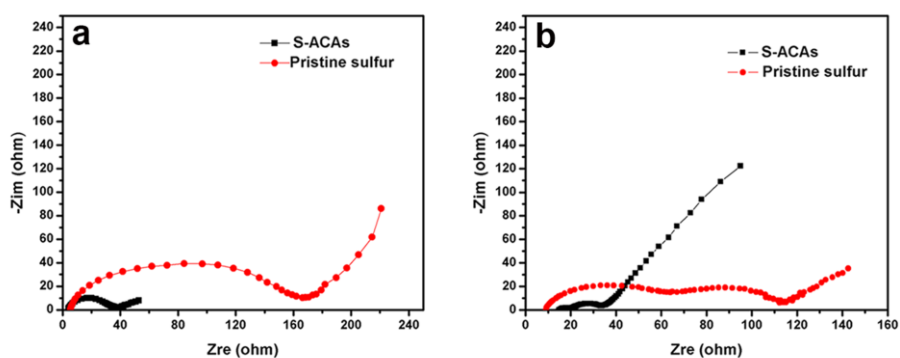


Fig. S6 EIS of S-ACAs cathode and the pristine sulfur cathode (a) before the first discharge and (b) after 100 cycles.

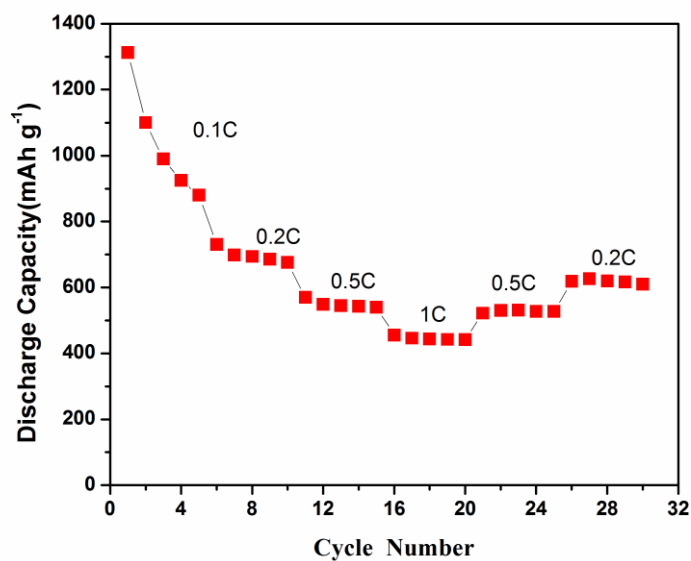


Fig. S7 The rate capability of the S/activated carbon aerogel composite as the current rate increased from
0.1C to 1 C