Supporting Information

Sulfur@Hollow Polypyrrole Spheres Nanocomposites for Rechargeable Li−S Batteries

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Experimental

Synthesis of SiO_2 microspheres. 125.6 mL ethanol, 50 mL DI water and 11mL ammonia (28%) were mixed to form a solution. Tetraethyl orthosilicate (TEOS) was dropped into the solution slowly and stirred for 24 h at room temperature. White precipitate was centrifuged and washed with DI water and SiO_2 microspheres with diameter of ~530 nm were received.

Synthesis of hollow polypyrrole (H-PPy). 0.4 g SiO_2 microspheres and 1 mL pyrrol were dispersed in 150 mL DI water in an ultrasonic bath to form a milky suspension. $FeCl_3$ was used as the oxidizing agent and the molar ratio of $FeCl_3$ and pyrrol is 1:1. $FeCl_3$ solution (0.15 M) was dropped into the to the suspension slowly and stirred for 24 h at room temperature. 10 wt % HF solution was used to remove the SiO_2 template.

Synthesis of sulfur−polypyrrole composites. Elemental sulfur and hollow polypyrrole with different weight ratio were mixed and ground, finally heated at 160 ^oC for 12 h to form homogeneous composites (S@H-PPy) with different mass percentage of sulfur.

Material characterization. Powder X-ray diffraction (XRD, Cu Kα radiation, Philips PW3040/60) was used to verify the component of the composite. The sulfur content in the S@H-PPy was ascertained by the thermogravimetric / differential thermal analysis (TG/DTA) measurement (Netzsch STA 449C thermal analyzer). The morphologies were examined by scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, JEM 2010F).

Electrochemical measurement. The electrodes were prepared by dispersing the

S@H-PPy (70 wt %), acetylene carbon black (20 wt %) and poly(vinylidene fluoride) binder (10 wt%) in N-methyl-2-pyrrolidone solvent to form a slurry. The slurry was pasted onto Al foil current collector and dried at 60 ^{o}C for 12 h in a vacuum oven. The electrochemical measurements were carried out by two-electrode coin cells with lithium foil as the counter electrode. The CR2025-type coin cells were assembled in an argon-filled glove box. The electrolyte solution was 1 M LiTFSI, 0.1 M $LiNO_3$ in a solvent of DOL : DME (1 : 1 in volume). Cyclic voltammetry (CV) was carried out on a CHI 660 C electrochemistry workstation from 1.5 to 3.0 V at a scan rate of 0.1 mV s^{-1}. The galvanostatic charge and discharge measurements were conducted on LAND battery test system at different current densities in the voltage range from 1.5 to 3.0 V.

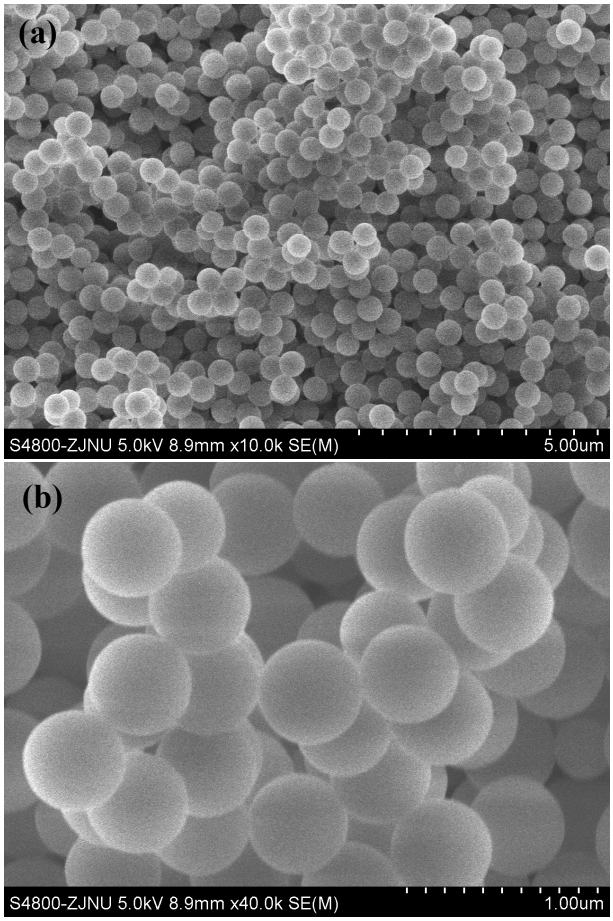

Figure S1. SEM images of SiO_2 spheres with an average diameter of 530 nm.

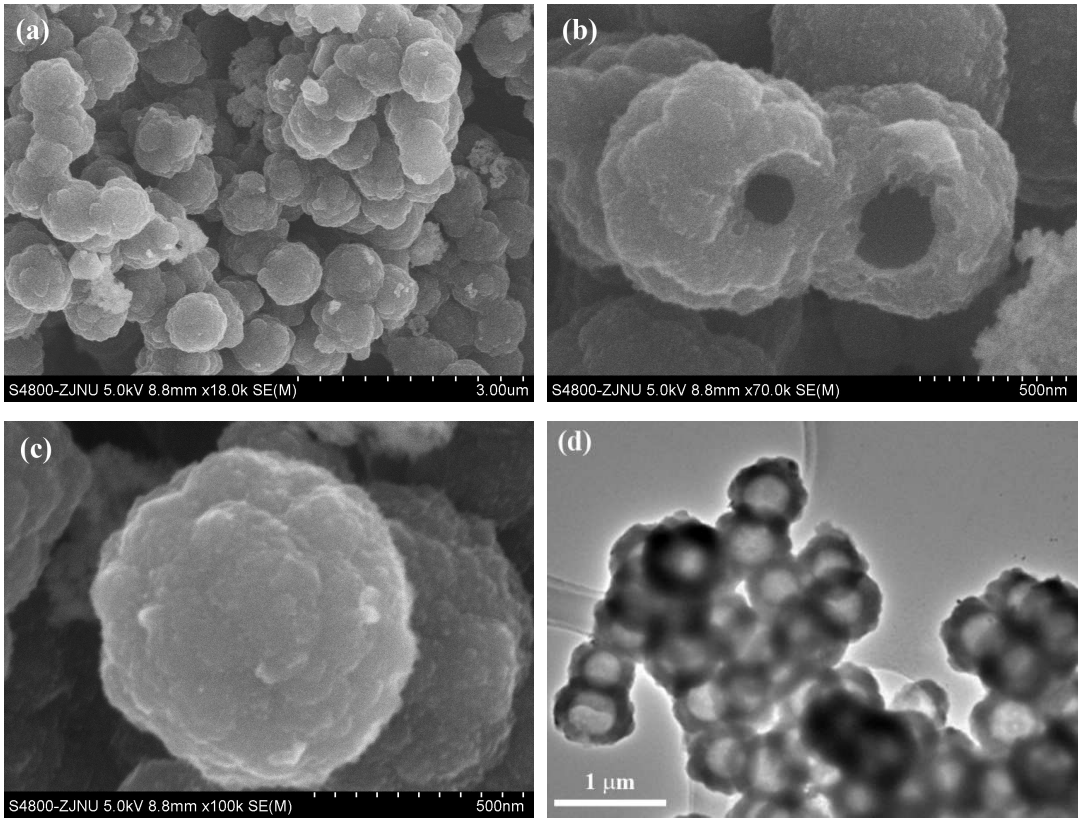

Figure S2. SEM images of H-PPy spheres.

TG curves of sulfur, H-PPy, and S@H-PPy with different pre-calculated sulfur percentage (1/2 and 3/4) are shown in Fig. 1b. Sulfur evaporates completely at ~350 ^{o}C, while PPy remains approximately unchanged. Comparing with the initial material ratio, it is found that a small amount of sulfur was lost in the mixing and heat treatment process. The sulfur content in the composites are 48% and 65%, respectively, which we denote as S@H-PPy-0.48 and S@H-PPy-0.65.

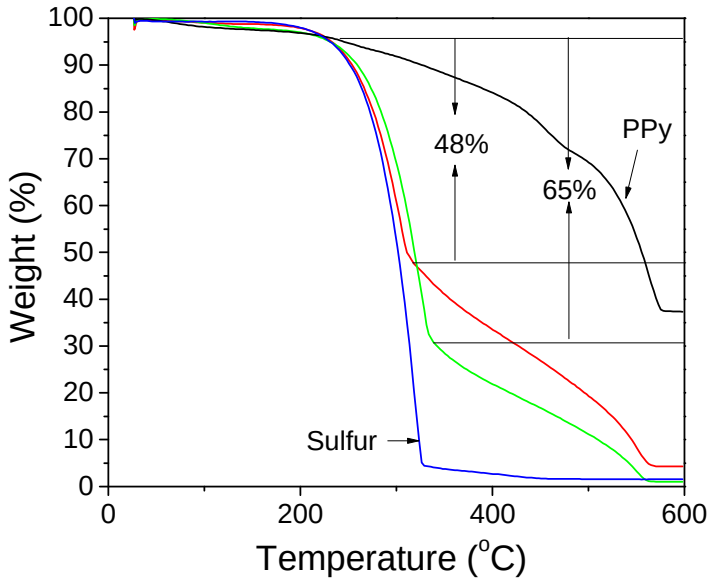

Figure S3. Thermogravimetric analysis of various materials.

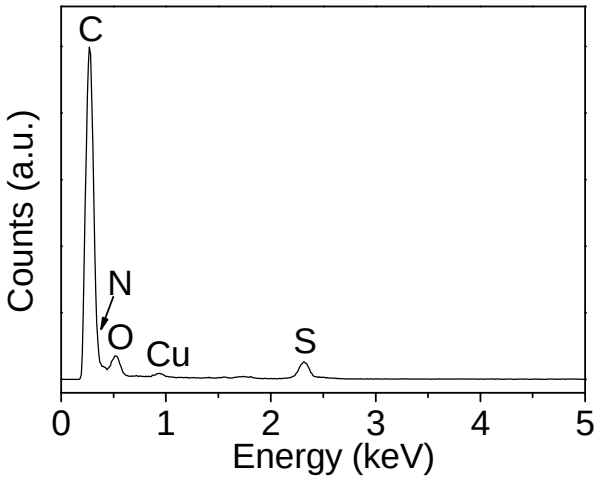

Figure S4. EDX pattern of the S@H-PPy composite corresponding to the TEM elemental mapping images in Figure 3.

The N_2 adsorption/desorption isotherm of sulfur@ppy hollow sphere shows a type III isotherm plot. The BET surface area of the sulfur@ppy hollow sphere is only 14.2 m^2/g, indicating a low porosity of the as-prepared nanocomposites.

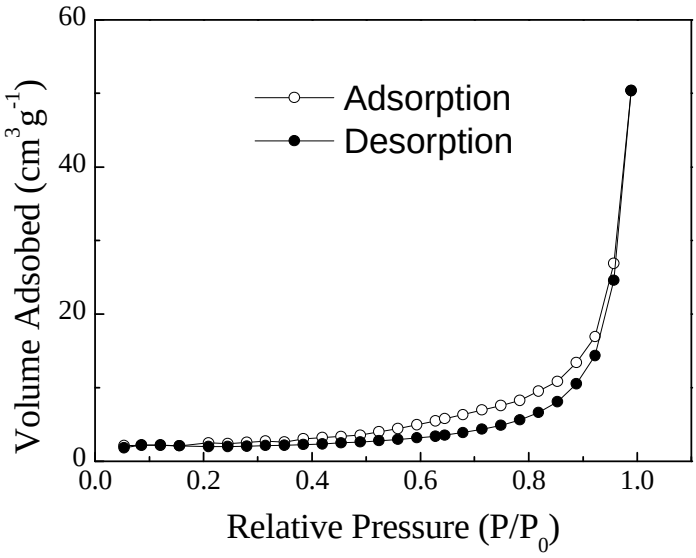

Fig. S5 N_2 adsorption/desorption isotherm of sulfur@ppy hollow sphere with 48 wt% sulfur.

We observed the electrode after 50 cycles using SEM and TEM. The electrode can keep the structure, though some pulverization is found.

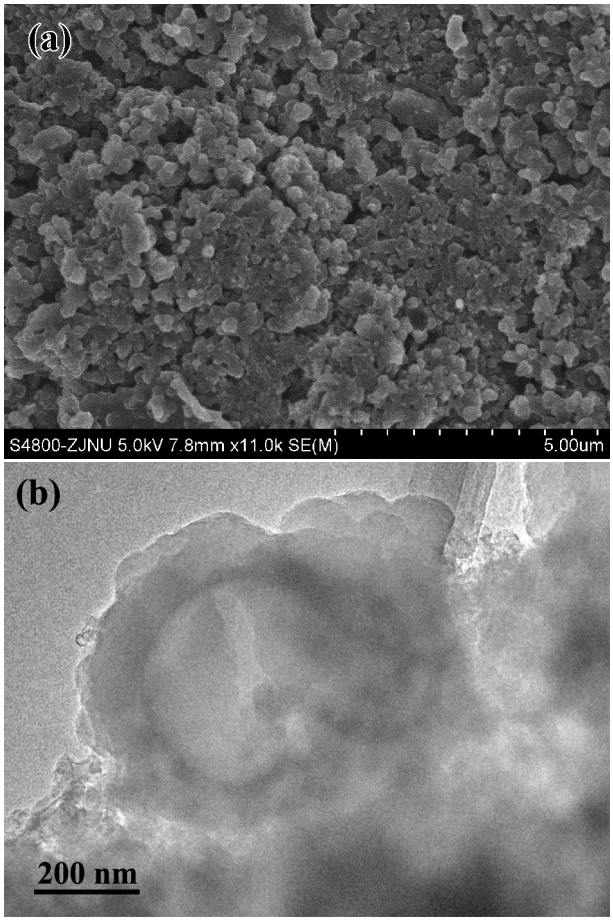

Figure S6. SEM (a) and TEM (b) images of the S@H-PPy composite electrode after 50 discharge/charge cycles.