

Electronic Supplementary Information for

**Core-shell Sulfur@polypyrrole Composite as a High-capacity Material for
Aqueous Rechargeable Batteries**

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Experimental section

Synthesis of the composites: *l*-S@PPy composite was synthesized by adding 40 mL of 1 mol L⁻¹ (NH₄)₂S₂O₈ aqueous solution into a mixing solution containing 7.2 g of Na₂S, 1.3 g of sulfur, and 1 g of pyrrole. 7.2 g of Na₂S, 2.6 g of sulfur, and 0.5 g of pyrrole were used for the preparation *h*-S@PPy composite. Activated carbon was purchased from Ningde Xinseng chemical and Industrial Co., Ltd., which has a BET surface area of about 2500 m²/g. Activated carbon impregnated sulfur composite was prepared by stirring 0.5 g of activated carbon in a 0.5 g sulfur-dissolved CS₂ solution at room temperature until CS₂ was evaporated. The obtained S@AC composite was then annealed at 150°C with the protection of Ar for 1 h to make sulfur diffuse into the pores of activated carbon thoroughly.

Characterization methods: XRD was collected using a Rigaku D/MAX-IIA X-ray diffractometer with Cu K α radiation. TG analysis was carried out with a SEIKO TG/DTA 7300 thermal analyzer. SEM images were obtained by Philip XL30 operated at 25 kV. XPS spectra were obtained by Perkin-Elmer PHI 5000C ESCA using Al K α radiation. TEM images were obtained with a JEOL JEM-2010 transmission electron microscope.

Electrochemical testing: For the electrochemical tests, the working electrodes were prepared by the following method. First, the active material, acetylene black (Shanghai Haohua Chemical and Industrial Co., Ltd.) and poly(tetrafluoroethylene) (PTFE, Sigma-Aldrich, 60 wt % dispersion in H₂O) with a weight ratio of 8:1:1 were dispersed homogeneously in ethanol. A mushy mixture was formed as ethanol evaporated in hot air. The mushy mixture was then pressed into a thin film, which was further punched into small disks with a diameter of 10 mm. At last, these disks were pressed onto a Ni-grid at a pressure of 12 MPa and then dried at 60 °C. Galvanostatic discharge and charge tests were performed with a cycle tester from LAND Electronic Co. The cyclic voltammograms and electrochemical impedance data were obtained using ZAHNER Electrochemical Workstation IM6.

Analysis about the redox reaction of sulfur in organic and aqueous electrolyte

Actually, the redox potential of a type of electrode material in organic electrolyte usually corresponds well to that in aqueous electrolyte if it undergoes the identical electrochemical reaction. For example, the average redox potential of LiMn₂O₄ in organic electrolyte is about 4.0 V vs. Li/Li⁺, equaling to 1.0 V vs. SHE, which is in good agreement with the experimentally measured redox potential of LiMn₂O₄ in aqueous electrolyte.

In lithium-sulfur batteries that use organic electrolyte, Li₂S and lithium polysulfides are formed during the charge-discharge ($S_8 \xleftarrow{Li_2S_8, Li_2S_6, Li_2S_4, Li_2S_3} Li_2S_2 / Li_2S$). The average redox potential of sulfur in organic electrolyte is reported at 2.30 V vs. Li/Li⁺,

which equals to -0.94 V *vs.* SCE. However, the measured redox potential of sulfur in aqueous Li₂SO₄ electrolyte is about -0.20 V *vs.* SCE. Therefore, the electrochemical reactions of sulfur in aqueous electrolyte must be different from that in organic electrolyte. Sulfur can be reduced to HS⁻ in the presence of water ($S + H_2O + 2e \Leftrightarrow HS^- + OH^-$).

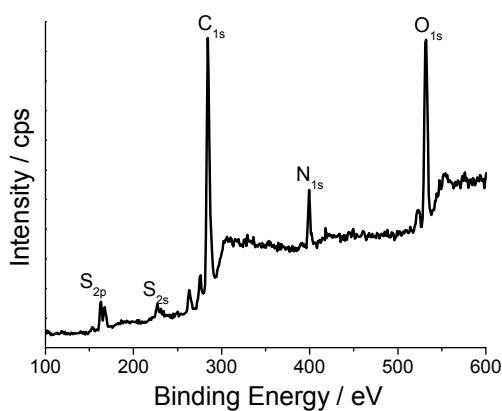


Fig. S1 The survey scan XPS spectra of *l*-S@PPy composite.

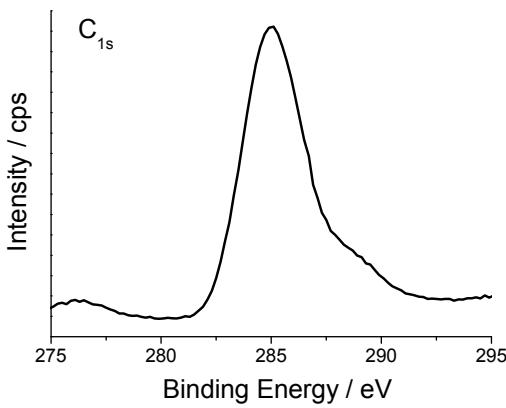


Fig. S2 C_{1s} XPS spectra of *l*-S@PPy composite.

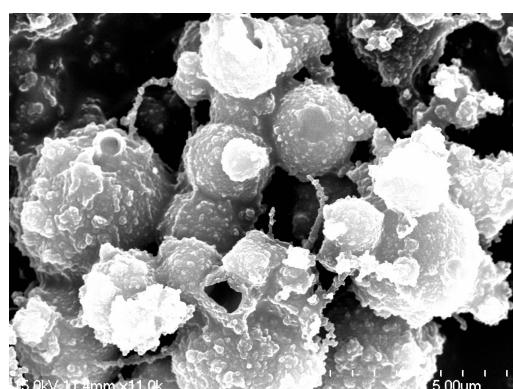


Fig. S3 Typical SEM image of *l*-S@PPy composite.

Similar to the SEM image of *h*-S@PPy, the core-shell structured S@PPy particles can also be observed.

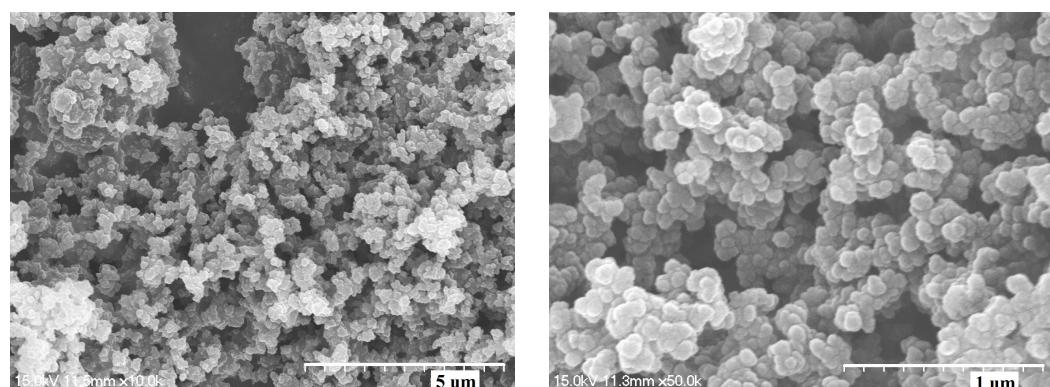


Fig. S4 Other SEM images of *l*-S@PPy composite.

Many extra PPy nanoparticles are dispersed in the composite so that the microscaled sulfur particles cannot be seen clearly in some places.

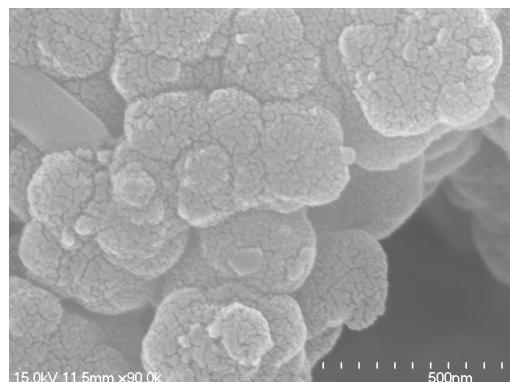


Fig. S5 SEM image of pure PPy.

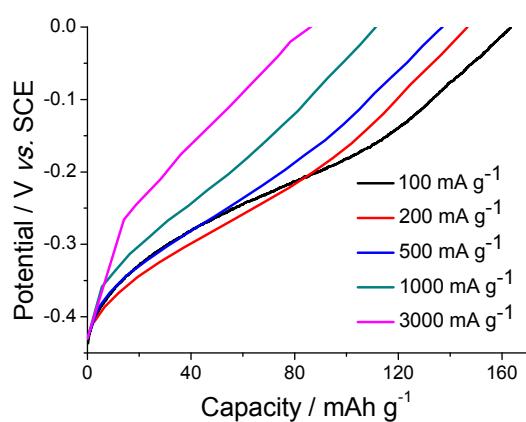


Fig. S6 Charge curves of *l*-S@PPy at different current densities.

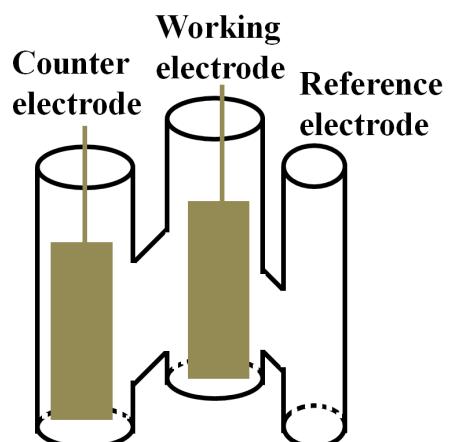


Fig. S7 Structure of the three-electrode cell.