

Supplementary Information

Sulfur-carbon yolk-shell particles based 3D interconnected nanostructure as cathode material for rechargeable lithium-sulfur batteries

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Experimental Section

Synthesis of ZnS Spheres: Zinc sulfide spheres were synthesized using a facile hydrothermal synthesis process. 0.03 mol of zinc acetate and 0.03 mol of thiourea were dissolved into 200 ml of deionized water and added into an autoclave. 3 g of gum arabic was then added as a surfactant for the formation of the spheres. The solution was stirred and sonicated to ensure complete dissolution of the reagents. The autoclave was sealed and placed into an oven at 120 °C for 12 hours. The resulting white precipitate of zinc sulfide was retrieved via centrifugation, washed several times with deionized water and dried in an oven at 70 °C for 3 hours.

Synthesis of ZnS@C core-shell particles: In a typical synthesis, 0.1 ml of phenol formaldehyde resin (PF) solution (0.5 g ml⁻¹ in acetone) was added to 0.5 g of zinc sulfide spheres, followed by the addition of 5 ml of acetone. The resultant mixture was stirred and sonicated thoroughly for 10 minutes and then dried in a vacuum over 5 hours. The samples were then subjected to high temperature treatment in a tube furnace at 900 °C under argon gas for 1 hour, and cooling down naturally to room temperature.

Synthesis of S@C Yolk-Shell Nanostructures: The obtained ZnS@C nanostructures were ground into fine powder, and mixed with 20 ml of ferric nitrate solution (2 M in water). The suspension was left with stirring in an ice-water bath for 15 hours. The samples were then recovered using centrifugation and hydrochloric acid was added

to each sample as a precaution to remove any remaining zinc sulfide. The residue was then removed via centrifugation and washed several times in deionized water. The sample, denoted as SC1, was dried in an oven at 70 °C for 3 hours.

Synthesis of S@C Yolk-Shell Nanostructures with different carbon content: To investigate the effect of carbon content on battery performance, 3 other samples with different carbon weight percentage were synthesized. In experiments this was realized by varying the volume of PF resin solution added to 0.2, 0.4 and 0.5 ml for samples SC2, SC3 and SC4, respectively, while keeping the mass of zinc sulfide spheres used at 0.5 g. The obtained weight ratio of sulfur to carbon was listed in Tab. S2.

Effect of concentration of ferric nitrate on oxidation stage of ZnS@C nanostructures: To investigate the conversion process, fresh batches of carbon-coated zinc sulfides were synthesized starting with 0.5 g of ZnS and 0.1 ml of PF resin. In oxidation experiments 5 different concentrations of ferric nitrate (0.4, 0.8, 1.2, 1.6, 2.0 M) were added to 5 separate containers, each containing equal amounts of the carbon-coated zinc sulfides. The respective oxidized intermediate (ZnS-S@C) or final product (S@C) was recovered by centrifugation and washed repeatedly with deionized water.

Synthesis of carbon-sulfur composite as control sample via melting diffusion (MSC): In the control experiment of introducing sulfur via melting diffusion method, sulfur in S@C yolk-shell (SC2) was removed by soaking in toluene for 1 hour. The resulting porous carbon material was then recovered by centrifugation, washed repeatedly with deionized water and then dried in the oven at 70 °C for 3 hours. Elemental sulfur was then added to the porous carbon material in a 1:1 weight ratio, sealed in an autoclave and placed in the oven at 150 °C for 12 hours to allow for sufficient diffusion of melted sulfur into the pores. The final product, the Melting-diffused Sulfur in Carbon, denoted as MSC, was ground into fine powder using a mortar and pestle prior to the electrode preparation for the battery test.

Morphology and Structural Characterization: SEM images were taken on a JEOL JSM-6700F FESEM with an accelerating voltage of 5 kV. TEM images were recorded on a Philips CM300 FEGTEM with an accelerating voltage of 200 kV. Energy-dispersive X-ray spectroscopy that was available in the TEM was used to conduct elemental analysis and mapping. X-ray diffraction patterns spectra were collected on a Bruker D8 General Area Detector Diffraction System using Cu K α radiation. Thermogravimetric analysis (TGA) was carried out on a TA instruments TGA Q500 at a heating rate of 10 °C min⁻¹ under nitrogen gas.

Electrochemical Measurements: To prepare the working cathodes for battery testing, the samples were each mixed with carbon black (Denka) and poly(vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidone in a weight ratio of (8:4:3) to form a black colored slurry. This slurry was then coated evenly onto an aluminum foil and dried in oven at 70 °C for 3 hours. The electrode was assembled into CR2032 coin cells with lithium foil as the anode in an argon-filled glove box. The electrolyte used (80 μ L) was 1,2-dimethoxyethane and 1,3-dioxolane in a 1:1 volume ratio containing 1M lithium bis(tri-fluoromethanesulfonyl)imide as the lithium salt. The electrolyte also

contained 0.5 M LiNO₃ and 0.2 M Li₂S₆ as electrolyte additives. Battery cycling tests were performed using Neware battery tester at a constant current of 0.3 mA from 1.5-3.2 V versus Li⁺/Li. Capacity values were calculated based on the mass of all components loaded on the aluminum foil. The mass loading of composites (including S@C composite, carbon black and binder) was around 2.75 mg per electrode. The areal sulfur loading density is 0.62 (CS1), 0.45 (CS2), 0.36 (CS3) and 0.28 mg cm⁻² (CS4).

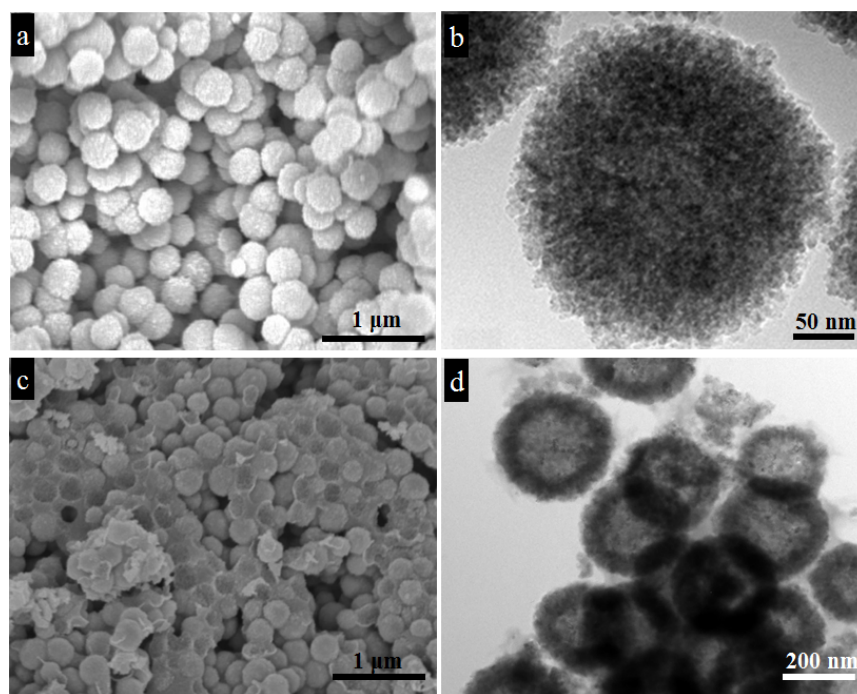


Fig. S1 (a) SEM and (b) TEM images of the obtained ZnS spherical particles via hydrothermal method. (c) SEM and (d) TEM images of “hollow-like” ZnS@C.

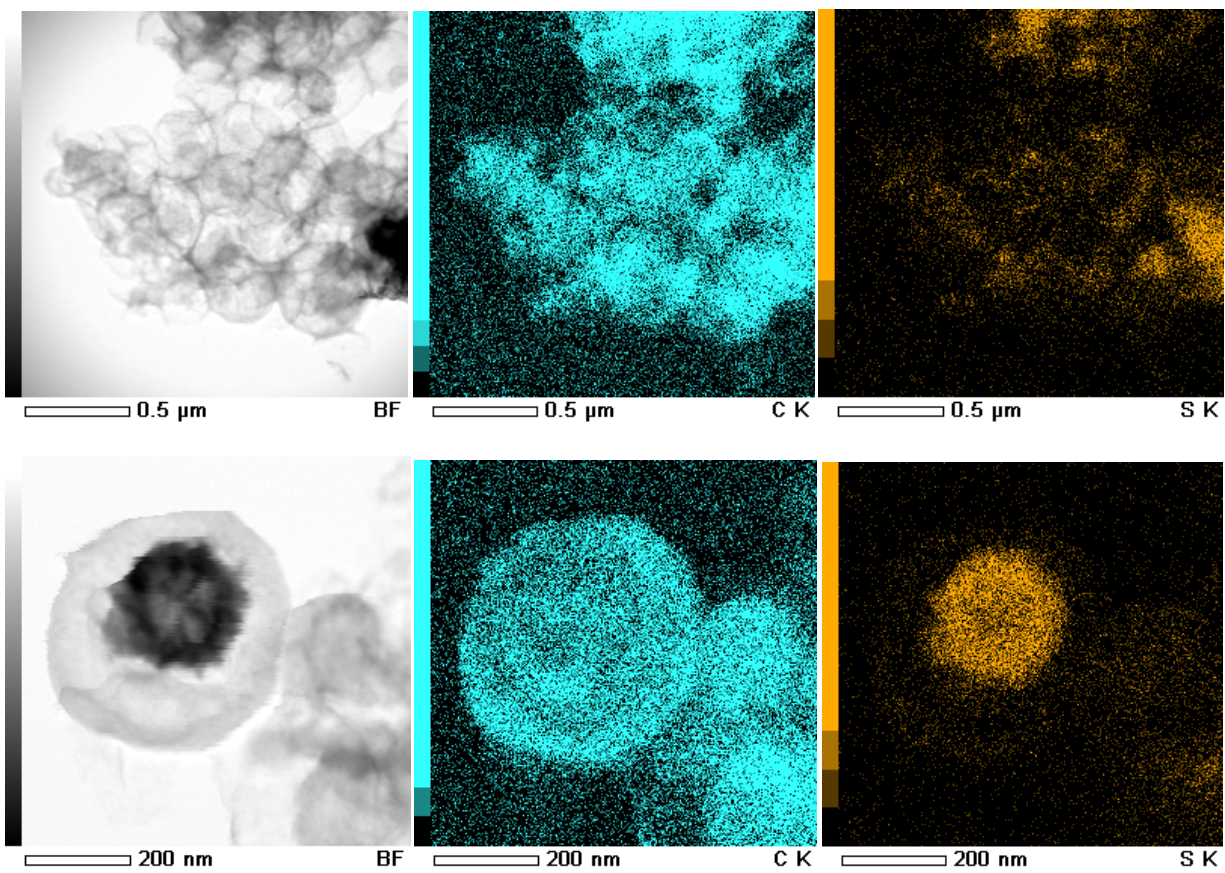


Fig. S2 Elemental mapping of S@C yolk-shell nanostructures with low (top) and high (bottom) magnifications. Due to the low signal-to-noise ratio in EDX mapping of S@C, the mapping images of high magnification were taken from the intermediate state: ZnS-S@C.

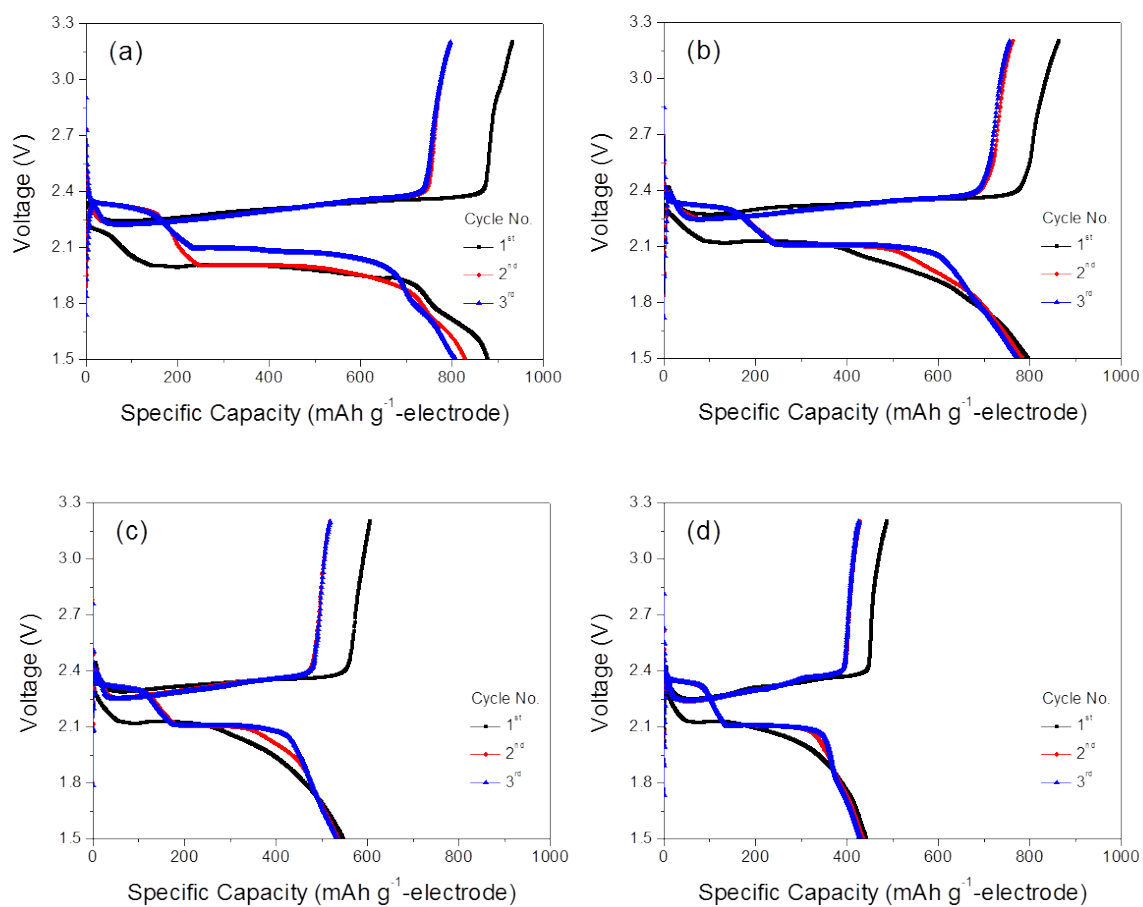


Fig. S3 Galvanostatic discharge-charge curves for the first three cycles for (a) SC1, (b) SC2, (c) SC3 and (d) SC4.

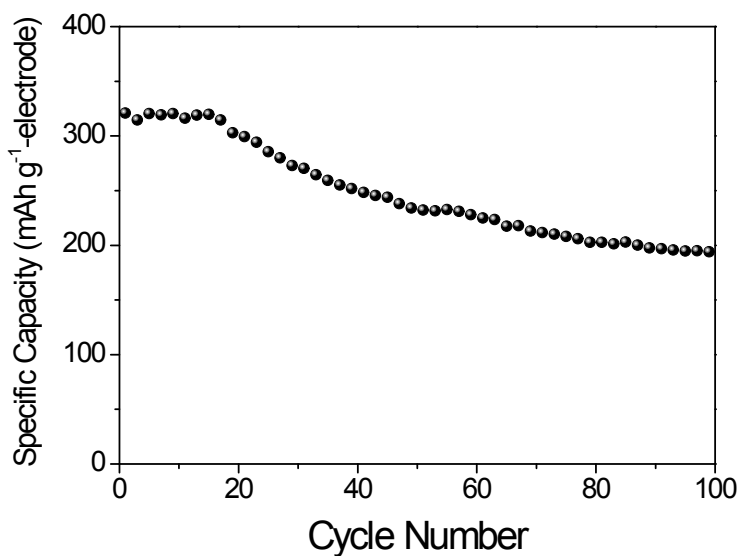


Fig. S4 Battery performance of the electrode comprised of carbon shell, carbon black and binder, cycled in the electrolyte containing Li_2S_6 (0.2 M) as electrolyte additives.

It is worth noting that the capacity of SC1 and SC2 is higher than previously reported results in literatures (typically about 500 mAh g^{-1} , based on the total mass of all components on cathode).¹⁻⁴ The higher capacity is partially introduced by the addition of Li_2S_6 , which was added as electrolyte additive to enhance the battery cyclability^{5,6} and may precipitate on carbon black and the carbon shell as sulfur during charging process. To calibrate the areal battery capacity, samples with only carbon shell were prepared by directly removing ZnS from ZnS@C (the precursor of SC1) by acid treatment. The cathode is fabricated using carbon black and carbon shell in a weight ratio of 1:1 with $\sim 20 \text{ wt\%}$ of binder, and the battery cycling performance is shown in Figure S4. One can see that the capacity resulted from Li_2S_6 is at most 320 mAh g^{-1} . Taking this as a reference, the maximum capacity of sulfur-carbon yolk-shell is obtained as $\sim 560 \text{ mAh}$ per gram of electrode or 1400 mAh per gram of sulfur in S@C yolk-shell nanostructure which is quite high.

Tab. S1 Selection of metal sulfides for the template to synthesize S@C yolk-shell nanostructures.

Sulfide	Ksp	Melting point	Max. Temperature stable in H ₂ ^a
MnS	3×10 ⁻¹¹	1610	1244
FeS	8×10 ⁻¹⁹	1118	273
CoS	5×10 ⁻²²	1117	134
NiS	4×10 ⁻²⁰	976	129
CuS	8×10 ⁻³⁷	507 ^b	-39.7
ZnS	2×10 ⁻²⁵	1700	979
PbS	3×10 ⁻²⁸	1114	423
Ag ₂ S	8×10 ⁻⁵¹	825	-76.6
CdS	1×10 ⁻²⁷	1750	741

^a Based on the thermal dynamic calculation $\Delta G = \Delta H - T\Delta S$

^b Decomposed into Cu₂S

Tab. S2 TGA results of carbon and sulfur content in the obtained S@C yolk-shell nanostructures.

Sample	Sulfur (wt%)	Carbon (wt%)
SC1	74.8	25.2
SC2	54.0	46.0
SC3	42.9	57.1
SC4	33.8	66.2

Reference

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