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.

## Supplementary Material

## C-S@PANI composite with polymer spherical network (PSN) structure for

## high performance lithium-sulfur batteries



Fig. S1 TGA curves of the C-S@PANI composite with different contents of sulfur



**Fig. S2** SEM images of Polyaniline sphere network-sulfur composites (contents of acetylene black, a: 0%, b: 5%, c: 10% and d: 15%)

The carbon content directly affects the growth morphology of the PSN. To synthesize the appropriate structure, comparison of different amounts acetylene black (based on the total mass of the composite material to calculate: 0%, 5%, 10% and 15% respectively) was tested. In figure S3, without the carbon particles, the growth of aniline is irregular in solution by diffusion, forming 3D network agglomeration (Figure S3a). When the carbon content of 10%, PANI chains graft onto the surface of oxidized carbon black to obtain a matrix. As shown in Figure S3c, the structure has a high porosity and volumetric capacity. A small amount of the cross-linked fibers occurs between the Polymer Spherical Networks (Figure S3d). By using the liquid phase deposition method to deposited sulfur, the internal pore network can accommodate the conversion of elemental sulfur and the large volume expansion can provide a stable reservoir for the electrolyte, during the charge-discharge process.



Fig. S3  $N_2$  adsorption-desorption isotherms for C-S@PANI composite, with insets showing the BJH pore-size distributions for the corresponding samples.



Fig. S4  $Li_2S$  (orange color) trapping within the PANI framework during lithiation / delithiation (Yellow and gray are the sulfur and lithium).