Electronic Supplementary Information (ESI)

An encapsulation-reduction-catalysis confined all-in-one microcapsule for lithium-sulfur batteries displaying high capacity and stable temperature tolerance

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Experimental

Material preparation

All chemicals were purchased from Aladdin without further purification. 0.58 g of $Co(NO_3)_2 \cdot 6H_2O$ and 0.5 g of polyvinylpyrrolidone were dissolved in 20 mL at a volumetric ratio of 1:1 in the mixture of ethanol and water. Then, 20 mL of 0.4 mol L^{-1} sodium hydroxide aqueous solution was added under stirring to make the mixture changed from red to blue, and the reaction suspension was quickly transferred to an autoclave, heated for 12 h at 200 °C. The sample was filtered, washed, and dried.

Subsequently, 0.1 g of Co_3O_4 and 4 g of *n*-hexadecane were dispersed ultrasonically for 20 min at room temperature to obtain a mixed solution A; 1.25 g of urea, 0.25 g of resorcinol, and 0.125 g of ammonium chloride were added in 50 mL of distilled water to obtain mixed solution B. Solution B was mixed with 25 mL of 2.5% methyl vinyl ether-maleic anhydride copolymer aqueous solution by mechanically

stirring, while adjusting the pH to 3.5 with triethanolamine. The solution A was added to the above solution, and the mechanical stirring was carried out for 0.5 h at a rate of 800 rpm. 3.2 g of formaldehyde aqueous solution with a mass concentration of 37% was added dropwise, and the stirring was continued for 2 h to obtain the microcapsules infilled with Co_3O_4.

The as-obtained sample was filtered, dried, and then carbonized at 800 ºC in nitrogen gas for 5 h, and the heating rate was set to 3 ºC min^{-1}. The microcapsules and sulfur powders were mixed uniformly according to the mass ratio of 1:2. The CNTs/S-infilled microcapsules were obtained by fumigating sulfur in a tube furnace at 155 ºC for 12 h under argon gas, and another rapid heat-treatment at 250 ºC for 10 min to remove the sulfur on the external surface of microcapsules.

Characterization

The samples were characterized by using scanning electron microscope (SEM, Hitachi S-8100, operated at 5 kV), transmission electron microscope (TEM, Hitachi HT7700), high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010), energy dispersive x-ray spectroscopy (EDS), x-ray powder diffraction (XRD, D8 Advance), Raman spectrometer (Renishaw inVia), and x-ray photoelectron spectroscopy (XPS, ESCALAB 250). The sulfur content in the microcapsule was measured on a thermogravimetric analyzer (TGA, Setaram Labsys Evo SDT Q600). The specific surface area of microcapsule was tested on a Brunauer-Emmett-Teller (BET, Nova 2000E).

Electrochemical tests

The microcapsules, conductive carbon black and polyvinylidene fluoride (mass ratio=65:25:10) were mixed for 5 h to form a slurry, and coated on an aluminum foil. After drying overnight in a vacuum oven at 60 °C, the foil was cut into small discs with a diameter of 12 mm by a microtome. Then, the CR2032 coin cell was assembled in a glove box (Mikrouna, Super 1220/750/900) in an argon gas. The lithium foil and the microporous polypropylene membrane were used as the counter electrode and diaphragm. The electrolyte was composed of DME and DOL (volume ratio 1:1), a mixture of 1.0 M LiTFSI and 1 wt% $LiNO_3$. The electrochemical performance of the battery was tested by the Neware CT-3008 battery test system, the voltage range was set to 1.7 to 2.8 V. The cyclic voltammetry (CV) measurement was performed on an electrochemical workstation (CHI-660E) at a scan rate of 0.1 mV s^{-1}. By using the same workstation, the electrochemical impedance spectroscopy (EIS) spectra of the cells were from 0.01 to 100 kHz.

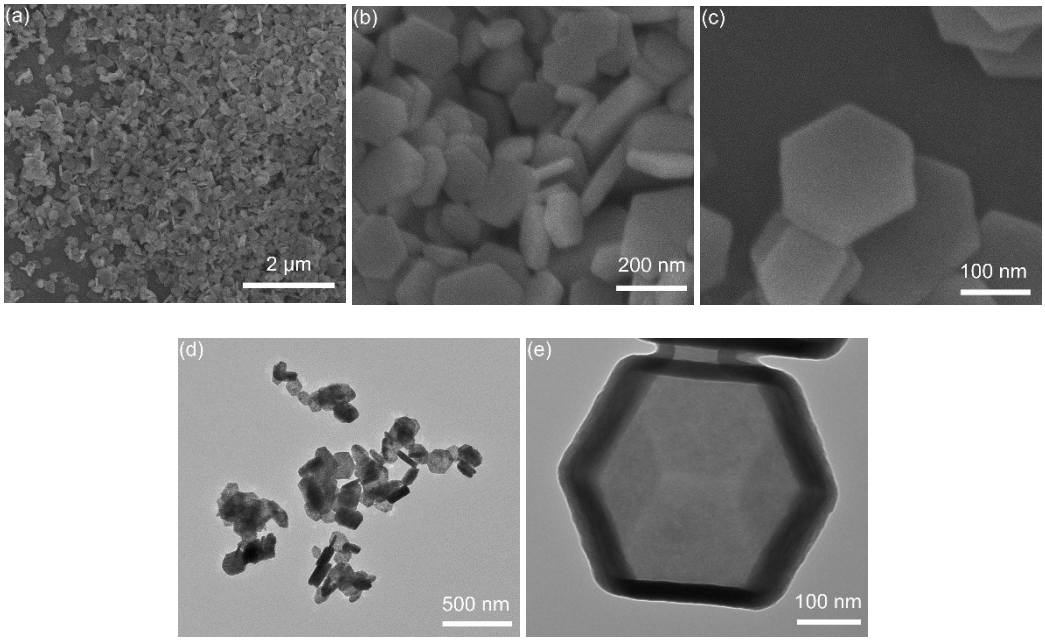

Fig. S1. (a-c) SEM and (d, e) TEM images of the Co_3O_4 nanoboxes.

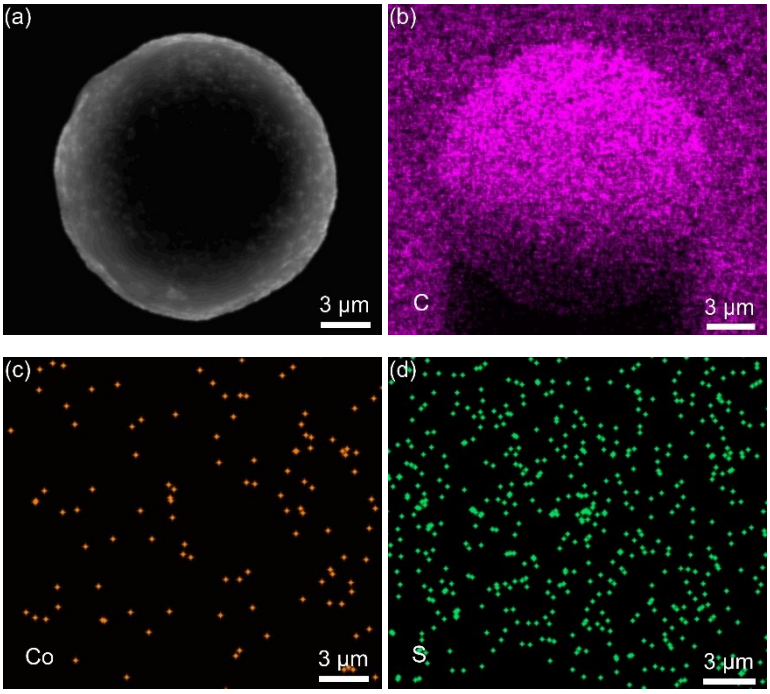

Fig. S2. (a) SEM image of a CNTs/S-infilled microcapsule. Elemental mapping images of (b) C, (c) Co, and (d) S.

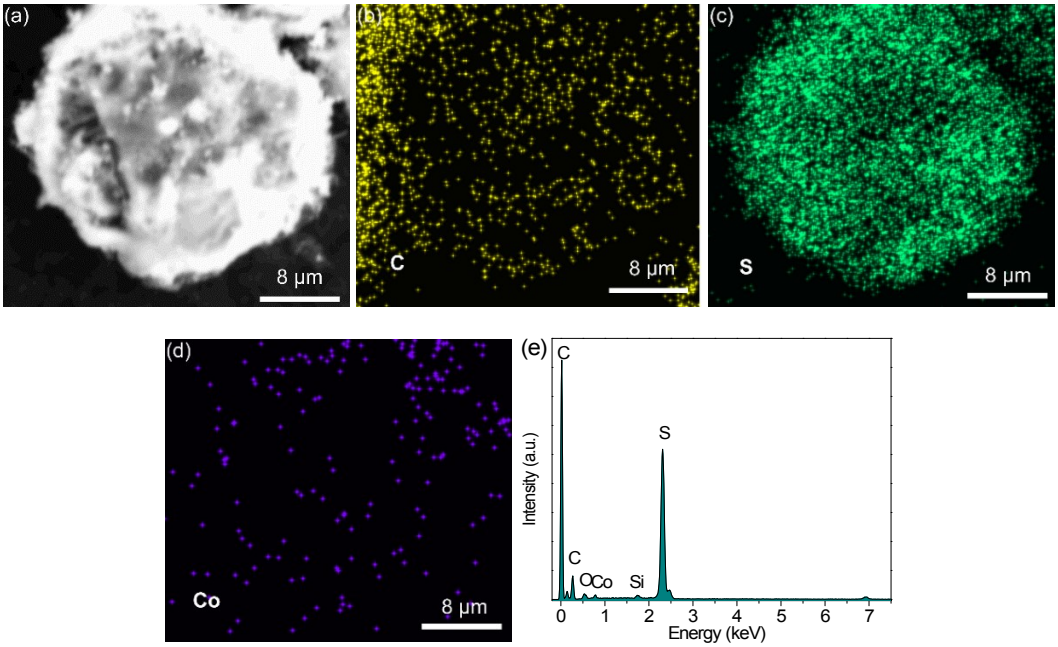

Fig. S3. (a) SEM image of a manually-broken CNTs/S-infilled microcapsule. Elemental mapping images of (b) C, (c) S, and (d) Co. (e) EDS spectrum.

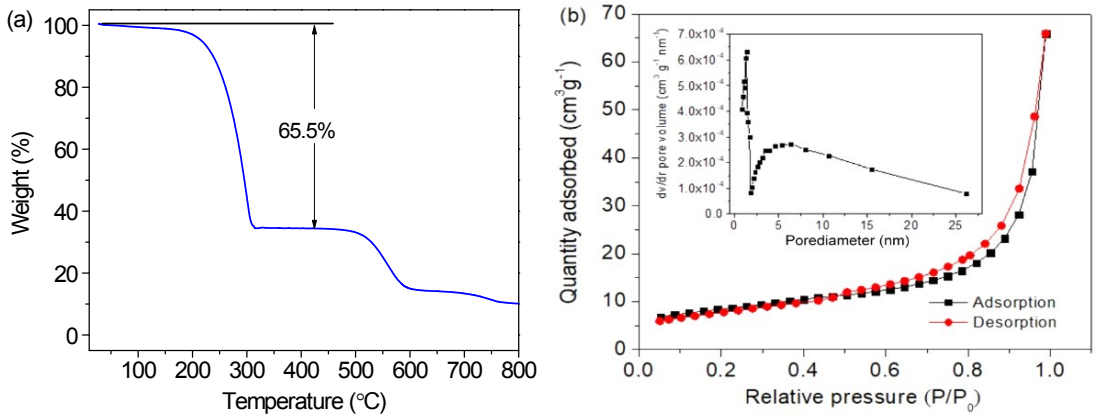

Fig. S4. (a) TGA curve of the CNTs/S-infilled microcapsules, (b) The N_2 adsorption-desorption isotherm of the microcapsules; and inset shows the pore-size distribution.

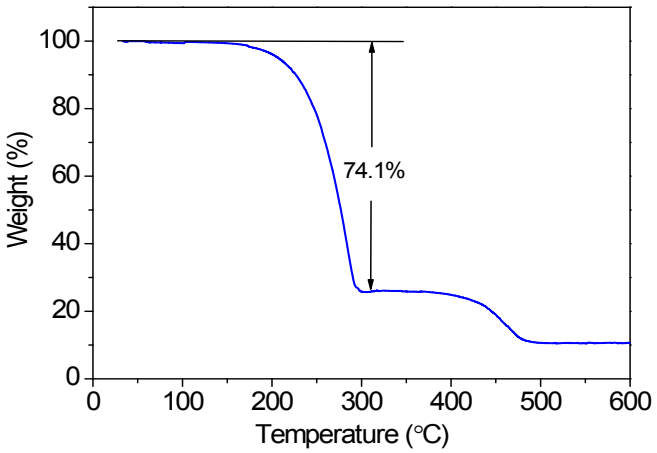

Fig. S5. TGA curve of the CNTs/S-infilled microcapsules with a sulfur content of 74.1%.

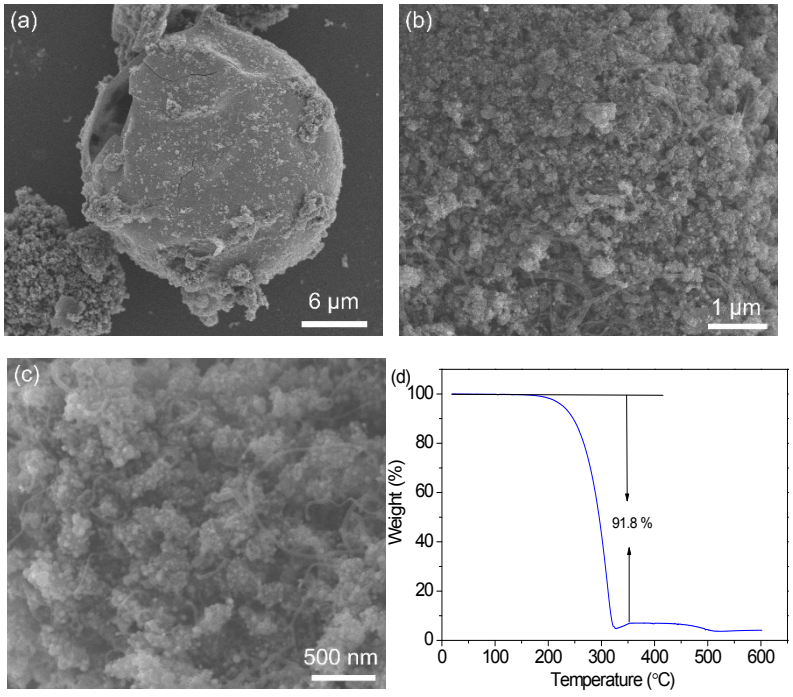

Fig. S6. (a-c) SEM images and (d) TGA curve of the CNTs/S-infilled microcapsules with a high sulfur content.

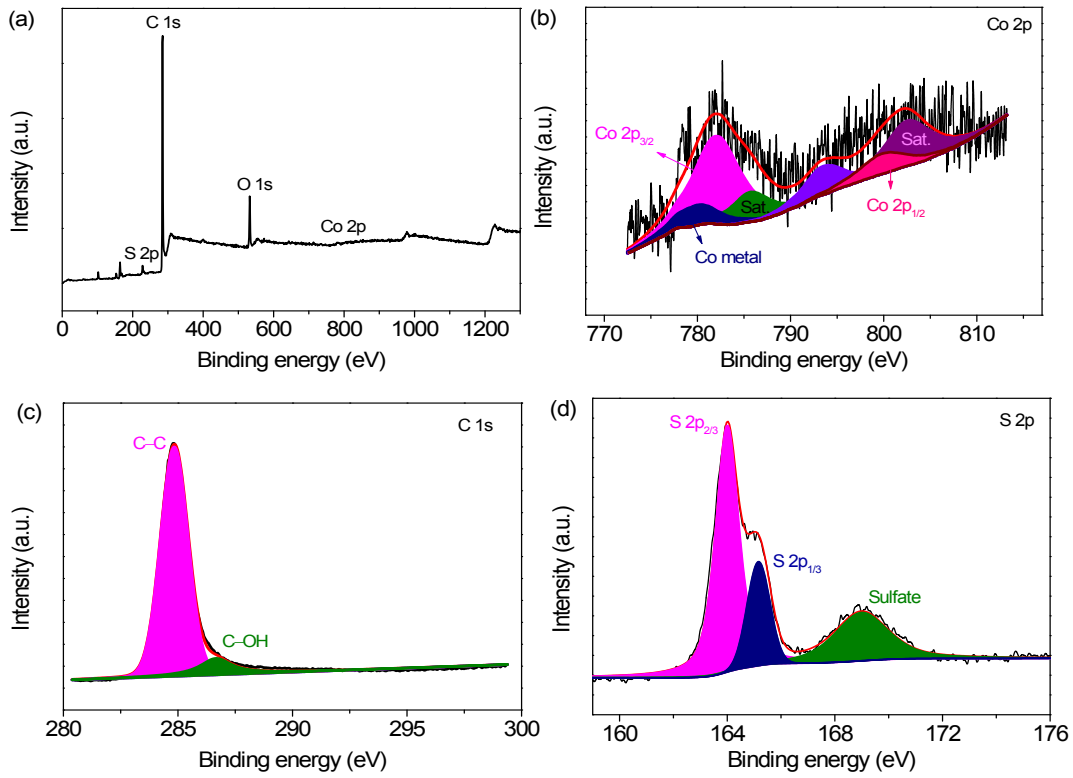

Fig. S7. XPS spectra of (a) Survey, (b) Co 2p, (c) C 1s, and (d) S 2p of the CNTs/S-infilled microcapsules.

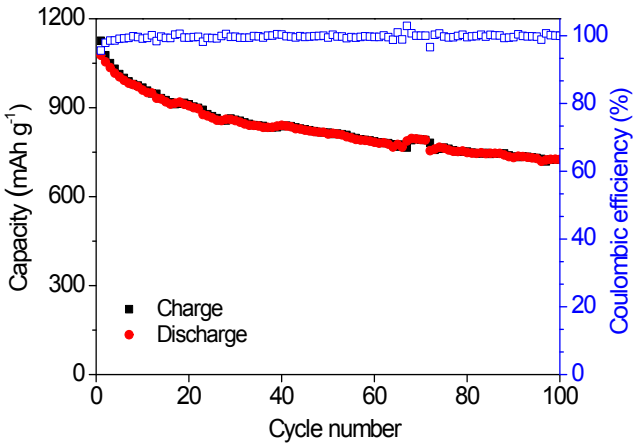

Fig. S8. Cycling performance of the CNTs/S-infilled microcapsules at 0.3 C.

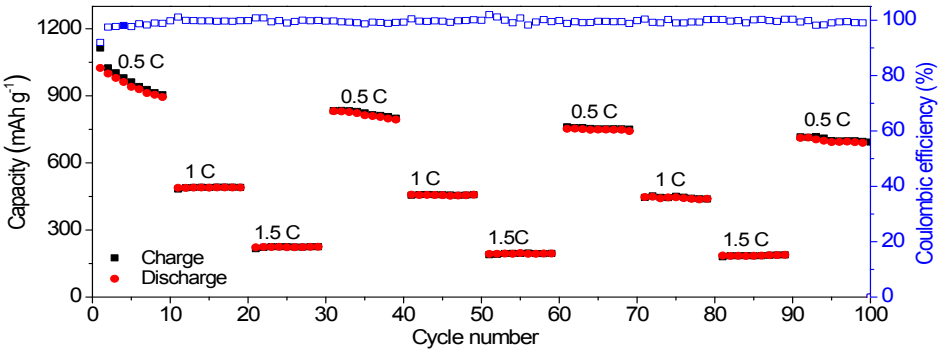

Fig. S9. Rate-performance of the CNTs/S-infilled microcapsules.

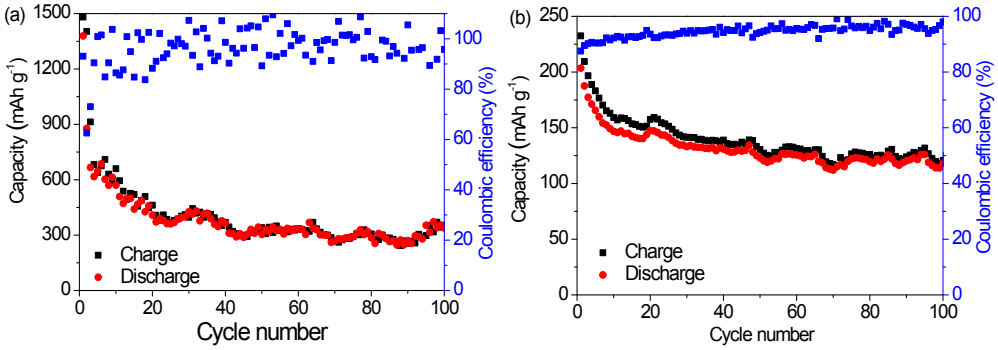

Fig. S10. Capacity and Coulombic efficiency of the CNTs/S composite cycling at 0.1 C under different temperatures: (a) 45 °C and (b) –5 °C.

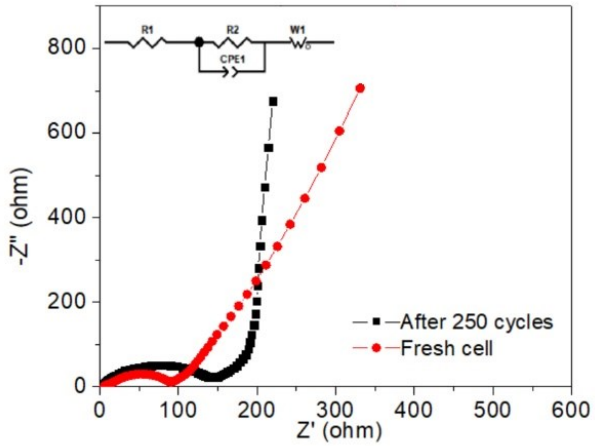

Fig. S11. Nyquist plots of the CNTs/S-infilled microcapsules before and after cycling at 0.1 C for 250 cycles.