Fully Integrated Hierarchical Double-Shelled Co₉S₈@CNTs Nanostructures with Superior Performance for Li-S Batteries

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Supporting Information

Experimental

Materials.

 $Co(NO_3)_2 \cdot 6H_2O$, thioacetamide (TAA), sublimed sulfur, glycerol, isopropanol and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All the chemical reagents used here were analytical grade without further purification.

Synthesis of double-shelled hollow Co₉S₈ nanospheres and Co₉S₈@CNTs composites.

Double-shelled Co_9S_8 nanospheres were prepared according to the literature with some modifications.¹ In a typical process, 109 mg Co(NO₃)₂·6H₂O and 8 ml glycerol were dissolved in 40 ml isopropanol. After 20 min stirring, the transparent pink solution was then sealed in a Teflon-lined stainless-steel autoclave and heated at 180 °C for 6 h. As the autoclave cooled down to room temperature, the light pink precipitate was collected by centrifugation and washed with ethanol several times. After dried in the oven at 60 °C, 30 mg of the obtained precursor Co-glycerate spheres and 75 mg TAA were added into 20 mL ethanol, stirred for 2 h and transferred into Teflon-lined stainless-steel autoclave. After heating at 160 °C for 6 h, the black product was obtained by centrifugation, washed with ethanol several times and finally dried in the vacuum oven at 60 °C. For the preparation of double-shelled Co₉S₈ nanospheres, the as-prepared samples were annealed at 800 °C under the Ar atmosphere for 6 h. For the preparation of Co₉S₈@CNTs composites, the as-prepared samples were annealed at 800 °C under the continuous acetylene/argon gas flow (1/9) for 6 h.

Synthesis of Co₉S₈@CNTs/S composites.

Sublimed sulfur and double-shelled Co_9S_8 @CNTs nanospheres were dispersed in the mixed solution of 10 mL ethanol and 10 mL carbon disulfide and stirred until the solution was evaporated. The sample was put into the oven at 60 °C to remove the remaining ethanol and carbon disulfide. Then the obtained dried sample was hand-milled and sealed in a quartz tube at 155 °C for 10 h. Upon cooling down, the Co_9S_8 @CNTs/S composites were prepared.

Structure characterizations.

The morphologies of the samples were characterized by scanning electron microscopy (SEM) (Carl Zeiss Supra 40 field emission scanning electron microscope); transmission electron microscopy (TEM) images were taken on a field emission Hitachi H7650 transmission electron microscope. The high angle annular dark-field scanning TEM (HAADF-STEM) energy-dispersive x-ray spectroscopy (EDS) element mappings and line scans were carried out with a JEOL ARM-200F transmission electron microscope. Powder X-ray diffractometer (XRD) was performed on the Philips X'pert Super diffract meter with Cu K α radiation (λ =1.54178 Å). Thermogravimetric analysis (TGA) was conducted to evaluate the content of sulfur in the composites. The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore distribution plots were measured on an ASAP 2020 accelerated surface area and porosimetry instrument. The pore size distribution was calculated from the adsorption branch of the isotherms using the non-local density functional theory.

The preparation of Li₂S₆ and the adsorption test.

0.2 M Li₂S₆ was prepared as follows: 2 mmol Li₂S and 10 mmol S was dissolved in 10 mL 1 M LiTFSI in the mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1, v/v). 20 μ L of 0.1 M Li₂S₆ solution was dropwise added into 1 mL tetrahydrofuran (THF) in a glass vial and then 5 mg different samples (CNT, Co₉S₈ and Co₉S₈@CNTs) was added into three vials, respectively. Finally, the adsorption capability was evaluated by comparing the color change of the solution.

Electrochemical Measurements.

The electrochemical performance was measured in the 2016-type coin cells, which were assembled in the argon-filled glove box (H₂O, $O_2 < 1$ ppm). For the symmetric electrochemical studies, the obtained sample (Co₉S₈@CNTs, Co₉S₈ or CNTs) and poly(vinylidene fluoride) binder were mixed in the N-methyl pyrrolidone with a weight ratio of 8:2, then dispersed onto the Al foil and dried at 110 °C for 12 h. The prepared electrodes with the same loading amount were assembled into a symmetric electrochemical cell with 0.2 M Li₂S₆ as the electrolyte. The electrodes for general Li-S battery studies were prepared by mixing the as-prepared composites, Ketjen Black and poly(vinylidene fluoride) binder in N-methyl pyrrolidone with a weight ratio of 7:2:1. The slurries were then pasted onto an Al foil and dried at 70 °C in the vacuum oven for 12 h. The obtained Al foil was cut into circular pieces with a diameter of 12 mm as the electrodes. Unless otherwise noted, the loading of sulfur in each electrode is about 1 mg cm⁻². The lithium foils were used as the counter electrode, celgard 2400 as the separator. The electrolyte was 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (1:1, v/v) with 1% LiNO₃. Cycling voltammograms (CV) and electrochemical impedance spectroscopy

(EIS) were measured on the electrochemical workstation CHI 660e. Glavanostatic measurements were performed on the LANDCT2001A instrument at room temperature with different rates. The galvanostatic intermittent titration technique (GITT) was conducted at the current density of 0.1 C for 0.5 h with the following rest for 3 h. The reaction resistant was evaluated via the difference in the potential of the end of current step and the end of the relaxation step. The visual tests of the polysulfides shuttling was performed in a sealed transparent bottle with the same electrolyte as the coin cell at the rate of 0.05 C.

Computational methods.

All calculations were performed using the plane-wave-based periodic DFT method in the CASTEP software as implemented in the Materials Studios package of Accelrys Inc. The electron exchange-correlation potential was treated by the Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA) and the DFT dispersion correction (DFT-D) method was used to treat the van der Waals interactions. The ultrasoft pseudopotentials was employed and the core electrons of atoms were treated using effective core potential (ECP). The energy cutoff was set to 400 eV for the plane-wave basis set with the Brillouin zone integration sampled with the 4 * 4 * 4 and 2 * 3 * 1 Monkhorst-Pack mesh k-point for bulk and surface calculations. Based on the corresponding optimized bulk unit cell, which is in good agreement with the experimental values, the $Co_{10}S_8$ terminated Co_9S_8 (1 1 0) surface was created by a periodic four-layer slab repeated in 1 * 1 surface unit cell with a vacuum region of 10 Å between the slabs along the Z axis, where the adsorbates together with four layers of surfaces atoms were all relaxed during the geometry optimizations. The convergence tolerances are set to 5.0 *

 10^{-6} eV per atom for energy, $5.0 * 10^{-4}$ Å for maximum displacement, and 0.01 eV Å⁻¹ for maximum force. The adsorption energy of Li₂S₆ on the surface was defined as E = $E_{Surface+Li2S6} - E_{Li2S6} - E_{Surface}$, where $E_{Surface+Li2S6}$ is the total energy of the adsorbed system, E_{Li2S6} is the energy of isolated Li₂S₆, and $E_{Surface}$ is the energy of the optimized clean surface slab.



Fig. S1 TEM image of the CNTs wrapping around the Co₉S₈@CNTs.



Fig. S2 (a) XRD pattern of Co₉S₈@CNTs. (b-d) SEM image of broken Co₉S₈@CNTs.



Fig. S3 (a) HAADF-STEM EDS line scan profiles of Co₉S₈@CNTs, (b) C-K (c) Co-L (d) S-K.



Fig. S4 (a) N_2 adsorption and desorption isotherms and (b) the pore size distribution of the Co_9S_8 @CNTs.



Fig. S5 XRD pattern of Co₉S₈@CNTs/S.



Fig. S6 Cyclic voltammograms of (a) Co_9S_8 @CNTs (b) Co_9S_8 (c) CNTs as the symmetrical electrodes at the scan rate of 7 mV s⁻¹, respectively.



Fig. S7 Cyclic voltammograms of Co_9S_8 @CNTs as the symmetrical electrodes at various scan rates.

Supplemental note : The optimization of the loading of Co₉S₈

We have studied the effects of Co_9S_8 loading weights on the electrochemical properties. The weight content of Co_9S_8 was tuned from 18.45 to 41.6 wt % by changing the CNT growth time in Ar/C₂H₂ atmosphere (Fig. S7). The electrochemical performance evaluated in the symmetrical cell, as shown in the Fig. S8a, S8b displays the sample with Co_9S_8 contents of 20.2 wt % exhibits lowest potential polarization and largest current density. Moreover, the Li-S battery performance measured in the 2016-type coin cells also reveals the sample with Co_9S_8 contents of 20.2 wt % has the best cycling stability and specific capacity (Fig. S8c). Taken together, the optimal loading of Co_9S_8 is ~20%. Increasing or reducing the loading amounts will affect the synergistic balance between of Co_9S_8 and CNTs on the interfacial electrical conductivity and polysulfide redox kinetics, and thus affect their electrochemical performances.



Fig. S8 TGA curves of Co₉S₈@CNTs with different loading contents of the Co₉S₈.



Fig. S9 (a) Cyclic voltammograms of Co_9S_8 @CNTs with different loading contents of Co_9S_8 in a symmetrical cell with Li_2S_6 as the electrolyte. (b) The comparison of peak potentials and current densities in Figure 2a. (c) Cycling performance of Co_9S_8 @CNTs with different loading contents

of Co_9S_8 at the rate of 2 C. Each sample was activated at the rate of 0.2 C for the first three cycles.



Fig. S10 UV-vis spectra of the polysulfide solution after exposure to the different absorbents.



Fig. S11 Optimized geometric configuration of free Li_2S_6 molecule with key bond lengths (bond orders).



Fig. S12 (a) XRD pattern, (b) TGA curve, (c) SEM image and (d) TEM image of Co₉S₈/S.



Fig. S13 (a) XRD pattern (b) TGA curve of CNTs/S. SEM images of (c) CNTs and (d) CNTs/S. TEM images of (e) CNTs and (f) CNTs/S.



Fig. S14 Voltage profiles of CNTs/S, Co₉S₈/S and Co₉S₈@CNTs/S, respectively.



Fig. S15 (a) the voltage profile and (b) the cycling performance of Co_9S_8 @CNTs without sulfur loading.



Fig. S16 The cycling performance and coulombic efficiency of Co_9S_8 @CNTs/S at 1 C with/without the LiNO₃ additive in the electrolyte.



Fig. S17 (a) Equivalent circuit and (b) electrochemical impedance spectra of Co_9S_8 @CNTs/S, Co_9S_8 /S and CNTs/S.



Fig. S18 Warburg coefficient plots of Co₉S₈@CNTs/S, Co₉S₈/S and CNTs/S, respectively.



Fig. S19 (a) the comparison of the GITT voltage profiles of CNTs/S, Co_9S_8/S and $Co_9S_8@CNTs/S$. (b-d) the corresponding potential response during GITT measurement of (b) $Co_9S_8@CNTs/S$ (c) Co_9S_8/S and (d) CNTs/S with the open-circuit voltages (OCV) and closed-circuit voltages (CCV) lined out.



Fig. S20 (a) The cyclic performance of Co_9S_8 @CNTs/S at 0.5 C with various loading amounts and (b) the corresponding areal capacity.



Fig. S21 Voltage profiles of Co_9S_8 @CNTs/S at 1st, 2nd, 100th, 150th and 200th cycle with different sulfur loading amounts of (a) 2 mg cm⁻² (b) 3 mg cm⁻² (c) 3.5 mg cm⁻², respectively. (d) the corresponding voltage polarization.



Fig. S22 The cyclic performance of Co_9S_8 @CNTs/S at 0.5 C with the loading amounts of 6.8 mg cm⁻².



Fig. S23 (a) the cycling performance of Co_9S_8 @CNTs/S with the different electrolyte amounts. The corresponding voltage profiles in (b) 1st cycle (c) 15th cycle and (d) 30th cycle.



Fig. S24 Visual tests of polysulfides shuttling effect of CNTs/S (upper panel) and $Co_9S_8@CNTs/S$ (lower panel) at 0.05 C.



Fig. S25 The SEM (a) and TEM (b) images of Co₉S₈@CNTs/S after cycling test.

Table S1. The specific capacities of Co_9S_8 @CNTs/S and the ever-reported sulfur cathodes with similar sulfur content at the rate of 10 C.

Cathode materials	Sulfur contents (wt%)	Rate	Capacity (mA h g ⁻¹)	Reference
C09S8@CNTs/S	68.67	10 C	676.7	this work
NbS2@S@IG	72	10 C	~500	ACS Nano, 2017, 11, 8488.
MWCNT-SnO/S	70	10 C	625.4	Nano Res., 2017 , 10, 2083.
PCNT-S@SNGE	68	10 C	600	<i>J. Mater. Chem. A</i> , 2016 , 4, 15343.
90S-Co-N-C	93.6	10 C	290	ACS Nano, 2017 , 11, 11417.
S@ISCF	70	10 C	650	Angew. Chem. Int. Ed., 2017 , 56, 1.

Table S2. Equivalent-circuit parameters obtained by fitting the experimental impedance spectra.

Electrodes	$R_s(\Omega)$	R _{CT} (Ω)
Co ₉ S ₈ @CNTs/S	2.060	26.48
Co ₉ S ₈ /S	2.054	43.98
CNTs/S	2.043	37.78

Sulfur loading amounts	2 mg cm ⁻²	3 mg cm ⁻²	3.5 mg cm ⁻²
Cycling rate	0.5 C	0.5 C	0.5 C
Charge-storage capacity (mAh g ⁻¹)	999.5	760.1	436.3
Capacity after 200 cycles (mAh g ⁻¹)	918.5	836.9	766.5
Areal capacity(mAh cm ⁻²)	1.999	2.2803	1.52705
Areal capacity after 200 cycles (mAh cm ⁻²)	1.837	2.5107	2.68275
Gravimetric Energy density after 200 cycles (mWh g ⁻¹)	1901	1732	1581
Areal energy density after 200 cycles (mWh cm ⁻²)	3.8	5.2	5.5

Table S3. Battery performances of Co_9S_8 (CNTs/S with different sulfur loading amounts.

Reference

[1] L. Shen, L. Yu, H. B. Wu, X.-Y. Yu, X. Zhang and X. W. D. Lou, Nat. Commun., 2015, 6, 6694.