# Supporting Information

# A labyrinth-like network electrode design for lithium-sulfur

## batteries

Wenwen Tang,<sup>a,b</sup> Youquan Zhang,<sup>a,b</sup> Wei Zhong,<sup>a,b</sup> Muhammad Kashif Aslam,<sup>a,b</sup>

Bingshu Guo,<sup>a,b</sup> Shu-Juan Bao,<sup>a,b,\*</sup> Maowen Xu<sup>a,b,\*</sup>

<sup>a</sup>Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, Institute of Materials and Energy, Southwest University, Chongqing 400715, PR China.

<sup>b</sup>Chongqing Key Laboratory for Advanced Materials and Technologies of Clean Energies, Chongqing 400715, P.R. China.

\* Corresponding author:

E-mail: baoshj@swu.edu.cn; xumaowen@swu.edu.cn.

# Catalog:

Exp	erimental Section3
1.	Synthesis of the coordination polymers spheres (CPs) precursor
2.	Synthesis of the multi-shelled NiO-Co $_3O_4$ hollow spheres
3.	Synthesis of the multi-shelled NiO-Co <sub>3</sub> O <sub>4</sub> @S hollow spheres
4.	Visualized adsorption experiment4
5.	Materials Characterization4
6.	Electrochemical Measurements5
Figu	re S1. a) Schematic synthesis of multi-shelled NiO-Co <sub>3</sub> O <sub>4</sub> @S spheres6
Figu	re S2. (a)TGA analysis of the multi-shelled NiO-Co <sub>3</sub> O <sub>4</sub> @S spheres (b) pure sulfur
in N	$_2$ at a heating rate of 10 °C min <sup>-1</sup> 7
Figu	re S3. (a,b) FESEM and (c) TEM images and (d) XRD pattern of CPs precursor8
Figu	<b>re S4.</b> HRTEM image of NiO-Co <sub>3</sub> O <sub>4</sub> 9
Figu	Ire S5. FESEM image of (a) NiO and (b) Co <sub>3</sub> O <sub>4</sub> 10
Figu	<b>re S6.</b> TGA of (a) NiO@S and (b) Co <sub>3</sub> O <sub>4</sub> @S in N <sub>2</sub> at a heating rate of 10 °C min <sup>-</sup>
1	
Figu	<b>re S7.</b> XRD pattern of (a) NiO@S and (b) Co <sub>3</sub> O <sub>4</sub> @S composite <b>12</b>
Figu	<b>Ire S8.</b> Cycling performance of the (a) NiO@S and (b) Co <sub>3</sub> O <sub>4</sub> @S at 1 C <b>13</b>
Figu	re S9. (a) The cycling performance (b) rate performance and (c) discharge-charge
curv	ves of pure NiO-Co <sub>3</sub> O <sub>4</sub> within the voltage window of 1.7-2.8V14
Figu	are S10. (a, c) $N_2$ adsorption-desorption isotherms and (b, d) pore-size
dist	ributions of the NiO-Co <sub>3</sub> O <sub>4</sub> and NiO-Co <sub>3</sub> O <sub>4</sub> @S composite15

## **Experimental Section**

#### 1.Synthesis of the coordination polymers spheres (CPs) precursor:

All chemicals were purchased from pharmaceutical companies and can be used without any treatment.

In a typical experiment, 34.9 mg Nickel (II) nitrate hexahydrate, 34.9 mg Cobalt (II) nitrate hexahydrate and 39.8 mg of isophthalic acid (H<sub>2</sub>IPA) were dispersed into a mixture of 15 ml DMF and 15 ml acetone solvent, followed by sonication for 10 min to form a clear solution. The solution was poured into a Teflon-lined stainless-steel autoclave and held at 150 °C for 10 h. Finally, the dark brown powder was obtained, washed three times with ethanol and dried in an oven at 60 °C for 12h.

#### 2. Synthesis of the multi-shelled NiO-Co<sub>3</sub>O<sub>4</sub> hollow spheres:

Then, the original products were placed in a muffle furnace and heated at 450 °C for 30 minutes with a temperature increase rate of 3 °C min<sup>-1</sup>.

### 3. Synthesis of the multi-shelled NiO-Co<sub>3</sub>O<sub>4</sub>@S hollow spheres:

The weight ratio of multi-shelled NiO-Co<sub>3</sub>O<sub>4</sub> hollow spheres to sulfur was set to

1:2. The mixtures were heated at 155 °C in an oven for 12 h.

#### 4. Visualized adsorption experiment:

 $Li_2S_4$  was synthesized by mixing sulfur and lithium sulfide ( $Li_2S$ ) together in a molar ratio of 2.75:1 in a mixture of 1,2-dimethoxyethane (DME) and 1, 3dioxolane(DOL) (v/v=1:1) and stirred vigorously until all sulfur content was fully dissolved. The same weight (10 mg) of NiO-Co<sub>3</sub>O<sub>4</sub> and CB were added respectively to the as-prepared  $Li_2S_4$  solutions, and stood for 24 h. The sediment of the adsorbing agent was collected after standing for further 48 h. All solutions were prepared in a relatively sealed environment which filled Ar.

#### 5. Materials Characterization.

The microstructure and internal structure of the material were characterized by field emission scanning electron microscopy (FESEM, JSM-7800F) and transition electron microscopy (TEM, JEM-2100), respectively. XPS data was presented on an ESCALAB 250Xi electronic spectrometer. X-ray diffraction (XRD) patterns were investigated with an X-ray diffractometer (Maxima-X XRD-7000) and Cu Kα radiation. The sulfur content of the sample was examined by a thermogravimetric analyzer (TGA, Q50). The BET specific surface area and pore size distribution were performed by Quadrasorb evo 2QDS-MP-30 (Quantachrome Instruments, USA). Furthermore, ultraviolet visible light spectrums were obtained on a Shimadzu ultraviole-2550 spectrophotometer.

### **6.Electrochemical Measurements**

NiO-Co<sub>3</sub>O<sub>4</sub>@S, conductive carbon black, and polyvinylidene fluoride (PVDF) were mixed in a weight ratio of 70:20:10, and an appropriate amount of n-methy1-2-pyrrolidone (NMP) was added to make slurry and grind uniformly, and then coated on Al foil using doctor blade.

The standard cell mass loading was  $0.8-1.2 \text{ mg/cm}^2$ . 2032 coin type cells consisted of lithium foil as the anode and NiO-Co<sub>3</sub>O<sub>4</sub>@S as a cathode using 2400-Celgard as a separator.

The coin type batteries were assembled in an Ar filled glove box. The electrolyte was 1 M lithium bis-trifluoromethanesulfonimide and 1,2-dimethoxyethane/ 1,3-

dioxolane solution (v/v=1:1) with 1 wt % of LiNO<sub>3</sub>. Cyclic voltammogram test proceeded on an Arbin instrument with a voltage range of 1.7-2.8 V and a sweep rate of 0.1 mV s<sup>-1</sup>. Electrochemical charge/discharge was carried out by a Land Instruments testing system (Wuhan Kingnuo Electronic Co., China) between 1.7 V and 2.8 V (vs. Li/Li<sup>+</sup>). The current density was on the basis of the mass of sulfur (1 C = 1675 mA h g<sup>-1</sup>).



**Figure S1.** a) Schematic synthesis of multi-shelled NiO-Co<sub>3</sub>O<sub>4</sub>@S spheres.



Figure S2. (a)TGA analysis of (a) the multi-shelled NiO-Co $_3O_4@S$  spheres (b) pure sulfur in N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>



Figure S3. (a,b) FESEM and (c) TEM images and (d) XRD pattern of CPs precursor.



Figure S4. HRTEM image of NiO-Co<sub>3</sub>O<sub>4</sub>.



**Figure S5**. FESEM image of (a)  $Co_3O_4$  and (b) NiO.



Figure S6. TGA of (a) NiO@S and (b)  $Co_3O_4@S$  composite in N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>.



Figure S7. XRD pattern of (a) NiO@S and (b) Co<sub>3</sub>O<sub>4</sub>@S composite.



Figure S8. Cycling performance of the (a) NiO@S and (b)  $Co_3O_4@S$  composite at 1 C.



**Figure S9**. (a) The cycling performance and (b) rate performance and (c)dischargecharge curves of pure NiO-Co<sub>3</sub>O<sub>4</sub> within the voltage window of 1.7-2.8 V.



Figure S10. (a, c)  $N_2$  adsorption-desorption isotherms and (b, d) pore-size distributions of the NiO-Co<sub>3</sub>O<sub>4</sub> and NiO-Co<sub>3</sub>O<sub>4</sub>@S composite

Samples	Initial capacity (mAh g <sup>-1</sup> )	Cycle number	Decay rate (per cycle)
$\mathrm{Co}_3\mathrm{O}_4\mathrm{HC}@\mathrm{S}^{[1]}$	730 at 0.5 C	550	0.067%
NiO HC@S <sup>[1]</sup>	620 at 0.5 C	550	0.12%
Co <sub>3</sub> O <sub>4</sub> CC@S <sup>[2]</sup>	1231 at 0.5 C	200	0.14%
NiO/RGO-Sn@S <sup>[3]</sup>	1058 at 0.1 C	150	0.12%
NiO-Co <sub>3</sub> O <sub>4</sub> @S	897 at 1 C	200	0.1 %

Table S1 The comparisons of cathode materials for Li-S batteries

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