# **Supporting information**

# Hollow multishelled structural NiO as a "shelter" for high-performance Li-S

## batteries

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## **Experimental section**

### Preparation of the multishelled structural NiO hollow spheres materials

The multishelled structural NiO hollow sphere materials: Carbonaceous microspheres (CMSs) were prepared by a hydrothermal method, as described elsewhere.<sup>1</sup> Different shell materials were synthesized by adjusting the composition of solvent, adsorption time and temperature, and calcination temperature. Double-shelled NiO hollow spheres (2S-NiO HoMSs) were taken as an example. Nickel acetate was added into the mixed solution of water and ethyl alcohol. The solution was stirred until completely dissolved. 0.6 g CMSs were added to the above solution and absorbed in 35 °C water bath for 6 h. The Ni-adsorbed CMSs were filtered out through vacuum filtration, washed with deionized water for three times, and dried at 70 °C for 12 hours. Finally, the dry materials were heated up to 500 °C in the muff furnace at 1 °C min<sup>-1</sup> for 1 hours. The single-shelled structural NiO hollow spheres, triple-shelled structural NiO hollow spheres and quadruple-shelled structural NiO hollow spheres were denoted as NiO hollow spheres, 3S-NiO HoMSs and 4S-NiO HoMSs, respectively.

Materials	CMSs	Solvent (H2O:C2H5O H)	Adsorption Time and Temperature	Calcination
NiO hollow spheres	0.6 g	œ	25 °C, 3 h	5 °C min <sup>-1</sup> , 500 °C, 1 h
2S-NiO HoMSs	0.6 g	5:1	35 °C, 6 h	1 °C min <sup>-1</sup> , 500 °C, 1 h
3S-NiO HoMSs	0.6 g	1:1	45 °C, 6 h	1 °C min <sup>-1</sup> , 500 °C, 1 h
4S-NiO HoMSs	0.6 g	3:2	45 °C, 12 h	1 °C min <sup>-1</sup> , 500 °C, 1 h

Table S1 Parameters of the preparation of NiO materials.

## Preparation of Li<sub>2</sub>S<sub>8</sub> solution

S and Li<sub>2</sub>S in a molar ratio of 7:1 were added the into the mixed solution of 1,3dioxolane (DOL) and ethylene glycol dimethyl ether (DME) and stirred until completely dissolved at 70 °C for 48 h.

## Preparation of CC-S, AB/CC-S and NiO/CC-S electrodes

The slurry was prepared by mixing AB and PVDF at a weight ratio of 9:1 with NMP. Then the slurry was doctor-blade coated onto CC, to obtain the AB/CC. NiO/CC was obtained by coating the slurry with NiO, AB and PVDF at a weight ratio of 4.5:4.5:1 with NMP. The S-cathode electrodes were fabricated by adding Li<sub>2</sub>S<sub>8</sub> solution dropwise.

## Assembly of coin cell

Coin cells (type: 2032) were assembled in an Ar-filled glovebox by using CC-S, AB/CC-S and NiO/CC-S electrodes as cathodes, Li foils as anodes and polypropylene membrane as separators. The electrolyte was 1 M lithium

(DOL) and 1,2-dimethoxyethane (DME) (DOL: DME = 1:1, v:v) with 2 wt% LiNO<sub>3</sub>.

# **Electrochemical measurement**

Galvanostatic charge and discharge process measurements were conducted on a Neware Battery Testing Systems between 1.7-2.8 V. Cyclic voltammetry (CV) measurements were performed on a CHI660e electrochemical workstation.

## Characterization

The SEM and TEM images were characterized using scanning electron microscopy (SEM, JSM6335f, JEOL, Japan) and transmission electron microscope (TEM, JEM-2011, JEOL, Japan). The crystal structure of NiO materials was characterized by an X-ray diffraction (XRD) system (Smartlab, Rigaku, Japan).



Fig. S1 TEM images of NiO materials. (a) NiO hollow spheres, (b) 2S- NiO HoMSs,

(c) 3S- NiO HoMSs, (d) 4S- NiO HoMSs.



Fig. S2 XRD patterns of NiO materials.



Fig. S3 SEM images of AB.



Fig. S4 EDX mapping images of CC-S electrode.



Fig. S5 Histogram of different electrode. Left to right: CC-S, AB/CC-S, NiO

hollow spheres/CC-S, 2S-NiO HoMSs/CC-S, 3S-NiO HoMSs/CC-S, 4S-NiO

HoMSs/CC-S.

1. Z. Li, X. Lai, H. Wang, D. Mao, C. Xing and D. Wang, General synthesis of homogeneous hollow core-shell ferrite microspheres. J. Phys. Chem. C 2009, 113, 2792–2797.