

**Electronic Supplementary Information**

**Carbon-coated core-shell Li<sub>2</sub>S@C nanocomposites as high performance  
cathode material for Lithium-Sulfur batteries†**

Chunguang Chen<sup>a,b</sup>, Dongjiang Li<sup>a</sup>, Lu Gao<sup>a</sup>, Peter Paul R.M.L. Harks<sup>c</sup>, Rüdiger-A. Eichel<sup>b,d</sup>  
and Peter H.L. Notten<sup>a,b,\*</sup>

<sup>a</sup>*Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

<sup>b</sup>*Forschungszentrum Jülich (IEK-9), D-52425, Jülich, Germany*

<sup>c</sup>*Delft University of Technology, P.O. Box 5, 2600 AA Delft, The Netherlands*

<sup>d</sup>*RWTH Aachen University, D-52074 Aachen, Germany*

*\*Corresponding author email: p.h.l.notten@tue.nl*

## Experimental Section

Due to the high water and oxygen sensitivity of  $\text{Li}_2\text{S}$ , powder preparation, electrode fabrication, cell assembly and electrochemical measurement were carried out in an argon-filled glove box with a moisture and oxygen content of less than 0.1 ppm.

### Materials Synthesis

The experimental setup to synthesize carbon-coated  $\text{Li}@C$  materials and uncoated Li NP primarily consisted of a plasma reaction chamber and sample collecting room (Fig. S1). In order to collect the samples produced in the reaction chamber conveniently, Ar was pumped by a circulation pump through the reaction chamber and the as-produced powders were collected at a filter (Advantec MFS, Inc., Toyo Roshi Kaisha, Ltd., Japan). 15 g Li rods (purity >99.9%, Sigma Aldrich) were put in the reaction chamber. A 50% Ar and 50%  $\text{CH}_4$  mixture of 0.1 MPa was brought into the chamber as sparking atmosphere. The plasma sparking arc was ignited at an arc current of 120 A at 25 V. The flow rate of the Ar/ $\text{CH}_4$  circulation gas was  $100 \text{ L}\cdot\text{min}^{-1}$ . After plasma arc melting about 20 min, the system was cooled down. Before the NP were taken out from the collection room, the powders were passivated with argon to minimize contamination. The  $\text{Li}@C$  powders were then transferred to the lab-designed sulfurization setup using an Ar-filled transfer shuttle. The sulfurization setup is shown in Fig. S3. The as-prepared  $\text{Li}@C$  powders were transferred into a quartz canoe, which is placed in a horizontal quartz tube. The S atmosphere (heated at  $170 \text{ }^\circ\text{C}$ ) was carried by Ar and the total gas flow was 50 Scm (standard cubic centimeter per minute). The  $\text{Li}_2\text{S}@C$  nanocomposites were synthesized by sulfurizing the  $\text{Li}@C$  powders under S atmosphere for 6 h at  $150 \text{ }^\circ\text{C}$  and then post-annealing the samples for 24 h to remove S residues. The  $\text{Li}@C$  powders were weighed before and after the sulfurizing process to determine the amount of  $\text{Li}_2\text{S}$  in the synthesized  $\text{Li}_2\text{S}@C$  nanocomposite materials (92 wt.%).

Commercial Li<sub>2</sub>S powders were milled using a high energy ball milling machine (SPEX 8000M Mixer/Mill, Thomas scientific, Swedesboro, NJ, USA) in a hardened stainless steel vial at 1060 cycles per minute for 4 h with an interval resting time of 30 minutes to avoid overheating of the samples. The ball milling setup was placed in an Ar filled glove box. The weight ratio between milling balls and the Li<sub>2</sub>S powders was set to 15:1 and Zirconia balls (with 10 and 5 mm diameters) were used as milling balls.

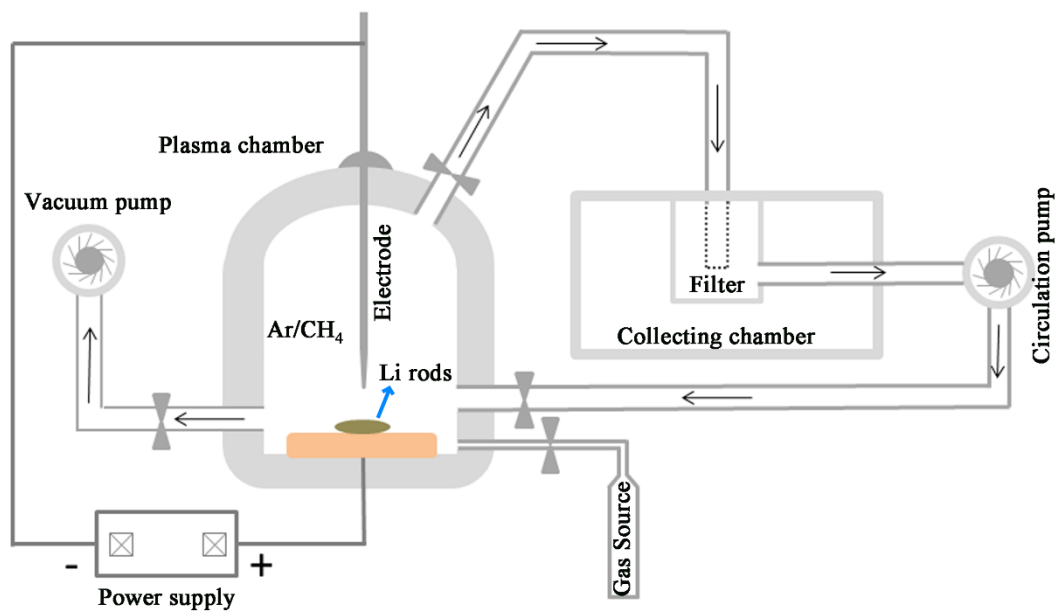
### **Materials Characterization**

Since Li<sub>2</sub>S is highly sensitive to oxygen and moisture, special precautions were taken during the materials characterization. The samples were tightly sealed by Kapton tape (no XRD background contribution) for X-ray diffraction (XRD) analyses and sealed in glass holders for the Raman measurements. Structural analyses (from 10° to 60° (2θ)) of the ball-milled Li<sub>2</sub>S, Li<sub>2</sub>S NP and Li<sub>2</sub>S@C were carried out by a XRD Diffractometer (Rigaku) with monochromatic CuKα radiation (λ=1.5406 Å). The Raman spectra were collected from 1800 to 200 cm<sup>-1</sup>, using a Renishaw Confocal Raman spectrometer with excitation wavelength of 488 nm. The morphology, particle size distribution and shape of the samples were measured by transmission electron microscope (TEM, JEOL-JSM-2100) at an accelerating voltage of 200 kV coupled with Energy Dispersive X-ray Spectroscopy (EDS). Scanning electron microscope (SEM, Philips/FEI XL 40 FEG) was used to check the morphology of the ball-milled Li<sub>2</sub>S powders.

### **Electrode fabrication and cell assembly**

The electrode slurries were prepared by mixing 65 wt.% of active material (ball milled Li<sub>2</sub>S, Li<sub>2</sub>S NP and Li<sub>2</sub>S@C), 30 wt.% of carbon, including the carbon coating in Li<sub>2</sub>S@C and Super-P carbon black as conductive additive, and 5 wt.% polymer binder (PVDF, polyvinylidene fluoride, Sigma-Aldrich) in N-methyl-2-pyrrolidinone. The slurries were casted onto the

surface (one side) of a two-sides of carbon coated aluminum foils (MTI Corp., USA), by means of the doctor blade method and dried by fully evaporating the solvent residues. The  $\text{Li}_2\text{S}$  mass loading on the current collector is about  $10 \text{ mg}\cdot\text{cm}^{-2}$ . The dried electrodes were punched into circular pieces. CR2032-type coin cells (MTI Corp., USA) were assembled with a polypropylene membrane (Celgard LLC., USA) used as separator and a metallic Li foil (Sigma-Aldrich) as counter/reference electrode. The electrolyte was composed of 1 M lithium bis(trifluoromethanesulphonyl)imide in 1:1 (v/v), 2-dimethoxyethane and 1,3-dioxolane with 1 wt.%  $\text{LiNO}_3$  additive. Galvanostatic cycling measurements of the assembled coin-type cells were carried out, using a M2300 galvanostat (Macoor, Tulsa, USA). Impedance spectroscopy (EIS) was carried out by an Autolab potentiostat in the frequency range from 200 kHz to 100 mHz.



**Fig. S1. Schematic representation of the plasma parking setup to synthesize Li NP and Li@C powders.**

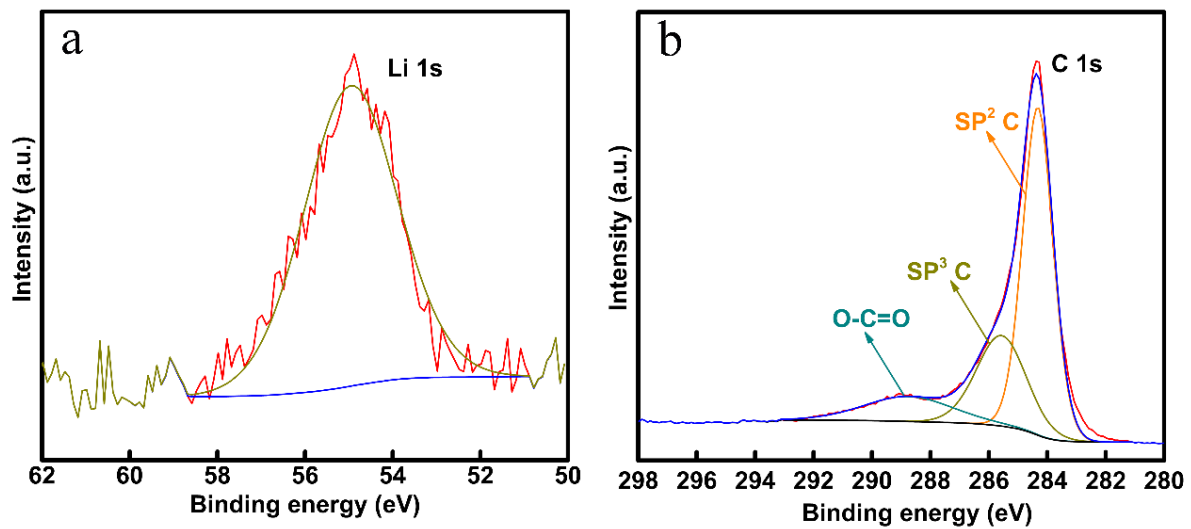
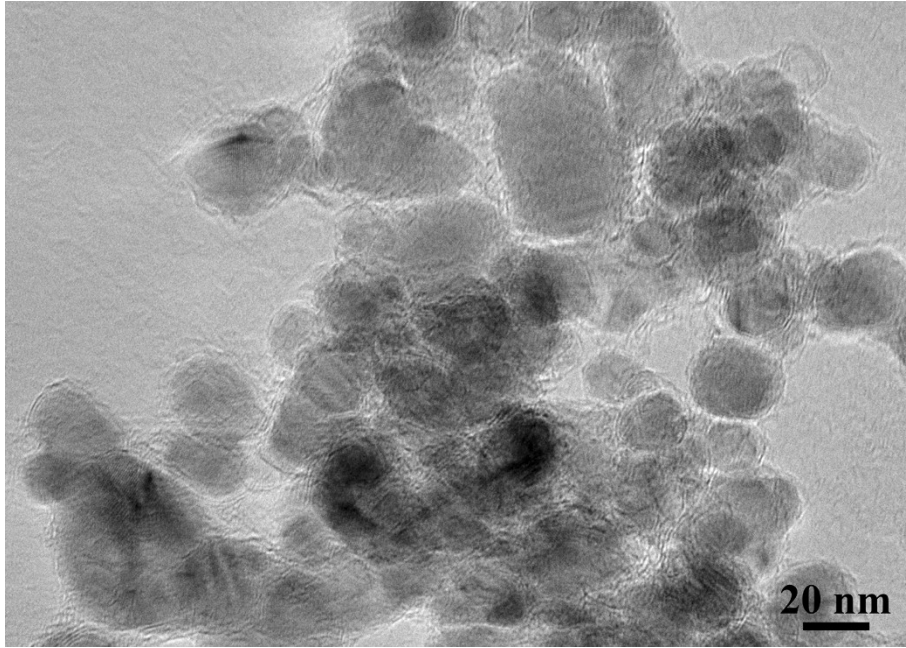
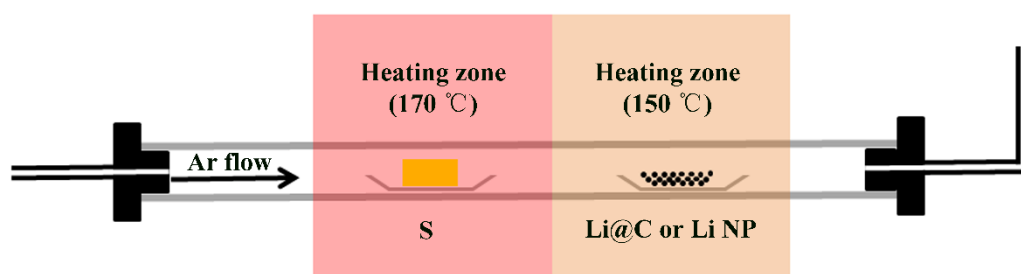


Fig. S2. XPS spectra of the as-synthesized Li@C powers. (a) Li 1s peak and (b) C 1s peak.

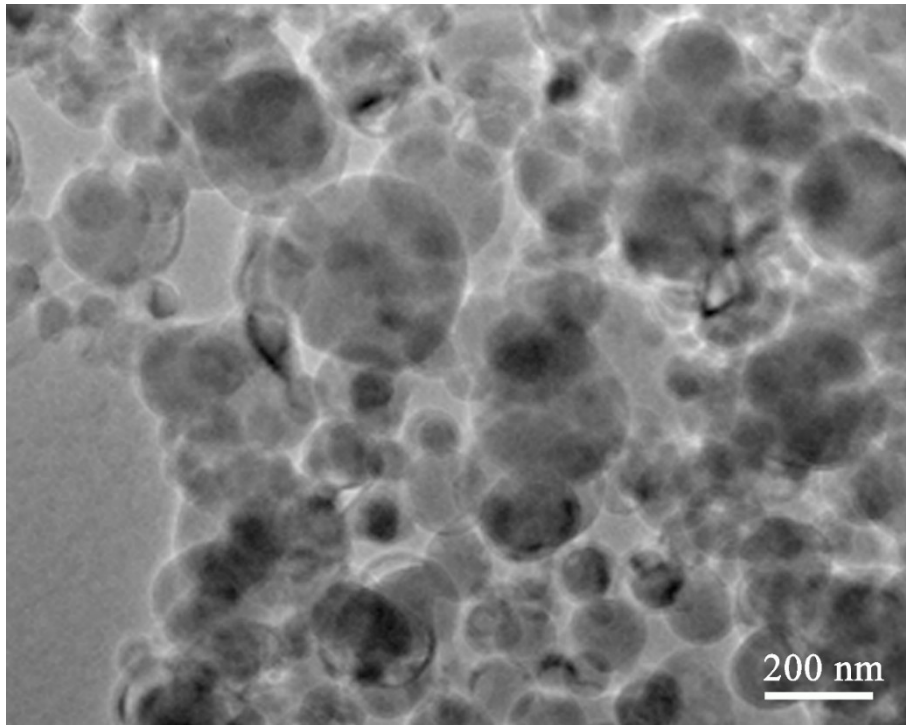


**Fig. S3. TEM image of as-synthesized Li@C power.**

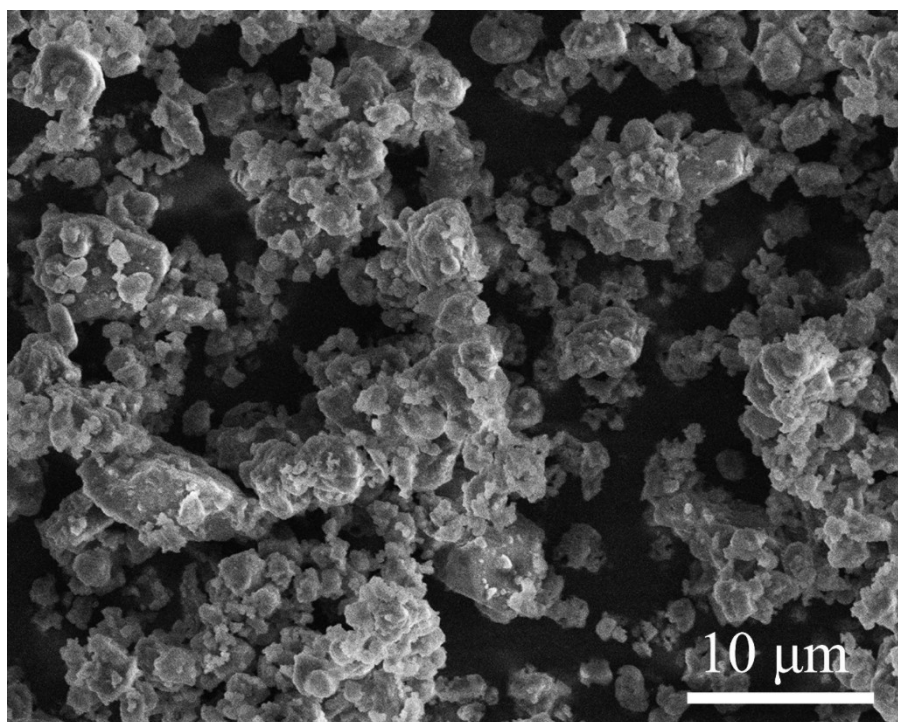


**Fig. S4. Sulfurization setup to convert Li into  $\text{Li}_2\text{S}$ .**





**Fig. S5. TEM image of the produced  $\text{Li}_2\text{S}$  NP.**



**Fig. S6. SEM image of ball-milled Li<sub>2</sub>S powders.**

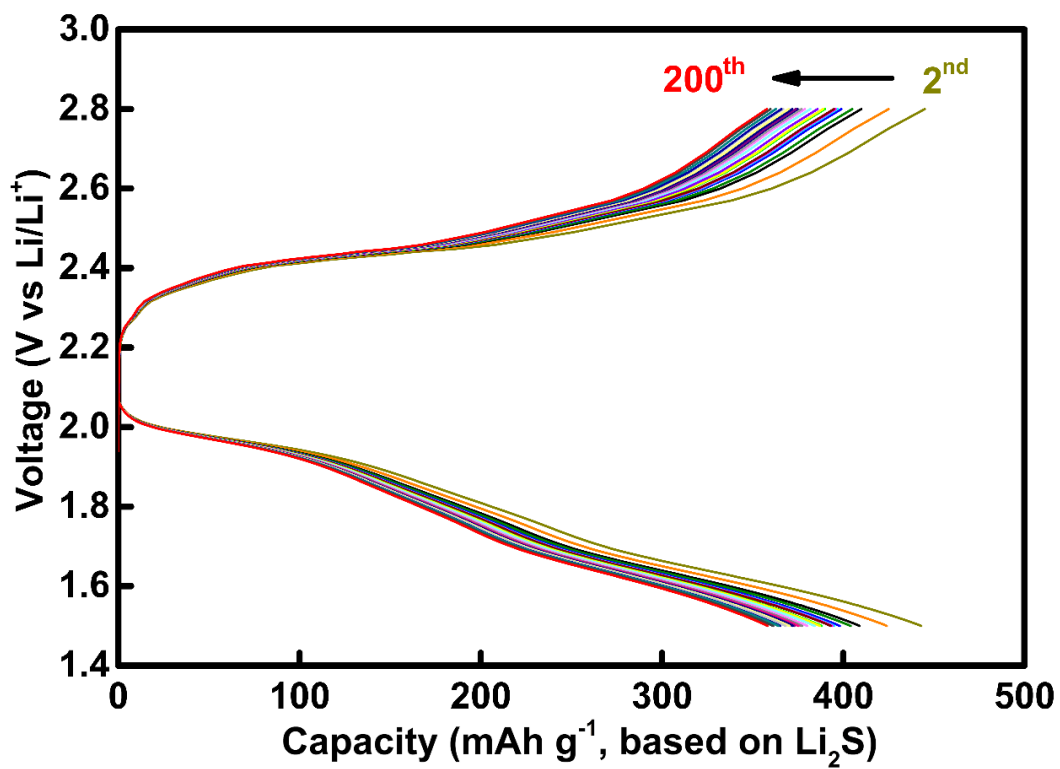
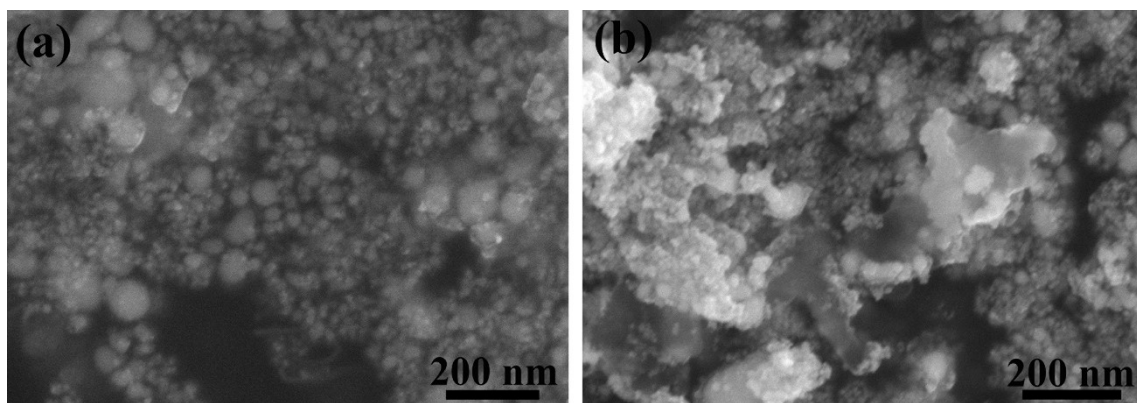


Fig. S7. Voltage profiles of a  $\text{Li}_2\text{S}@C$  electrode cycled at 10 C between cycle 2 and 200, only 10 cycle intervals are shown.



**Fig. S8. SEM images of a pristine (a) and cycled (200 cycles at 10 C discharge rate)  $\text{Li}_2\text{S}@C$  electrode (b).**