

Supporting Information

Improving the capacity of lithium–sulfur batteries by tailoring the polysulfide adsorption efficiency of hierarchical oxygen/nitrogen-functionalized carbon host materials

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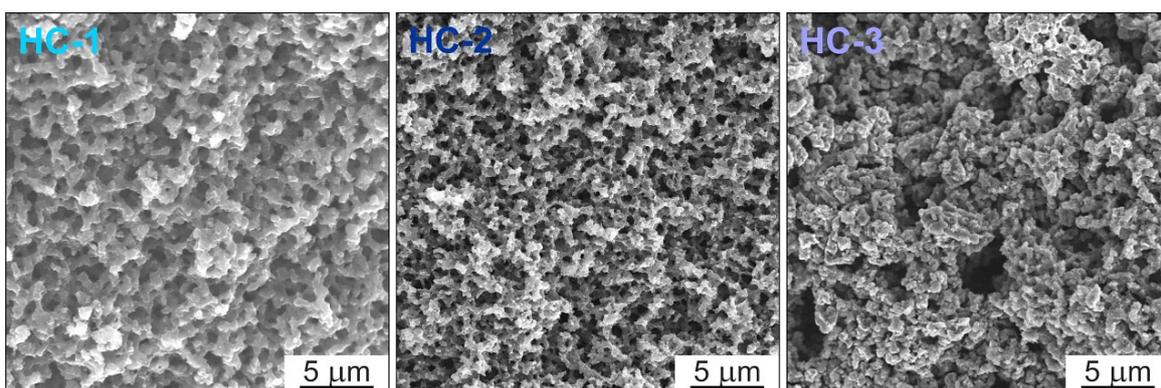


Fig. S1 Top view SEM images of HC-1, HC-2, and HC-3 showing the hierarchical architecture of the silica-templated carbons with varying amounts of nitrogen functionalities. As can be seen, there are no significant differences in macropore structure, in agreement with results from mercury intrusion porosimetry.

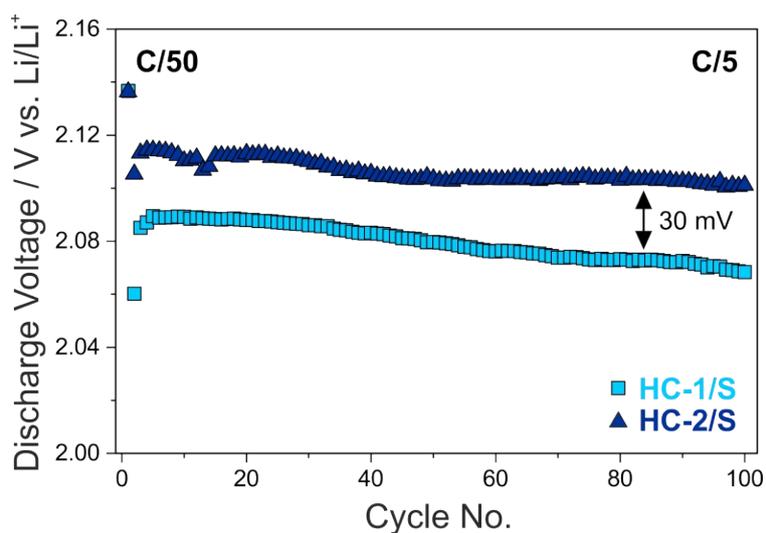


Fig. S2 Average discharge voltage versus the cycle number for HC-1/S and HC-2/S-based lithium–sulfur cells. After the activation cycle at C/50 was completed, the cells were cycled at a rate of C/5. The average discharge voltage was higher by up to 30 mV for the nitrogen-functionalized carbon/sulfur composite and decreased at a lower rate during cycling operation.

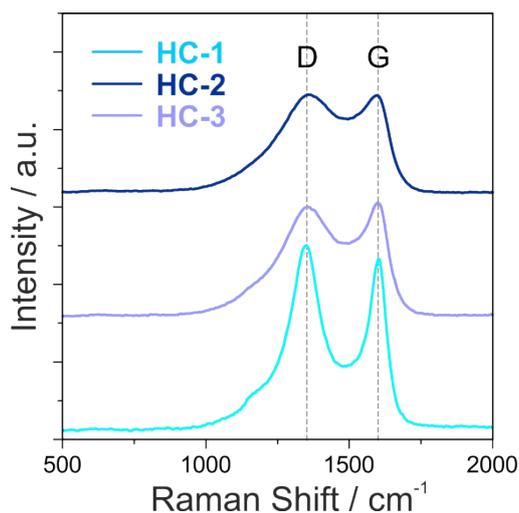


Fig. S3 Raman spectra of HC-1, HC-2, and HC-3. The D and G modes, which are characteristic of turbostratic carbon, are located at 1350 and 1600 cm^{-1} , respectively. As is evident, the degree of crystallinity decreased with increasing nitrogen content. According to Tuinstra and Koenig,¹ the lateral extent of the graphene layers was calculated to be in the range of 4.5 to 5.5 nm, which agrees with expectations for precursor-derived material carbonized at temperatures <1000 $^{\circ}\text{C}$ in the absence of any catalysts. We note that the room temperature electrical conductivity of HC-1 could not be determined with certainty by four-probe measurements. In contrast, the N-rich carbon revealed high electrical conductivity of around 5 S/cm, despite the apparent lack of crystallinity. The primary reason is that nitrogen dopants increase the electronic conductivity through injection of additional electrons into the structure.

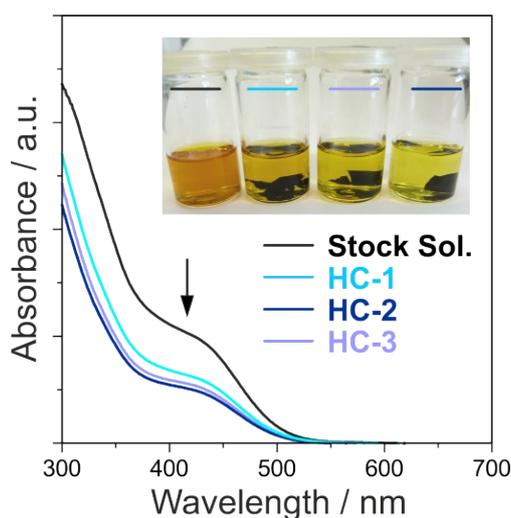


Fig. S4 UV-Vis spectra of lithium polysulfide solutions after adsorption by silica-templated carbons with varying amounts of nitrogen functionalities. The arrow indicates the change in absorption at 415 nm, on the basis of which the adsorption capacity was calculated. (inset) Photograph of vials showing the discoloration: stock solution, HC-1, HC-3, and HC-2 (from left to right).

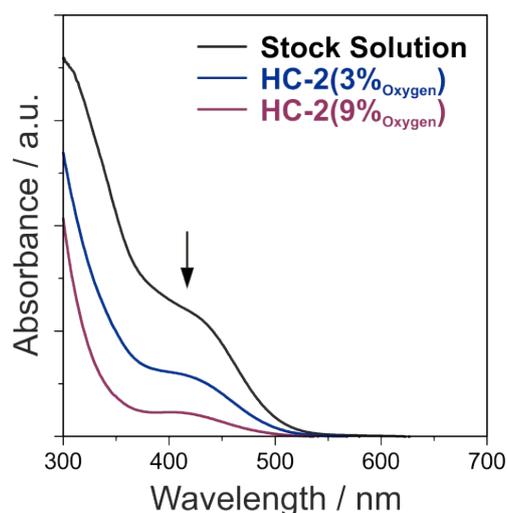


Fig. S5 UV-Vis spectra of lithium polysulfide solutions after adsorption by nitrogen-functionalized carbon HC-2 with varying amounts of oxygen functionalities. The incorporation of oxygen-containing surface groups significantly increased the polysulfide adsorption efficiency. The arrow indicates the change in absorption at 415 nm.

Appendix S1 Surface area requirement

To estimate the surface area requirement of a representative model polysulfide intermediate species, we made two general assumptions: (i) all the sulfur dissolves into the electrolyte to form Li_2S_4 , and (ii) the molecules adsorb as a monolayer on the carbon surface. First, we calculated both the total amount of sulfur and the concentration of Li_2S_4 in the ethereal electrolyte.

$$n(\text{S}_8) = \frac{\text{sulfur loading} \times \text{electrode area}}{\text{molar mass}} = \frac{0.003 \frac{\text{g}}{\text{cm}^2} \times 1.3 \text{ cm}^2}{256 \frac{\text{g}}{\text{mol}}} = 15.2 \mu\text{mol}$$

$$c(\text{Li}_2\text{S}_4) = \frac{\text{amount}}{\text{electrolyte volume}} = \frac{30.4 \mu\text{mol}}{39 \mu\text{l}} = 0.78 \frac{\text{mol}}{\text{l}}$$

Assuming the carbon surface (from BET analysis) to be fully accessible, we then calculated the total surface area of the hierarchical carbon host in the cathode (neglecting the carbon black additives).

$$S_{\text{Carbon}} = S_{\text{BET}} \times \text{total mass} = 400 \frac{\text{m}^2}{\text{g}} \times 0.0008 \text{ g} = 0.32 \text{ m}^2$$

Assuming S–S and Li–S bond lengths of 2.1 Å and 2.4 Å, respectively, the molecule length was estimated to be 11.1 Å (no bond angle) or 9.6 Å (bond angle of 120°).^{2,3} For horizontal adsorption configuration, the molecule occupies an area between 20 Å² (roughly rectangular area) and 70 Å² (roughly spherical area). And this corresponds to monolayer areas of the order of a few square meters (for closed packed structures), which is much larger than that provided by the hierarchical carbon. Even if we assume multilayer formation during the electrochemical reactions (or “larger” polysulfide species in the calculation), the area requirement would still exceed the carbon surface by far. In other words, the specific surface area is apparently not large enough to provide sufficient sites for the sulfur species to react.

1. F. Tuinstra and L. Koenig, *J. Chem. Phys.*, **1970**, *53*, 1126-1130.
2. M. Vijayakumar, N. Govind, E. Walter, S. D. Burton, A. Shukla, A. Devaraj, J. Xiao, J. Liu, C. Wang, A. Karim and S. Thevuthasan, *Phys. Chem. Phys. Chem.*, **2014**, *16*, 10923-10932.
3. X. Yu and A. Manthiram, *Chem. Mater.*, **2016**, *28*, 896-905.