Electronic Supplementary Information

Facile synthesis of Li_2S–polypyrrole composite structures for high-performance Li_2S cathodes

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Experimental Methods

Materials synthesis. Due to the sensitivity of Li_2S to moisture, all the material synthesis procedures were carried out in an argon-filled glove box with moisture and oxygen levels below 0.5 ppm. Commercial Li_2S particles (100 mg) were first dispersed in anhydrous methyl acetate (20 mL) containing anhydrous $FeCl_3$ (100 mg) as an oxidant and poly(vinyl acetate) (20 mg) as a stabilizing agent.[1] The monomer pyrrole (20 μL; 0.97 mg/μL) was then added, followed by overnight reaction at room temperature. The solution of as-synthesized Li_2S–PPy composites was washed by centrifugation three times with methyl acetate and allowed to dry in the glove box. For comparison, PPy nanocolloids were also prepared in the same way as that of Li_2S–PPy composites except without the Li_2S particles (Fig. S2).

Characterization. To prevent moisture contamination of Li_2S, special precautions were taken during characterization. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and elemental mapping were performed using a FEI XL30 Sirion SEM. High-resolution X-ray photoelectron spectroscopy (XPS) was carried out using a PHI 5000 VersaProbe. For SEM, EDX and XPS, the samples were first tightly sealed in foil/poly bags before being transferred into the chamber via an argon-filled glove bag. X-ray diffraction (XRD) patterns were obtained on a PANalytical X'Pert Diffractometer (Cu Kα radiation) after the samples were tightly sealed using Kapton tape. Raman spectroscopy was performed using a WITEC Raman spectrometer (531 nm excitation laser) after the samples were tightly sealed in a glass holder.

***Ab initio* simulations.** *Ab initio* simulations were performed using the Vienna *Ab Initio* Simulation Package (VASP) in the framework of density functional theory (DFT).[2,3] The projector augmented-wave (PAW) pseudopotential[4] and the generalized gradient approximation (GGA) exchange-correlation function described by Perdew-Burke-Ernzerhof (PBE)[5] were adopted. To ensure convergence, 500 eV was chosen as the cut-off energy of the plane-wave basis. The vacuum between PPy and its image exceeds 30 Å, while the distance between Li_2S and its image is no less than 15 Å along the periodic direction. These systems were large enough to avoid any artificial interaction caused by periodicity. The binding energy, E_b, was defined as the energy difference between the Li–S·/Li_2S–PPy adsorbed system (E_{tot}) and the summation of pure Li–S·/Li_2S cluster ($E_{LiS/Li2S}$) and pure PPy (E_{PPy}): $E_b = (E_{LiS/Li2S} + E_{PPy}) - E_{tot}$. The three-dimensional visualization models were constructed using VESTA 3 software.[6]

Electrochemical measurements. Due to the sensitivity of Li_2S to moisture, all the electrode preparation and cell assembly procedures were carried out in an argon-filled glove box with moisture and oxygen levels below 0.5 ppm. The Li_2S–PPy composites were ground with conductive carbon black (Super P) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 60: 35: 5 using a mortar and pestle, followed by dispersion in *N*-methyl-2-pyrrolidinone (NMP) to form a slurry. After overnight stirring, the slurry was then coated onto aluminum foil (carbon-coated; Exopack) using doctor blade and dried at 60^{o}C to form the working electrode. For comparison, pristine Li_2S cathodes were also prepared in the same way by mixing commercial Li_2S with Super P and binder in a weight ratio 60: 35: 5. 2032-type coin cells were assembled using lithium foil as the counter electrode. The electrolyte used was a freshly-prepared solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 1 M) in 1:1 v/v 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) containing $LiNO_3$ additive (1 wt%). Galvanostatic cycling was carried out using a 96-channel (Arbin Instruments) or a 8-channel (MTI Corporation) battery tester. The Li_2S–PPy composite cathodes were first activated at C/20 (1C = 1,166 mA g^{-1}) by charging to a high cutoff voltage of 3.8 V vs. Li^+/Li to overcome the initial potential barrier (Fig. S4),[7] followed by discharge to 1.8 V. Galvanostatic cycling was then carried out from 1.8 to 2.6 V vs. Li^+/Li. The typical mass loading of Li_2S was ~1 mg cm^{-2} and specific capacity values were calculated based on the mass of Li_2S.

Electrolyte testing. For analysis of sulfur content in the electrolyte, a sulfur-free lithium salt of $LiClO_4$ (1 M) in 1:1 v/v DME/DOL solution with $LiNO_3$ (1 wt%) was used as the electrolyte (25 μL in each cell). All other cell assembly procedures are the same as that described above. The cells were disassembled at various points 1 to 10 during a discharge/charge cycle (Fig. 4c), where 100% depth of discharge (point 6) and 100% state of charge (point 10) corresponds to the maximum discharge and charge capacities attained by the cells respectively. The contents of the disassembled cells (cathode, anode and electrolyte-soaked separator) were washed with DOL solution. This polysulfide-containing solution was then oxidized with concentrated HNO_3 and diluted with deionized water for analysis of sulfur content using inductively coupled plasma-optical emission spectroscopy (ICP-OES; Thermo Scientific ICAP 6300 Duo View Spectrometer).[8]

References:

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	Li	**S**	**C**	**N**	**H**
at% (measured)	-	63.2	29.4	7.4	-
wt% (calculated)	25.9	59.9	10.4	3.1	0.7
Composition	85.8 wt% Li_2S		14.2 wt% PPy		

Table S1. Elemental composition of the Li_2S–PPy composites determined using large-area EDX analysis, showing the measured at% of the various elements (except Li and H which cannot be measured by EDX). The wt% of Li was calculated from the at% of S based on the empirical formula Li_2S. The relative at% of C: N is close to the empirical formula of PPy (C_4H_3N), from which the wt% of H can be deduced. From the results, we can determine the overall Li_2S content in the Li_2S–PPy composites to be ~86 wt%. This is consistent with the relative amounts of Li_2S and pyrrole monomer added during the synthesis process.

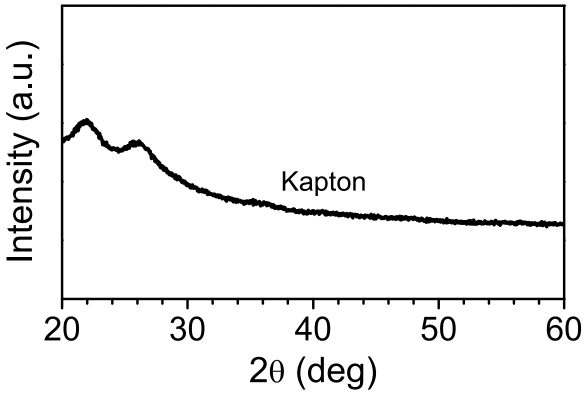

Fig. S1 XRD pattern of Kapton tape used to protect the air-sensitive Li_2S samples during XRD characterization.

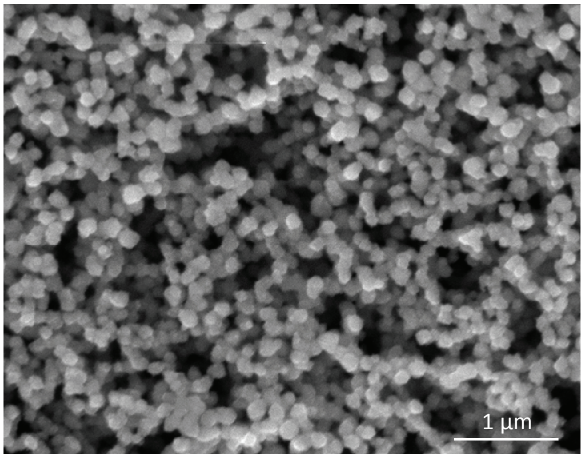

Fig. S2 SEM image of PPy nanocolloids prepared in the same way as that of Li_2S–PPy composites except without the Li_2S particles.

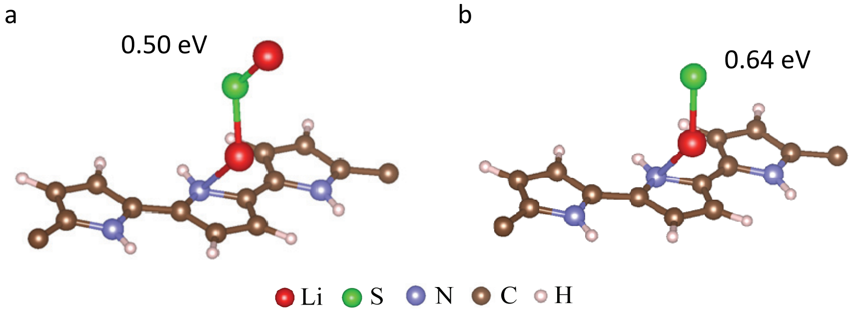

Fig. S3 *Ab initio* simulations showing the most stable configuration (Li–N interaction) and calculated binding energies of PPy with **(a)** Li_2S and **(b)** $Li\text{–}S\cdot$ species (which can be used to represent the relevant end groups in the general class of lithium polysulfides ($Li\text{–}S\text{–}S_{n-2}\text{–}S\text{–}Li$; Li_2S_n in short, $4 \le n \le 8$)).[8]

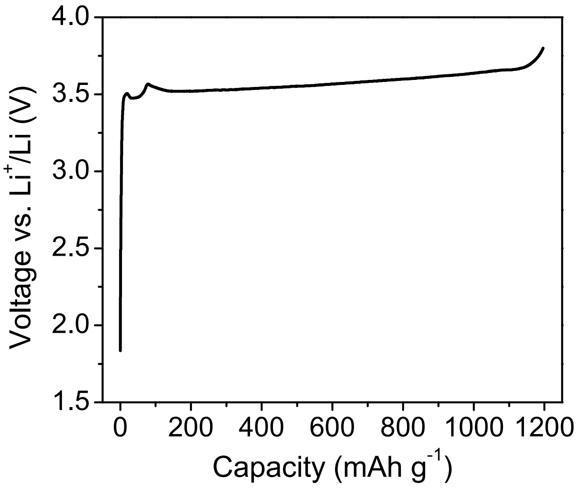

Fig. S4 Typical activation charge profile of the Li_2S–PPy composite cathodes. A high cutoff voltage of 3.8 V vs. Li^+/Li was used to overcome the initial potential barrier.[7] The initial charge process involves removal of Li^+ and e^- from Li_2S ($Li_2S \rightarrow Li_{2-x}S + x\,Li^+ + x\,e^-$), which is kinetically difficult due to the insulating nature of Li_2S, both ionically and electronically. Moreover, because of the micrometer-size range of Li_2S particles used in our work, the diffusion of Li^+ in the bulk of the particles is expected to be kinetically difficult as well.

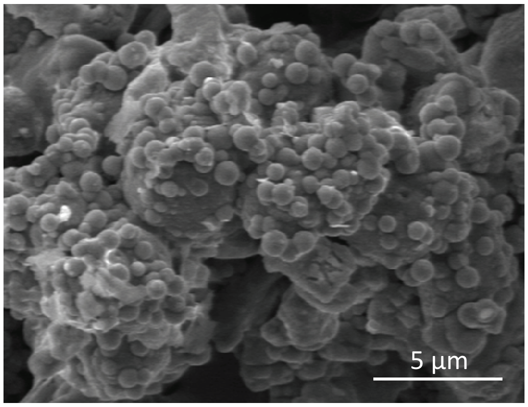

Fig. S5 Morphology of the Li_2S–PPy composite cathodes after 50 cycles at 0.2 C. The cell was disassembled in the discharged state after the voltage was maintained at 1.8 V vs. Li^+/Li for over 20 h. Because of effective constraining of intermediate polysulfide species during cycling, the solid Li_2S formed at the end of discharge does not precipitate randomly and irregularly all over the electrode and the original morphology is largely preserved.