Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Lowering Charge Overpotential of Li_2S via Inductive Effect of Phenyl Diselenide in Li-S Batteries

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Experimental Section:

Materials: Commercial lithium sulfur electrolyte (1.0 M LiTFSI in DOL:DME =1:1 vol with 1.0 wt.% $LiNO_3$, Canrd), phenyl diselenide (PDSe, $C_{12}H_{10}Se_2$, >97%, Tokyo Chemical Industry Co. Ltd), Lithium sulfide (Li_2S, 99.98%, Alfa Aesar), anhydrous ethanol (99.7%, Sinopharm Reagent Co. Ltd) were purchased and used as received.

Preparation of PDSe catholyte and Li_2S/PDSe mixture solutions: The PDSe catholyte was prepared by dissolving PDSe in lithium sulfur electrolyte to form 0.5 M solution. The Li_2S solution was prepared by dissolving Li_2S power in anhydrous ethanol to render 0.5 M solution. To prepare Li_2S/PDSe mixtures, Li_2S and PDSe solutions with appropriate amounts of Li_2S and PDSe (Li_2S: PDSe molar ratios = 2:1, 4:1, 6:1 and 8:1) were mixed to render 0.5 M solutions.

Preparation of Li_2S and Li_2S/PDSe composite electrodes: Commercial binder free carbon nanotube paper called buckypaper (NanoTechLabs, Inc) was used as the current collector in this study. The carbon paper was cut into 1.13 cm^2 discs (d = 12 mm, about 2.2 mg each) and dried at 110 ºC 24 h in a vacuum oven before use. First, 10 μL of Li_2S solution was added into the carbon paper, and then the Li_2S electrode was dried at room temperature inside the glove box. The Li_2S electrode was flipped, and additional Li_2S solution was added, and then the electrode was dried again. This procedure was repeated at least three times until the mass of Li_2S in the electrode was calculated to be 1.13 mg, corresponding to 1 mg cm^{-2} in the electrode. Finally, the Li_2S electrode was dried in the gloved box at room temperature for another 48 h to completely remove ethanol for the control experiment. The Li_2S/PDSe composite electrodes were prepared by following the same procedure, the mass of Li_2S in the Li_2S/PDSe composite electrodes was controlled to be 1.13 mg. The masses of PDSe in the Li_2S/PDSe composite electrodes are 3.85 mg (Li_2S:PDSe molar ratio = 2:1), 1.92 mg (Li_2S:PDSe molar ratio = 4:1), 1.28 mg (Li_2S:PDSe molar ratio = 6:1), and 0.96 mg (Li_2S:PDSe molar ratio = 8:1).

Cell fabrication and electrochemical evaluation: CR2032 Coin cells were fabricated in an Ar-filled glove box. First, 20 μL electrolyte was added into the prepared Li_2S and Li_2S/PDSe composite electrodes. Then a Celgard 2400 separator was placed on the top of the electrode followed by 20 μL additional electrolyte and lithium metal anode. Finally, the cell was crimped and taken out of the glove box for electrochemical evaluation. PDSe cells were fabricated for control experiments. An appropriate amount of PDSe catholyte was added into carbon paper, the following procedure is same as that in preparing the Li_2S/PDSe cells.

Cells were galvanostatically cycled on a LANHE battery cycler at different C rates (1C = 1166 mA g^{-1}, based on the mass of Li_2S in the cells). The Li_2S and Li_2S/PDSe cells were initially charged to 2.8 V at 0.05 C rate, then cycled between 1.8-2.8 V at 0.1 C and 0.2 C rates, 1.75−2.8 V at 0.5 C rate, 1.7−2.8 V at 1 C rate, and 1.65−2.8 V at 2 C. For the Li_2S and Li_2S/PDSe cells, the cyclic voltammetry (CV) was performed on a Bio-Logic VMP-3 potentiostat with a scan rate of 0.02 mV s^{-1} between 2.8-1.8 V after the initial anodic scan from OCV to 2.8 V. For the PDSe cell, the potential was swept from OCV to 1.8 V and then swept back to 2.8 V at a scan rate of 0.02 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) data were collected with a Bio-Logic VMP-3 impedance analyzer in the frequency range of 100 kHz−0.1 Hz.

Characterizations:

The morphological characterizations were conducted with a Carl Zeiss Sigma 500 field emission scanning electron microscopy (SEM). The elemental mapping was performed with energy-dispersive X-ray spectroscopy (EDX) attached to the SEM. X-ray photoelectron spectroscopy (XPS) were analyzed with a 5000 VersaProbe II XPS spectrometer with monochromatic Al Kα radiation.

Fourier Transform Infrared (FTIR) absorption spectra were collected using a Nicolet NEXUS-470 FTIR spectrometer. Samples were prepared by grinding the compounds with dried KBr power and then pressing it into tablet using an FTIR die set in an Ar-filled glove box.

A Waters ACQUITY UPLC I-Class PLUS liquid chromatogram coupled to a Waters Xevo G2-XS QTof mass spectrometer was used to verify the existence of PhSe• in the Li_2S/PDSe composite electrode. The column is ACOUITY UPLC BEH C18 LC Column (2.1-100 mm, Waters). The fresh Li_2S/PDSe electrode sample was dissolved in chromatographic methanol and it was filtered. 0.5 µL of the solution was tested in electrospray ionization (ESI) positive mode, and the first-order mass spectrometry model was applied to ensure that no fragment ions are produced during the testing process.

Theoretical Computation:

The Li_2S and PDSe were optimized at the density functional theory (DFT) with PBE0/6-31G(d) level implemented with polarizable continuum model (PCM) to consider the solvent effect, and the static dielectric constant of DME ($\epsilon = 7.07$ at 298.15K) was used. The vibrational frequency analysis was performed to verify the optimized geometries are local minima. All the optimizations were manipulated by the Gaussian 09 suite.

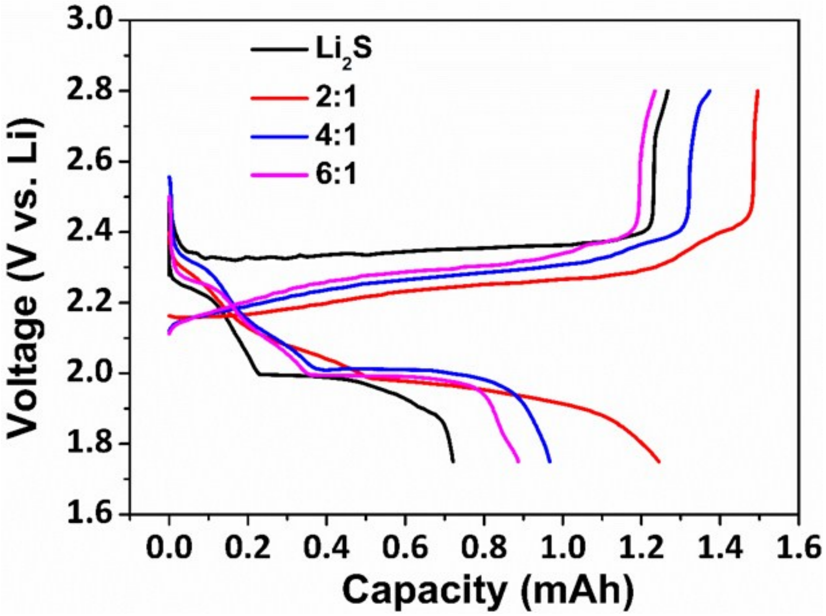

Figure S1. Initial charge/discharge voltage profiles of the Li_2S and Li_2S/PDSe electrodes with Li_2S:PDSe molar ratios of 2:1, 4:1, and 6:1.

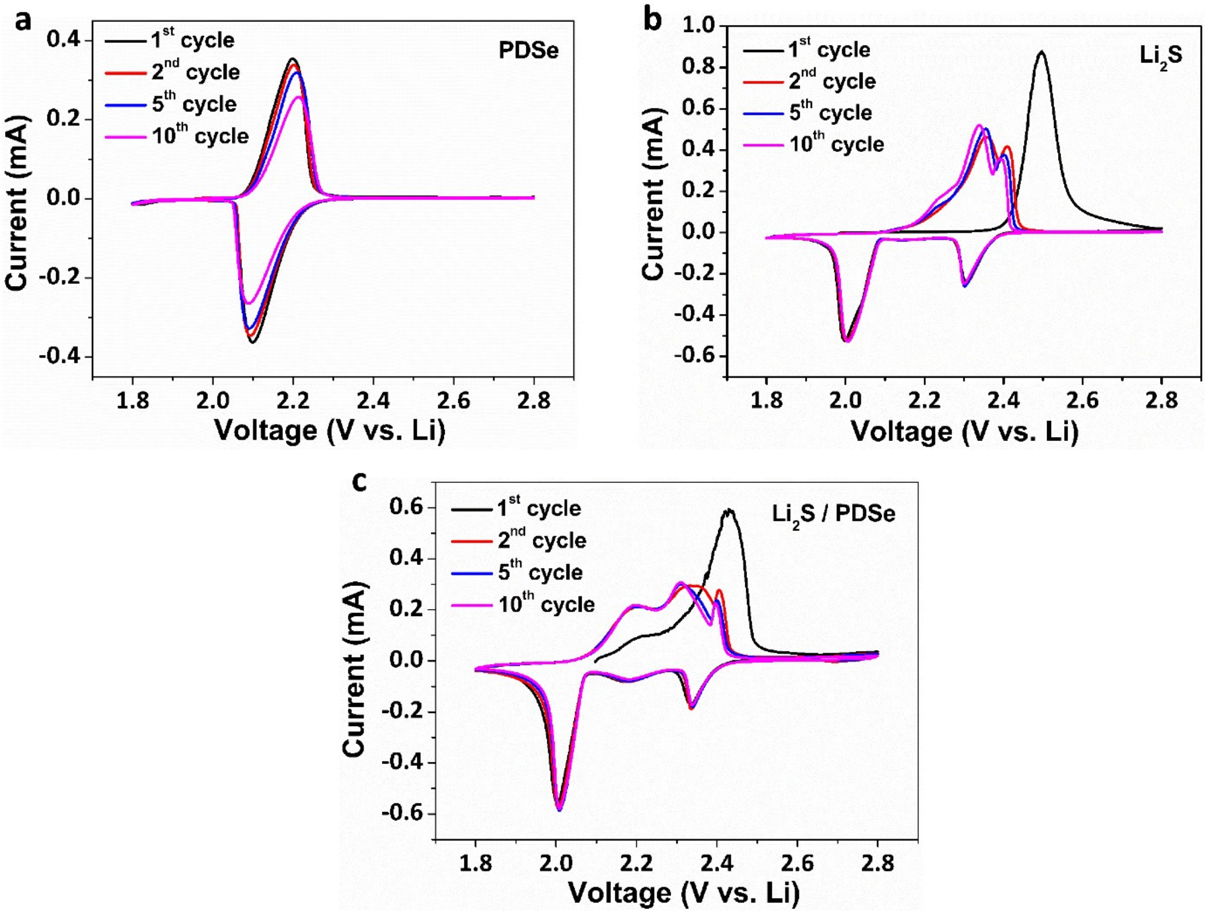

Figure S2. CV of cells with (a) PDSe, (b) Li_2S, and (c) Li_2S/PDSe electrodes cycled at a scanning rate of 0.02 mV s^{-1}. The Li_2S:PDSe molar ratio is 8:1.

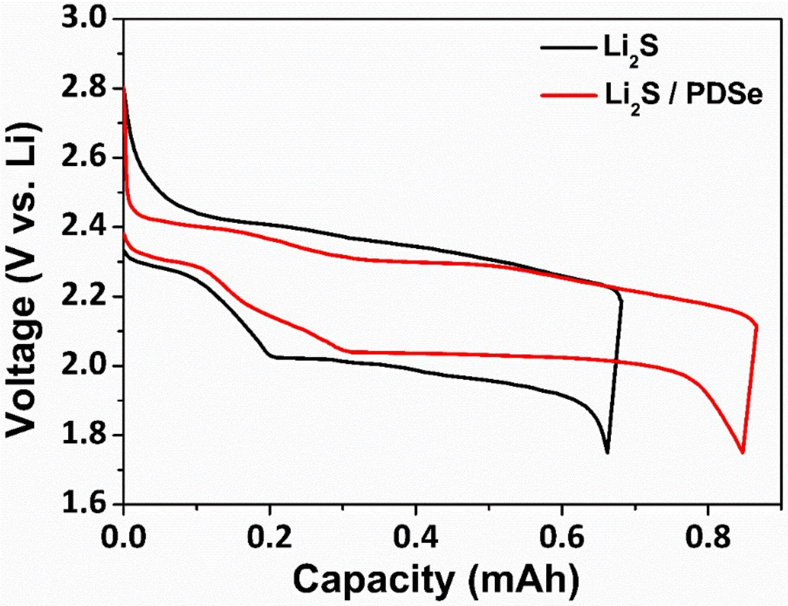

Figure S3. Voltage profiles of Li_2S and Li_2S/PDSe electrodes with the Li_2S:PDSe molar ratio of 8:1 at 0.5 C rate. The Li_2S:PDSe molar ratio is 8:1.

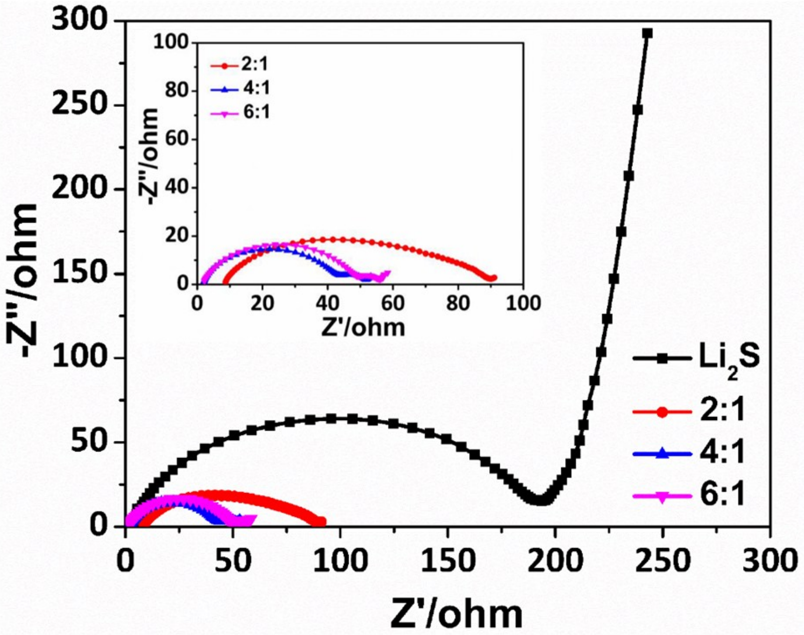

Figure S4. Nyquist plots of Li_2S and Li_2S/PDSe cells with the Li_2S:PDSe molar ratios of 2:1, 4:1, and 6:1. The insert shows the local amplification of impedance spectra of the Li_2S/PDSe cells.

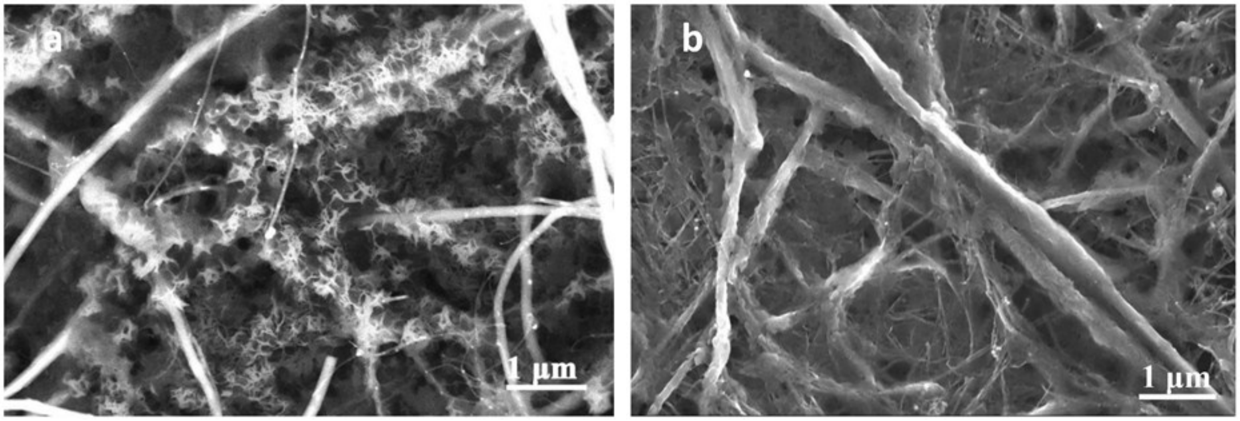

Figure S5. High magnification SEM images of (a) the fresh Li_2S and (b) Li_2S/PDSe electrodes when the molar ratio of Li_2S to PDSe is 8:1.

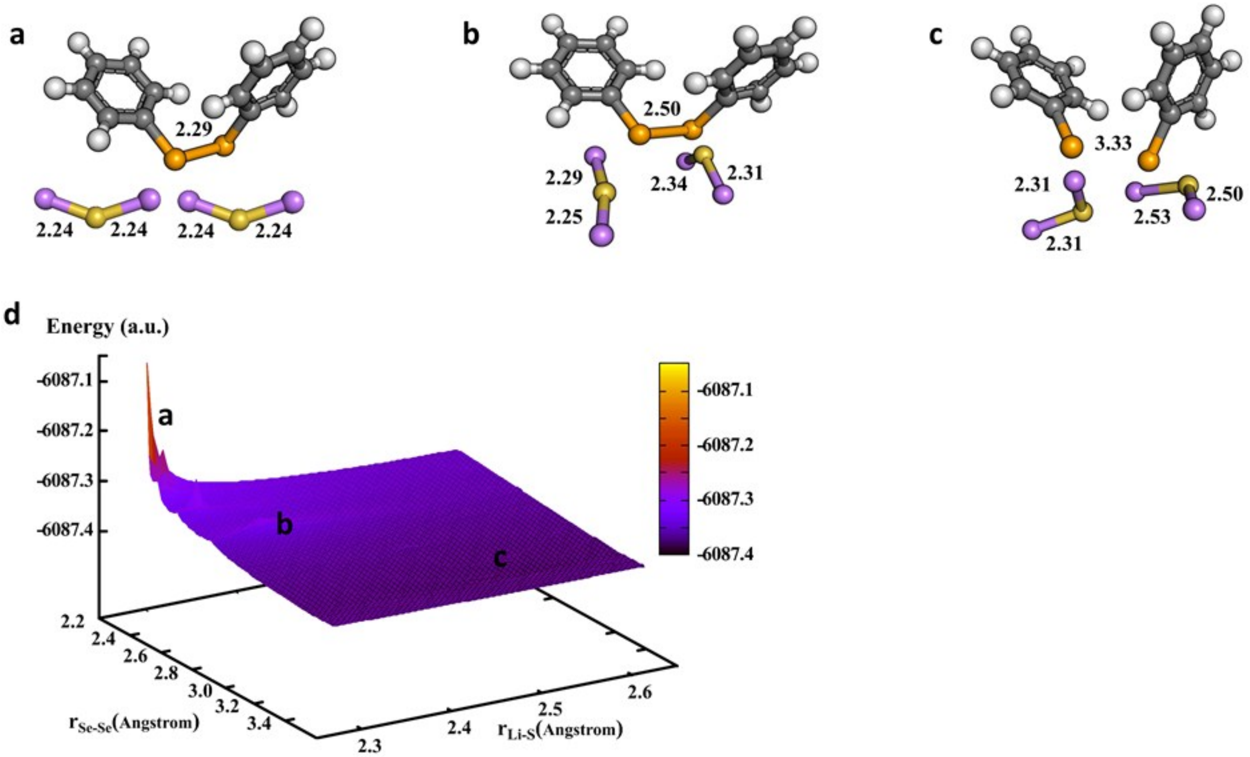

Figure S6. (a-d) Theoretical models for the interactions between Li_2S and PDSe in ethanol environment with the dielectric constant of 24.852 used. The monomers of Li_2S and PDSe are shown in (a), and the initial and final complexes are shown in (b) and (c) as well as the possible potential energy surface is given in (d). In the models, the carbon, hydrogen, lithium, sulfur and selenium elements are shown in green, white, purple, yellow and dark yellow, respectively.

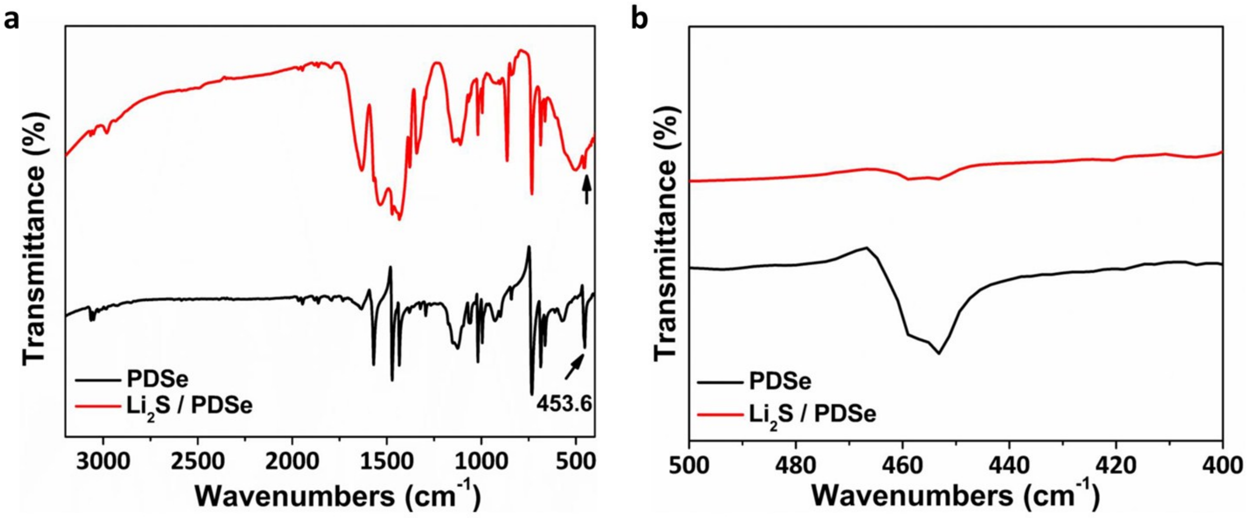

Figure S7. (a) FTIR spectra of PDSe and Li_2S/PDSe. (b) The enlarged spectra of the out of plane phenyl ring twist peaks in PDSe and Li_2S/PDSe. The Li_2S:PDSe molar ratio is 8:1.

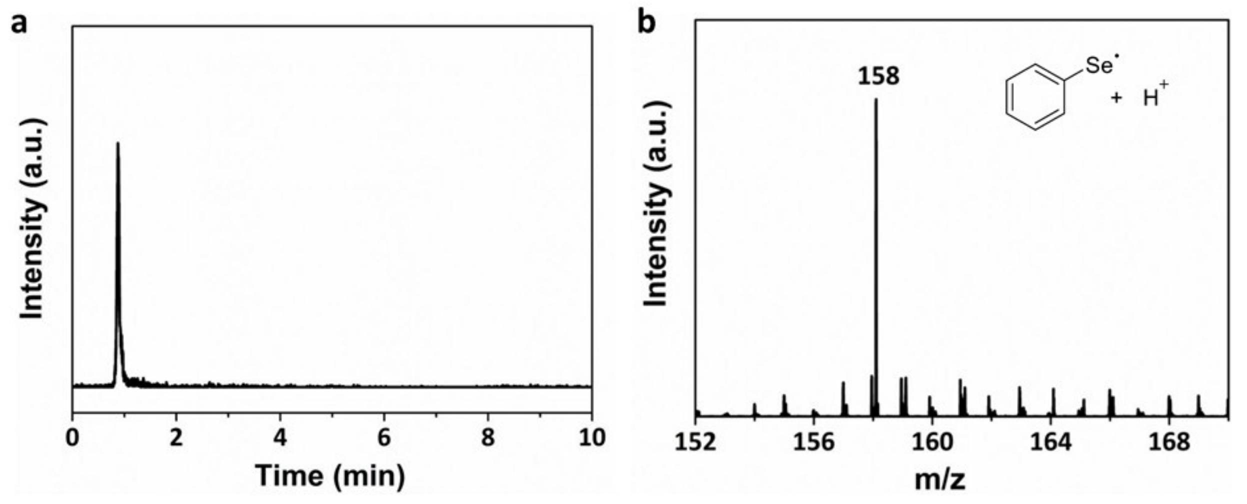

Figure S8. Extracted ion chromatogram of the fresh Li_2S/PDSe composite electrode and corresponding mass spectrum.

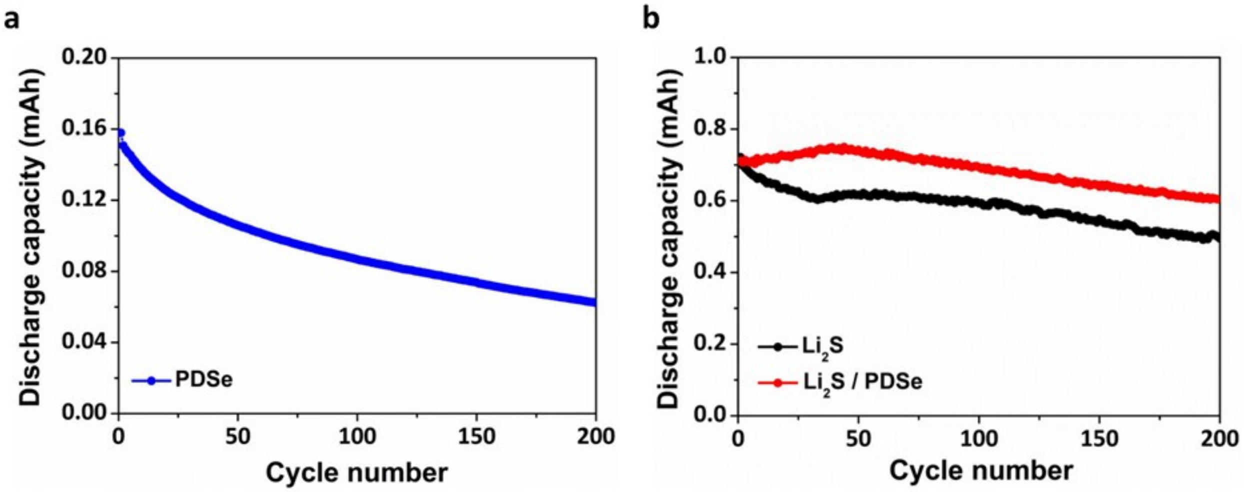

Figure S9. Cycling performance of (a) PDSe and (b) Li_2S and Li_2S/PDSe electrodes at 0.5 C rate, the contributed capacities of PDSe as shown in (a) were extracted from those of the Li_2S/PDSe electrode shown in (b). The Li_2S:PDSe molar ratio is 8:1.

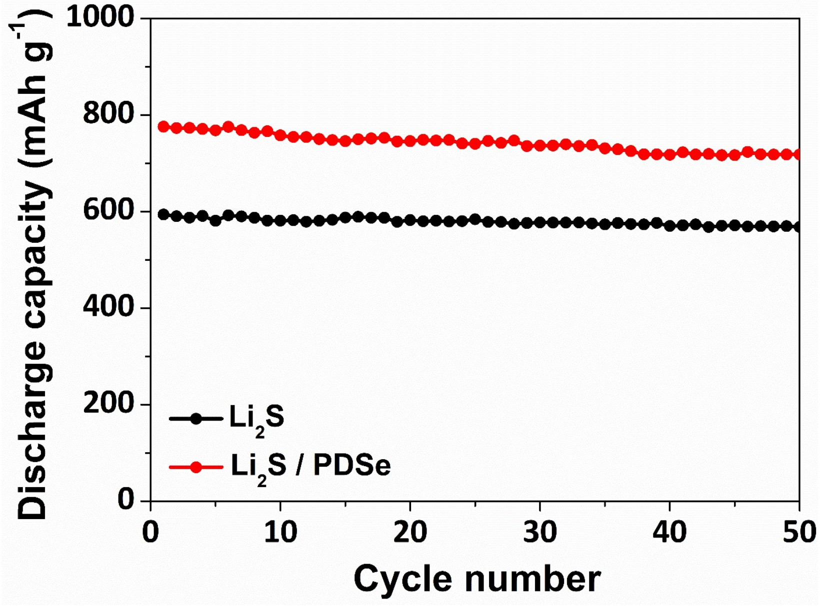

Figure S10. Cycling performance of Li_2S and Li_2S/PDSe cells at 0.2 C rate.

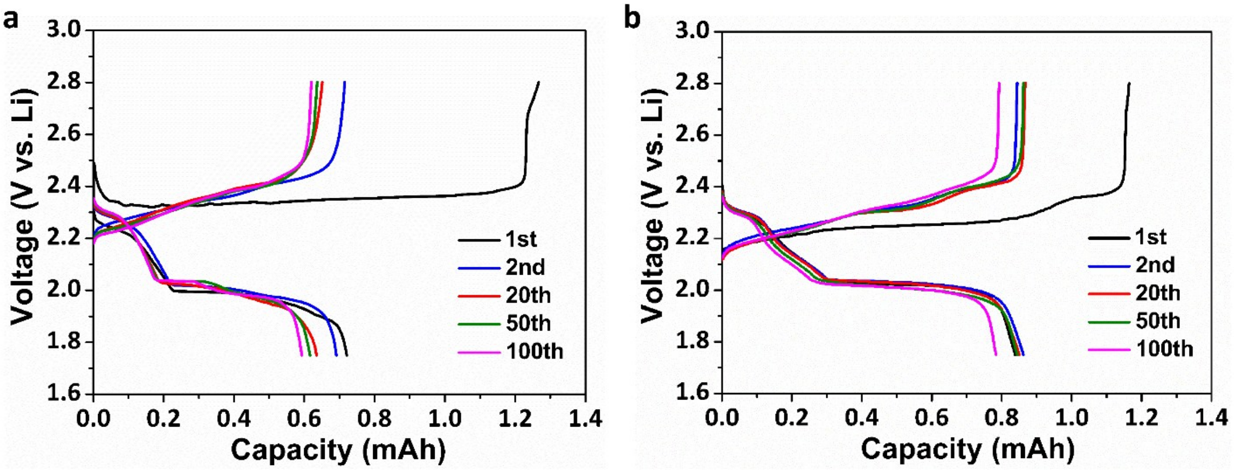

Figure S11. Charge/discharge voltage profiles of (a) Li_2S and (b) Li_2S/PDSe electrodes at different cycles at 0.5 C rate. The Li_2S:PDSe molar ratio is 8:1.

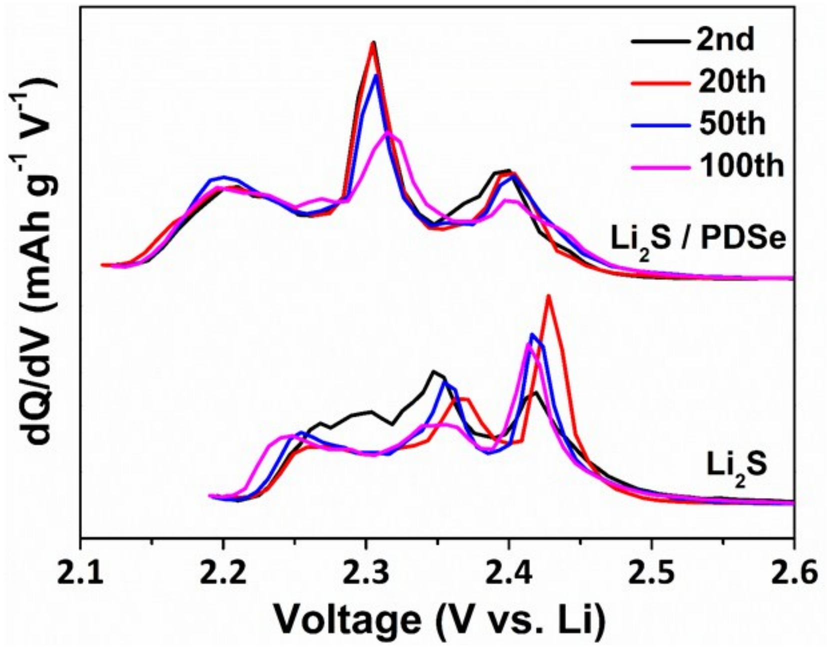

Figure S12. dQ/dV of Li_2S and Li_2S/PDSe electrodes derived from data presented in Figure S11.

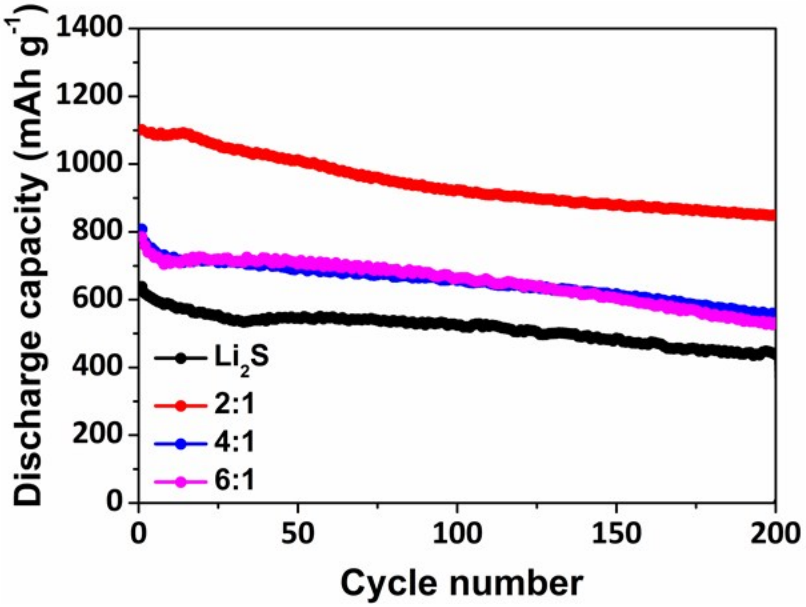

Figure S13. Cycling stability of Li_2S and Li_2S/PDSe cells with the Li_2S:PDSe molar ratios of 2:1, 4:1, and 6:1 at 0.5 C rate, the cells were first charged at the 0.05 C rate, and then cycled between 1.75 and 2.8 V at the 0.5 C rate.

Table S1. Coordinates of complexes b and c at the PBE0/PCM/6-31G(d) level.

Coordinates of complexes b and c:

Complex b:

Element	X	Y	Z
C	-2.13551300	-2.38552400	-0.26150100
C	-0.95883800	-1.64737200	-0.02339400
C	-0.00943300	-2.15456100	0.88014800
C	-0.23486100	-3.36996200	1.52477800
C	-1.40032500	-4.10145900	1.28265600
C	-2.34764000	-3.60253900	0.38972300
H	-2.89048100	-1.99381600	-0.94264500
H	0.89790400	-1.58928500	1.07553500
H	0.51315000	-3.75417500	2.21564900
H	-1.56731800	-5.05085400	1.78496200
H	-3.26172700	-4.16091600	0.19768800
C	2.73636200	0.47052200	-0.19449500
C	3.89591700	0.95208700	0.43016900
C	2.87391200	-0.45376400	-1.23568400
C	5.15962700	0.52774300	0.02125200
H	3.81716100	1.67226700	1.24592600
C	4.13985500	-0.87975800	-1.64130800
H	1.98429400	-0.84335500	-1.72728000
C	5.28701900	-0.39148000	-1.01865900
H	6.04723000	0.91577400	0.51801400
H	4.22620600	-1.59971200	-2.45304100
H	6.27100900	-0.72495900	-1.33856100
Se	-0.71693000	0.02832400	-0.97573800
Se	0.95886500	1.15704500	0.48058900
S	0.78159500	2.67484700	2.14265400
Li	0.69578000	4.02282700	0.27577200
Li	-0.11439800	3.15095500	4.24455900
S	-2.85709200	1.25791600	-1.60476300
Li	-2.76798500	0.28180200	0.46476100
Li	-3.36273500	2.02980600	-3.65345800

Complex c:

Element	X	Y	Z
C	-1.38070800	-3.09816700	-1.28413700
C	-0.80967400	-1.86645600	-0.93184500
C	-0.34090400	-1.70952800	0.38282500
C	-0.45475700	-2.74333700	1.30970500
C	-1.02847900	-3.96039000	0.94839000
C	-1.48778200	-4.13107100	-0.35699000
H	-1.74430900	-3.24337200	-2.29806300
H	0.12440400	-0.77052800	0.67560200
H	-0.08418900	-2.59419800	2.32143300

H	-1.11302200	-4.76666400	1.67210800
H	-1.93433000	-5.07616500	-0.65800400
C	2.56504900	0.66683600	-0.10370300
C	3.49938100	0.96548400	0.88536100
C	2.75737800	-0.43349600	-0.94421800
C	4.63472400	0.16934300	1.02670300
H	3.34783200	1.82960900	1.52705100
C	3.89134600	-1.22582600	-0.78762200
H	2.00369200	-0.68203400	-1.68807400
C	4.83655300	-0.92693800	0.19209700
H	5.36209200	0.40984500	1.79810200
H	4.03489300	-2.08174600	-1.44216800
H	5.72240700	-1.54590200	0.30552200
Se	-0.67270300	-0.45076200	-2.20830900
Se	0.96859600	1.74266800	-0.33594300
S	1.50162500	3.62294500	0.77815000
Li	1.71529600	3.83656500	-1.66140400
Li	-0.67657600	3.02424400	1.74596400
S	-2.75048100	2.45879500	0.91061600
Li	-1.83751200	0.95221800	-0.56932400
Li	-4.98923300	2.06644900	0.89448500