Supplementary Figure 1. The lithium polysulfide distribution on the patterned electrode. SEM image of the ITO-carbon electrode after dipping into Li$_2$S$_8$ solution and drying, which shows the random distribution of Li$_2$S$_8$ on ITO-carbon hybrid electrode.

Supplementary Figure 2. Morphologies of Li$_x$S deposited on the ITO surface. SEM image of Li$_x$S nanoparticles deposited on ITO surface showing the vertical platelet-like morphologies.
Supplementary Figure 3. Effect of width and spacing of the ITO patterns on the spatially controlled deposition. EDX mapping of different sizes of ITO patterns on glassy carbon electrodes after discharging to 1.7 V showing clearly patterned distributions of carbon (red), indium (blue), and sulfur (green). (a) ~1 µm size of ITO patterns. (b) ~10 µm size of ITO patterns. (c) ~100 µm size of ITO patterns. The variation of sulfur distribution on ITO patterned glassy carbon electrode is marked by the line scan.
Supplementary Figure 4. $S_{2p}$ spectra of products deposited on glassy carbon and ITO-coated glassy carbon, respectively.

Supplementary Figure 5. $Li_{1s}$ spectra of products deposited on glassy carbon and ITO-coated glassy carbon, respectively.
Supplementary Figure 6. Raman spectra of initial Li$_2$S$_8$ and the product charging to 2.6 V. The peaks at 376 cm$^{-1}$ and 428 cm$^{-1}$ can be assigned to the Raman peaks of Li$_2$S$_8$. The peaks at 219 cm$^{-1}$ and 472 cm$^{-1}$ can be assigned to Raman peaks of S$_8$.

Supplementary Figure 7. The effect of charge current density on the spatially controlled deposition of polysulfides. EDX mapping of ITO patterns-glassy carbon electrodes after directly charging the cell to 2.6 V under different current densities. (a) 20 µA/cm$^2$. (b) 200µA/cm$^2$. Both mapping show clearly patterned distributions of carbon (red), indium (blue), and sulfur (green).
Supplementary Figure 8. Micropatterns of Li$_x$S-ITO on glassy carbon electrode after 20 charge/discharge cycles. SEM image of ITO micropattern-glassy carbon hybrid electrode after 20 charge/discharge cycles and corresponding elemental scanning: carbon (red color), indium (blue color), and sulfur (green color).

Supplementary Figure 9. Nanofiber morphologies of ITO-C and carbon electrodes. SEM images of ITO-carbon hybrid nanofibers (a-b) and carbon nanofibers (c-d).
Supplementary Figure 10. EDX analysis of ITO-carbon hybrid nanofibers.

Supplementary Figure 11. XRD of ITO-carbon hybrid nanofibers indicating the cubic phase of ITO.
**Supplementary Figure 12.** Free-standing nanofiber electrode. Photograph of as-fabricated freestanding nanofiber mat as binder-free and current-collector free electrode.

**Supplementary Figure 13.** Impedance of Li-S cells with nanofiber electrodes before cycling. Electrochemical impedance spectroscopy plots of Li–S cells using ITO-C hybrid nanofiber mat and carbon nanofiber mat as electrodes.
Supplementary Figure 14. TEM characterization of carbon nanofiber electrodes after discharge. (a) EDX and TEM image of ITO-C nanofibers after the initial discharge indicating the formation of lithium sulfide nanoparticles on the fibers. (b) Dark field STEM image of ITO-C nanofibers after the initial discharge. (c-e) Corresponding line scan profiles of sulfur, carbon, and indium across the nanofiber, respectively.

Supplementary Figure 15. SEM characterization of carbon nanofiber electrodes after discharge. SEM and sulfur elemental EDX mapping of ITO(surface)-carbon nanofiber electrode (a and b) and carbon nanofiber electrode (c and d) after the initial discharge.
Supplementary Figure 16. Typical charge/discharge voltage profile of the cell in the following cycles. The profile indicates the complete reversible conversion between sulfur and lithium sulfide in the cell.

Supplementary Figure 17. Schematic illustration of the cell assembly process.
Supplementary Figure 18. Polysulfide content in the electrolyte after cycling, at the charged state. Percentage of sulfur in the electrolyte relative to the total sulfur mass on the electrode after cycling at 0.2 C using ITO-carbon hybrid electrode.

Supplementary Figure 19. Schematic illustration of ITO particle-engineered deposition of polysulfide. a-c) the nucleation and growth process of lithium sulfide on the ITO-C hybrid nanofiber electrode. d-e) the nucleation and growth process of lithium sulfide on the carbon nanofiber electrode.
Supplementary Figure 20. $S_{2p}$, $O_{1s}$, $C_{1s}$, and $N_{1s}$ XPS spectra collected from the lithium metal surface after 20 cycles at C/5, respectively.

Supplementary Figure 21. SEM images of lithium metal surface after 20 cycles at C/5.
Supplementary Note 1. Effect of width and spacing of the ITO patterns on the spatially controlled deposition.

To show the size effect of the space, we studied the deposition of polysulfides on three different sizes (~1 μm, ~10 μm, and ~100 μm) of ITO patterns on the glassy carbon. The ~1 μm and ~10 μm ITO patterns were fabricated by the lift-off process with e-beam lithography patterning and ~100 μm size of ITO patterns were fabricated by using a copper mesh as the mask. The fabricated patterned ITO-glassy carbon electrode was used for lithium polysulfide deposition in a pouch cell.

To fabricate 1 μm and 10 μm scale ITO patterns on glassy carbon substrates, the patterns were written using electron beam lithography. The glassy carbon substrates were cleaned by using ethanol. A two-layer electron beam resist process was used. First, 9% MMA (8.5)-MAA copolymer dissolved in ethyl lactate (Microchem Corp) was spin-coated onto the substrate at 4000 RPM for 60 seconds and then baked at 150°C on a hotplate for 90 seconds. Next, 4% 950K PMMA dissolved in anisole (Microchem Corp) was spin-coated onto the substrate at 4000 RPM and baked at 180°C on a hotplate for 90 seconds. A JEOL JBX-6300 electron beam lithography system operating at 100 kV beam voltage and 2 nA beam current was used to write the square array pattern. The dose was set to 1500 μC/cm². The pattern was developed in 1:1 methyl isobutyl ketone:isopropanol for 90 seconds and the bottom of the pattern was de-scummed by a 5 second exposure to oxygen plasma in a Plasmatherm LL-ICP etcher. A thin layer of ITO (50 nm for the ~1 μm size pattern and 100 nm for the ~10 μm size pattern) was sputtered (AJA ORION sputtering system) onto
obtained glassy carbon substrate. After dissolving the dual-layer resist mask with acetone, the ITO patterned glassy carbon electrodes were obtained.

To confirm the spatial distribution of deposited lithium sulfide species on different sizes of ITO patterns we mapped out the relevant elemental (C, S, In) distribution with EDX in SEM. As shown in Supplementary Figure 3, in all sizes of ITO patterns, the sulfur map (green, bottom right) overlays very well with the indium map (blue, bottom left) while there is only little sulfur on carbon map (red, top right), suggesting the discharged Li,S species are mostly deposited on the ITO surface. The line scan of the sulfur signal across the sample displayed sharp variations in signal intensity consistent with the patterned morphologies and high contrast between the ITO and the carbon surfaces. These EDX mapping results indicate that the preferential deposition of Li,S species onto ITO is effective on ITO patterns with various widths and spacings.

**Supplementary Note 2. The effect of charge current density on the spatially controlled deposition of polysulfides.**

Spacially selective deposition of polysulfides on patterned electrode was also observed even under directly charging the lithium polysulfide catholyte to sulfur. As shown in Supplementary Figure 7a, with a current density of 20 µA/cm², the EDX mapped distribution of sulfur displayed similar patterns as that of indium indicating the preferred deposition of polysulfides on the ITO surface during the direct charging process. This also means that the interaction of ITO and polysulfides is the main
driving force for the nucleation and deposition of sulfur related species on the ITO surface.

The charge current density was increased to show its effect on the lithium polysulfide selective deposition. Supplementary Figure 7b shows the mapped elementary distribution of ITO patterned-glassy carbon electrode after charging the cell to 2.6 V with a current density of 200 μA/cm² (one order higher than previously used 20 μA/cm²). Similar selective deposition behavior was observed.

**Supplementary Note 3. The cell fabrication process by using the nanofiber mat as the electrode.**

In our cell assembly process, the separator was fully wetted by the electrolyte. The amount of electrolyte absorbed into the separator was ~20 μl. The assembly steps is shown in Supplementary Figure 17. The fresh lithium metal was firstly put into the coin cell shell. The separator wetted by the electrolyte was put on the lithium metal. Then the nanofiber mat was put on the separator and the polysulfide was dropped onto the nanofiber mat. Finally, the coin cell was sealed by the MTI battery sealing system. Through this assembly process, the lithium polysulfides would diffuse from the top surface of nanofiber mat to the separator, enabling the full dispersion of lithium polysulfides into whole hybrid electrode.
**Supplementary Note 4. Polysulfide content in the electrolyte after cycling, at the charged state.**

For analysis of sulfur content in the electrolyte after cycling, 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. After 1, 5, 15 and 30 cycles at 0.2 C, the cells were charged to 2.6 V vs. Li$^+/\text{Li}$ and the voltage was maintained for over 20 h, following which they were disassembled and the contents (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).

The polysulfide content in the electrolyte after 1, 5, 15, and 30 cycles, at the charged state were tested. As shown in Supplementary Figure 18, the percentage of dissolved sulfur is in the range of 20%~35% indicating the good cycling reversibility of the cell. Moreover, the sulfur dissolution in the electrolyte increased from 23% at 1 cycle to 35% at 5 cycles and then decreased to 26% at 30 cycles, which is consistent with the specific capacity variation in cycling.

**Supplementary Note 5. Polysulfide (Li$_2$S$_8$) volumetric energy density calculation.**

In the calculation, $E = \frac{C_{\text{Li}_2\text{S}_8} \cdot C_{\text{Li}}}{C_{\text{Li}_2\text{S}_8} + C_{\text{Li}}} \cdot V$, where $C_{\text{Li}_2\text{S}_8}$ and $C_{\text{Li}}$ are volumetric specific capacities of Li$_2$S$_8$ and Li, respectively, and $V$ is the average voltage of discharge. The gravimetric specific capacity of Li$_2$S$_8$ is equal to $1675 \cdot \frac{7}{8} = 1466$ mAh/g. For 5M
Li$_2$S$_8$, the volumetric specific capacity, $C_{\text{Li}_2\text{S}_8} = 1466 \text{ mAh/g} \times 32 \text{ g/mol} \times 5 \text{ mol/L} = 234.56 \text{ Ah/L}$. The volumetric specific capacity of Li is 2000 Ah/L. The average voltage of discharge is 2.2 V. Thus, the polysulfide (Li$_2$S$_8$) volumetric energy density, $E = \frac{234.56 \times 2000}{234.56 + 2000} \times 2.2 = 461 \text{ Wh/L}$.

**Supplementary Note 6. Sulfur and polysulfide (Li$_2$S$_8$) mixture volumetric energy density calculation.**

With replacing 50 wt.% of the Li$_2$S$_8$ by solid sulfur, the volumetric specific capacity of the mixture, $C_{\text{mix}} = \frac{C_{\text{S}} \times V_{\text{S}} + C_{\text{Li}_2\text{S}_8} \times V_{\text{Li}_2\text{S}_8}}{V_{\text{S}} + V_{\text{Li}_2\text{S}_8}} = C_{\text{S}} \times \frac{V_{\text{S}}}{V_{\text{S}} + V_{\text{Li}_2\text{S}_8}} + C_{\text{Li}_2\text{S}_8} \times \frac{V_{\text{Li}_2\text{S}_8}}{V_{\text{S}} + V_{\text{Li}_2\text{S}_8}} = 3350 \times 0.075 + 243.56 \times 0.925 = 464.86 \text{ Ah/L}$. Thus, the mixed catholyte volumetric energy density, $E = \frac{464.86 \times 2000}{464.86 + 2000} \times 2.2 = 829 \text{ Wh/L}$.

**Supplementary Note 7. Proposed mechanism of spatial control of polysulfide deposition on ITO-C nanofiber electrode.**

Based on the strong binding between ITO and polysulfides demonstrated by the micro-pattern, the mechanism for ITO nanoparticles mediating polysulfide deposition on nanofibers is proposed and illustrated in Supplementary Figure 19. As shown in Supplementary Figure 19 a and d, with the same concentration of polysulfide solution ($c_i = c_i'$), the concentration of polysulfides around the surface of ITO-C nanofibers ($c_i$) is higher than that around the surface of carbon nanofibers ($c_i'$) due to the strong adsorption effect of polysulfides on the ITO. With $c_i > c_i'$, the reduction of polysulfides on the ITO-C hybrid nanofibers is expected to be faster than that on the
carbon nanofiber as a result of faster reaction kinetics induced by the higher concentration of reactants at the ITO-C hybrid interface. In addition, the ITO nanoparticles on the carbon surface would act as 'anchors' to provide more nucleation sites for lithium sulfide deposition than smooth carbon surface due to the stronger polar-polar affinity between ITO and lithium sulfide (Supplementary Figure 19 b and e). Thus, at the initial stage of polysulfide deposition on the electrode, more lithium sulfide nuclei were formed on the ITO-C hybrid nanofiber electrode than pure carbon nanofiber electrode due to the faster reduction kinetics and more nucleation sites on the ITO-C hybrid electrode. Influenced by the initial nucleation of Li_{x}S, ITO-C hybrid electrodes had more effective surfaces for following precipitation and growth processes. Since there were fewer nuclei on the carbon electrode, the sizes of Li_{x}S particles were much larger than that on the ITO-C hybrid electrode after the same amount of polysulfide deposition (Supplementary Figure 19 c and f). Finally, the polysulfide deposition on carbon electrodes was limited by the inefficient electron transfer from the electrode to the surface of Li_{x}S particles. Therefore, as the result of fewer nucleation sites of Li_{x}S on carbon nanofiber surfaces, the utilization of polysulfides in the carbon nanofiber electrode is lower than that of the ITO-C hybrid electrode.

Supplementary Note 8. XPS and SEM characterization of SEI formed on the lithium metal anode after cycling.

We used XPS and SEM to characterize the SEI on the lithium metal surface after
cycling. As shown in Supplementary Figure 20 the S, C, N, O elements were detected by XPS indicating the complicated reactions among electrolyte, polysulfide, and lithium. The $S_{2p}$ spectra shows that the polysulfide was reduced to form the lithium sulfide species ($Li_2S$, $Li_2S_2$) on the anode surface. The existence of S-O ($Li_2SO_4$, $Li_2S_2O_3$) and $-CO_2Li$ ($CH_3CO_2Li$, $CH_3OCO_2Li$) indicates that LiNO$_3$ plays an important role as oxidizing agent in the formation of the SEI. Meanwhile, the decomposition products of electrolyte (RCH$_2$OLi, ROLi) and the reduced products of LiNO$_3$ ($LiN_xO_y$, $Li_2N_2O_2$) were also contributed to the formation of SEI. Furthermore, the smooth surface of lithium metal anode after 20 cycles (Supplementary Figure 21) indicates that the lithium dendrite was suppressed by the SEI formed on the lithium metal surface.