
Supplementary information

**Visualizing interfacial collective reaction
behaviour of Li–S batteries**

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Supporting Information

Visualizing Interfacial Collective Reaction Behaviour of Li-S Batteries

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Supplementary Discussions

1. Instrumental advancements for high-resolution observation

1.1 Spacer thickness: Generally, the image resolution limitation in liquid cells have limited image resolution in TEM due to the chromatic aberration coefficient (C_c) caused by inelastic scattering from both the liquid layer and SiN_x window, resulting in a broader range of transmitted electron energy compared to the original spread at the source¹⁻³. To improve the spatial resolution, we first reduced the liquid layer thickness by using a spacer with ~ 100 nm thickness to build electrochemical liquid cells. We investigated the spatial resolution of liquid cells sealed using spacers of varying thicknesses, ranging from 100 to 1000 nm. In the TEM images taken with spacers of 100 and 200 nm (Supplementary Fig. 2a, b), the edges of the Ti electrode were clearly visible. However, as the spacer thickness was increased to 500 nm (Supplementary Fig. 2c), the electrode surface became less distinct due to the increased thickness of the electrolyte layer. The resolution further deteriorated with a spacer thickness of 1000 nm (Supplementary Fig. 2d), where SiN_x observation windows can hardly be located. These results clearly demonstrate the importance of using thinner spacers to obtain high-resolution TEM images in liquid cells. It is worth noting that there is a trade-off between spatial resolution and liquid layer thickness. While a thin liquid layer can enhance spatial resolution, it may not accurately reflect the operando environment due to restricted reactant species and slow diffusion processes. To mitigate this effect, our *in situ* EC-TEM experiments focused on the early nucleation and growth of Li_2S rather than the long-term cycle process, thereby ensuring that reactant species were readily available. The growth rate statistics of solid $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ indicated that the early nucleation was reaction-limited (Supplementary Fig. 16), demonstrating that there was an abundant supply of LiPSs reactant at the electrode/electrolyte interfaces.

1.2 Bulging effect: The bulging effect of SiN_x membrane is a common issue that arises from the window geometry, particularly the large length and width sizes, as well as the pressure difference between the sealed liquid cell and the high-vacuum chamber of the electron microscope. This issue is usually observed in commercial flow holder systems and can lead to a considerable increase in the liquid layer thickness and a decrease in the resolution due to beam broadening and chromatic aberrations³. To address this issue in our liquid cells, we have reduced the size of the observation areas to a width of 5-8 μm and a length of 50 μm . Additionally, the volume of the closed cell is in the range of hundreds of picolitres, which is significantly smaller than that of a flow system. This means that even slight bulging can lead to a considerable decrease in pressure inside the liquid cell, thereby compensating for the difference in pressure between the inside and outside. As a result, the bulging effect of the SiN_x observation windows in our liquid cells has been greatly reduced. We have quantitatively measured the thickness of the liquid layer in our electrochemical liquid cell with EELS and the log-ratio method $t/\lambda = \ln(I_t/I_0)$ ⁴⁻⁷. In this equation, t represents the absolute thickness of the liquid layer, λ is the mean free path, I_t is the integration of the entire EELS, and I_0 is the integration of the zero-loss peak. Here, we sealed deionized water in liquid cells to measure the thickness, where the mean free path (λ_{water}) is 330 nm at an acceleration voltage of 300 kV⁸. In addition to the high-resolution TEM image and the clear Ti electrode (Supplementary Fig. 3a), EELS revealed similar values of liquid layer thickness across different areas in the liquid cell, providing further evidence of the alleviated bulging effect. The thickness of the liquid layer can be obtained using the following equation (Supplementary Fig. 3b, c), once the relative thickness of the two SiN_x observation windows has been measured (Extended Data Fig. 5h):

$$t_{\text{water}}/\lambda_{\text{water}} + 2 \times t_{\text{SiN}_x}/\lambda_{\text{SiN}_x} = \ln(I_t/I_0)$$

The thickness of the liquid layer was determined to be approximately 124.74 ± 8.54 nm.

1.3 SiN_x thickness: While SiN_x windows are commonly considered transparent for beam energy, thick SiN_x windows can lead to an increased background contrast and reduced image resolution. Therefore, we investigated the impact of SiN_x window thickness on TEM image resolution by loading Li₂S@graphene on single bottom chips with different thicknesses of SiN_x windows (11.2, 48, and 94.8 nm). HRTEM images and the corresponding FFT patterns showed that in SiN_x windows with thicknesses of 48 and 94.8 nm, the background noise impeded HRTEM image resolution (Supplementary Fig. 4). However, in the 11.2 nm-thick SiN_x window, the atomic structure of Li₂S@graphene was clearly and stably observed in (111), (200), and (220) crystal planes over 103.4 s (Extended Data Fig. 1e, f). Through the modification of the thickness of the liquid layer and SiN_x window, we have successfully achieved the high-resolution observation in liquid cells, as reported in our previous works⁹⁻¹¹.

2. E-beam effects

2.1 E-beam effects on the LiPSs intermediates in liquid cells: The solid discharge products and LiPSs intermediates are susceptible to e-beam damage. Time-series TEM images revealed that a medium dose rate of 11.5 e Å⁻² s⁻¹ caused the decomposition after 34.4 s, with the generation of voids simultaneously (Supplementary Fig. 5a). By contrast, decreasing the dose rate to 1.54 and 1.13 e Å⁻² s⁻¹ effectively prevented the side reactions over the same observation time, stabilizing both solid deposits and LiPSs electrolyte (Supplementary Fig. 5b, c). Meanwhile, the spatial resolution was maintained for real-time observation. The above investigation indicates that the deposition of Li₂S triggered by an external electric field can mitigate e-beam damage to metastable intermediates during observation under low e-beam dose rates. Electrochemical studies in liquid cells were conducted with dose rates below 1.5 e Å⁻² s⁻¹.

2.2 E-beam effects on Li₂S: Imaging Li-S batteries in electron microscope has always been inherently challenging^{12,13}, due to the spontaneous sublimation of sulfur under high vacuum, the high sensitivity of Li₂S to moisture ($\text{Li}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2\text{S}\uparrow$, Supplementary Fig. 6a), and the unstable structure of LiPSs intermediates. We first focused on the e-beam damage mechanism on Li₂S. Time-series TEM images revealed that commercial Li₂S was extremely vulnerable to e-beam, which shrank and decomposed with the generation of voids inside crystal in 8.6 s under a dose rate of 69 e Å⁻² s⁻¹ (Supplementary Fig. 6b–d). To better understand the e-beam damage mechanism, we conducted *in situ* heating experiments on commercial Li₂S in vacuum from 20°C to 800°C, with a dose rate of 3 e Å⁻² s⁻¹ (Supplementary Fig. 7a–c). When subjected to an individual e-beam without an increase in temperature, we observed no obvious structural variations in Li₂S over 30 s. This indicates that observations under a low e-beam dose rate would not cause severe structural damage (Supplementary Fig. 7d). By contrast, as the temperature increased (Supplementary Fig. 7e), voids appeared inside the Li₂S crystal (160.2 s), which shrank continuously (207 s), and worsened during heating up to 800°C (267.2 s). The results were similar to e-beam damage on the commercial Li₂S shown in Supplementary Fig. 6b–d. Therefore, the e-beam effect on Li₂S can be mainly attributed to the ionization, radiolysis, and heating, due to its poor electrical and thermal conductivity^{13,14}. However, we discovered that by simply ultrasonically mixing commercial Li₂S with graphene (Supplementary Fig. 8a, b), the e-beam effect can be significantly alleviated. This should be attributed to the excellent electrical and thermal conductivity of graphene, enabling atomic-resolution and long-time observation of Li₂S@graphene. In the time-series HRTEM images (Supplementary Fig. 8c), we were able to clearly observe the atomic structure of Li₂S@graphene even at a high dose rate of 11000 e Å⁻² s⁻¹ and a long period of 134.6 s. Similar atomic structure of carbon-coated Li₂S have also been observed in previously reported works¹⁵⁻¹⁷. E-beam damage mechanism was further confirmed after Li₂S deposition in coin-type cells. Time-series HRTEM images revealed the stable atomic

structure of Li_2S nanocrystalline deposited on Mo NCs/N-G nanosheet (Supplementary Fig. 9a), while rod-like Li_2S deposited on bare Ti electrode was highly susceptible to e-beam damage (Supplementary Fig. 9b). This also explains how we were able to observe the atomic structure of Li_2S -Mo NCs/N-G after electrochemical deposition in liquid cells (Fig. 3).

2.3 SiN_x effects on the electrochemical deposition: To investigate the SiN_x effect on electrochemical deposition, we conducted discussions or experiments in three aspects: liquid cell preparation, e-beam effect, and *ex situ* characterization in coin-type cells. Initially, SiN_x layers on Si substrate are hydrophobic after production and are vulnerable to be contaminated by organic adsorption layer. This can cause the charging of SiN_x window during electron transfer across the solid/liquid interface, due to inelastic scattering. To avoid air contamination, we prepared and assembled the liquid cells in a clean room with specialized nanofabrication setups, and conducted electrolyte injection and chip sealing in an argon-filled glovebox ($\text{H}_2\text{O} < 0.01$ ppm, $\text{O}_2 < 0.01$ ppm). Next, we conducted a quantitative analysis of the e-beam effect on electrochemical reactions in a liquid cell under a dose rate of $1.2 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$ (Supplementary Fig. 10a, b), which accounted for only 2.46% of the measured current density. We found that if the electric field was excluded, the individual e-beam cannot drive the heterogenous deposition of Li_2S on SiN_x or Ti electrode during 164 s observation (Supplementary Fig. 10c). This suggested that the charging effect of SiN_x window was negligible. Instead, Li_2S deposition mainly occurred on the electrode surface during potentiostatic discharge (Fig. 2 and Extended Data Figs. 3 and 4), due to the necessity of charge transfer for LiPSs electrochemical reactions, which can only be driven by an electric field, not an e-beam. Similar electrochemical behavior at electrode/electrolyte interface under low dose rates has also been reported in the deposition of Li metal or SEI layer¹⁸⁻²¹. Finally, we constructed a SiN_x layer via plasma enhanced chemical vapour deposition (PECVD) on a Ti current collector to investigate the effect of SiN_x layer on electrochemical reactions over a large observation region. After disassembling the coin-type cells, *ex situ* SEM images showed that Li_2S nucleation occurred only on the conductive Ti surface (Supplementary Fig. 10d). By contrast, the conversion from Li_2S_6 to Li_2S was blocked on SiN_x surface due to its insulating properties. Overall, the above investigation revealed that the surface functionality of SiN_x layer would not affect the electrochemical conversion of LiPSs on electrode/electrolyte interfaces.

3. HRTEM observation in liquid cells

In addition to the instrumental advancement, we also used an "e-beam bubble generation" method to further enhance the spatial resolution experimentally by locally squeezing out the liquid layer, which had been previously adopted in our works⁹⁻¹¹. E. A. Stach et al. systematically conducted a thorough analysis of the chemical and structural properties at the nanoscale level in liquid cells²². Their findings indicate that when a gas bubble is generated, the spatial resolution and signal-to-noise ratio (SNR) of images obtained in the thin-film condition are comparable to those observed for samples in a dry state. In our experiments, after completing the electrochemical deposition of Li_2S nanocrystalline on Mo NCs/N-G nanosheets, we generated bubbles by focusing e-beam, and adjusted their shrinkage or enlargement by changing magnification, as schematically illustrated (Extended Data Fig. 5a). After generating and stabilizing the bubbles, TEM images revealed a significant reduction in the thickness of liquid layer and the background was almost transparent (Extended Data Fig. 5b). If the thin-film wetting layer was completely removed (Extended Data Fig. 5c, d), imaging resolution would depend on the thickness of the bottom/top SiN_x layers theoretically, thereby achieving the ultimate spatial resolution. We measured the relative thickness (t/λ , where t is the absolute thickness and λ is the mean free path) of different areas in liquid cells after bubble stabilization⁴⁻⁷, as revealed by ADF-STEM and EELS images (Extended Data

Fig. 5e, f). The average values of Li₂S nanocrystalline (I) and Mo NC/N-G nanosheets (II), accounting for 0.77 ± 0.16 and 0.29 ± 0.02 , were slightly larger than that of SiN_x layers (III) with 0.16 ± 0.04 (Extended Data Fig. 5g, h). Time-series HRTEM images revealed the atomic structure of Li₂S nanocrystalline along the [100] direction (Extended Data Fig. 5i). Above all, benefited from the efforts of both instrumental (spacer, bulging, and SiN_x layer) and experimental advancements, we can track the high-resolution electrochemical reactions and obtain the atomic structure of the solid discharge products in liquid cells simultaneously. It should be noted that the structure characterization of the rod-like Li₂S deposited on Ti electrode (without active center) was carried out at low e-beam dose rates, due to its intrinsic susceptibility to e-beam damage. Atomic-scale HRTEM characterization was only conducted on Li₂S-Mo NCs/N-G after the complete electrochemical reactions, since the structure stability of Li₂S@graphene under high e-beam dose rates has already been verified in *Supplementary Discussions 2.2*.

4. Image acquiring conditions and post-image processing

For image acquiring conditions, we used the FEI Talos-F200s TEM operating at 200 kV. The HRTEM image was captured using Velox software at various dose rates (Supplementary Fig. 21), with a resolution of 4096×4096 pixels and an exposure time of 500 ms. To mitigate the impact of carbon contamination and amorphous SiN_x layer-induced background noise in HRTEM images of Li₂S nanocrystals, we utilized the radial Wiener filter for post-image processing, with the highest frequency of 80 and edge smoothing of 5%. While a simple Fourier space periodic mask is commonly used to extract crystal structure, this method can introduce artifacts or periodic features that are not part of the crystal structure. Therefore, we employed the radial Wiener filter to eliminate amorphous background noise^{23,24}. This method estimates the background by taking the average value after excluding the intensity corresponding to Bragg diffraction from periodic structures, and it calculates the rotation average of the Fourier transform of the entire image. The HRTEM images in Fig. 3i before and after applying the radial Wiener filtering, and the corresponding FFT patterns, were provided in Supplementary Fig. 25. The original FFT patterns of Li₂S nanocrystalline showed concentric rings corresponding to diffraction patterns of non-crystalline materials (I). These ring patterns were caused by non-periodic parts of the image arising from amorphous surface layers. The Fourier transform (F_o) of the observed image is the sum of the true signal from the crystalline part (F_c) and the non-periodic background from the non-crystalline part (F_b), represented as $F_o = F_c + F_b$. The true signal F_c is limited to diffraction spots and is typically strong, while the non-periodic background F_b is more uniformly distributed. The Wiener filter seeks a solution that minimizes the sum of the square differences between the true signal F_c and its estimated value $\hat{F}_w$ ($\sum |\hat{F}_w - F_c|^2 \rightarrow \text{minimum}$). As a result, after applying the radial Wiener filter, the concentric rings from non-crystalline surface layers were greatly reduced, while diffraction spots from the periodic Li₂S nanocrystalline were preserved in the processed HRTEM images and FFT images (II).

5. Simulations of gathering and charge transfer in dense phase

5.1 MD simulations of the LiPSs gathering: We first constructed the randomly dispersed S₆²⁻ and Li⁺ ions at varying concentrations (2.51 wt%, 5.28 wt%, 9.68 wt%, and 17.93 wt%) without electrode surface and investigated their movement behavior in bulk electrolyte (Extended Data Fig. 8a and Supplementary Figs. 28 and 29). Time-series MD simulations revealed that S₆²⁻ ions tended to aggregate spontaneously in solution, forming clusters with varying sizes. By calculating the average number of S atoms in these clusters (Extended Data Fig. 8b), we found a direct correlation between cluster size and the concentration of S₆²⁻ and Li⁺ ions. Specifically, the cluster size increased as the ion concentration increased. To verify the interaction between the electrode surfaces and Li₂S₆ molecules, we constructed

MD models of S_6^{2-} and Li^+ ions with different concentrations over Mo NCs/N-G and Ti electrode surfaces (Extended Data Fig. 8c and Supplementary Fig. 30). The simulations revealed that Mo NCs/N-G gathered the S_6^{2-} and Li^+ ions from bulk solution to the electrode surface, which was independent of electrolyte concentration. Statistical analysis confirmed that Mo NCs/N-G exhibited stronger long-range attraction than Ti surface. Specifically, at the Mo NCs/N-G interface, the number of S atoms gradually increased over time (Extended Data Fig. 8d).

5.2 AIMD simulations of the charge transfer in droplet-like dense phase: We simulated the charge transfer and distribution in a model system containing Li_2S_6 molecules in the dense phase with the concentration of 17.9 wt% before and after applying an electrode potential. The electrode potential was provided by electron-donating Li atoms added below Mo NCs/N-G electrode. From the top view, we defined S_6 ions in the external, middle, and internal layers based on their distance from the Mo active centers (Extended Data Fig. 8g and Supplementary Fig. 31e). Considering the dynamic charge distribution, the polysulfide ions in the dense phase were defined as S_6 ions. At the moment when electrode potential was applied (II-Applied potential at 0 ps), the number of electrons in S_6 ions remained almost unchanged compared to its original state (I-Pristine). However, after a relaxation period of 8 ps (III-Applied potential at 8 ps), S_6 ions underwent an obvious increase of electrons numbers and transfer. Specifically, compared with S_6 ions in the internal layer ($3.78 - 3.34 = 0.44e$), S_6 ions in the middle layer received even more electrons ($2.42 - 1.73 = 0.69e$), and S_6 ions in the external layer also gained some electrons ($1.52 - 1.37 = 0.15e$). AIMD results revealed that electrons can be transfer from Mo active centers to S_6 ions in the droplet-like dense phase from internal to external layers, not just the LiPSs molecules closest to active centers. Overall, our MD simulations showed that Mo active centers can induce a long-range gathering effect, while AIMD simulations demonstrated extremely fast electron transfer in these gathered LiPSs molecules. Therefore, Mo active centers can induce an instant reduction of LiPSs dense phase into solid Li_2S , which suppresses the step-by-step evolution of soluble LiPSs in the electrode without active centers.

5.3 Discussion of collective charge transfer behavior compared with step-by-step mechanism: In our *in situ* EC-TEM experiments, we observed that the reaction at bare Ti electrode surface followed a step-by-step nucleation-growth process: (Step-I) the formation of Li_2S_2/Li_2S nuclei, (Step-II) the continuous growth of rod-like/plate-like Li_2S . Conversely, at Mo NCs/N-G nanosheet surface, we observed that the gathering of LiPSs induced the direct Li_2S crystallization. No other soluble or insoluble intermediates were formed during this process, indicating that LiPSs reacted as a whole in the droplet-like dense phase, and transformed directly from the LiPSs dense phase into crystallized Li_2S . Since the conversion from soluble Li_2S_6 to Li_2S requires sustained electron transfer ($Li_2S_6 + 10Li^+ + 10e^- = 6Li_2S$), the gathered LiPSs should be continuously reduced under an electric field. AIMD simulations revealed that electrons can be transfer from Mo active centers to S_6 ions in the droplet-like dense phase from internal to external layers, not just the LiPSs molecules near the active centers (Extended Data Fig. 8g). Based on the structural characterization (HRTEM, SAED, EDS, and EELS in Fig. 4c and Extended Data Fig. 7) of LiPSs droplets and Li_2S nanocrystalline, we further confirmed the direct transformation from droplet-like dense phase into crystallized Li_2S . Therefore, both the experimental and simulation results demonstrate that during the gathering process, the gathered long-chain LiPSs in the dense phase are continuously reduced to short-chain LiPSs under an electric field, inducing a direct crystallization of solid Li_2S .

6. Consistency of *in situ* and *ex situ* experiments

The gathering-induced collective charge transfer of LiPSs primarily involved the gathering of soluble LiPSs and their fast conversion into solid Li_2S . To confirm this phenomenon, we conducted

parallel investigations on the soluble and insoluble discharge products through *ex situ* characterizations, including Raman spectra, XRD patterns, UV-vis spectra, SEM, and high-resolution (S)TEM.

6.1 Raman spectra: After galvanostatic discharge to 1.7 V, the coin-type cells were disassembled in an argon-filled glovebox. Subsequently, they were transferred to a stainless-steel device with a quartz window for Raman spectra characterization, which was crucial in preventing air pollution (Supplementary Fig. 32a). The peaks at 473 and 458 cm^{-1} were primarily attributed to the S–S stretching vibration of the surface-adsorbed soluble Li_2S_n ($2 < n < 6$), while the peak at 374 cm^{-1} was associated with solid Li_2S ²⁵⁻²⁷. The previous *in situ* and *ex situ* Raman studies have highlighted the challenge in identifying Li_2S peaks due to their low intensity. In our Raman spectra, both soluble and insoluble discharge products exhibited significantly stronger signals when detected from the Mo NCs/N-G decorated surface, compared to the bare Ti electrode before/after deposition. This should be attributed to the Li_2S_n ($2 < n < 6$) dense phase and the abundant Li_2S nanocrystalline deposited on the Mo NCs/N-G nanosheet. Subsequently, the discharge products of solid Li_2S were investigated by XRD patterns and the soluble Li_2S_6 was investigated by UV-vis spectra. The structures of solid Li_2S deposited on different surfaces were further visualized by SEM and TEM images.

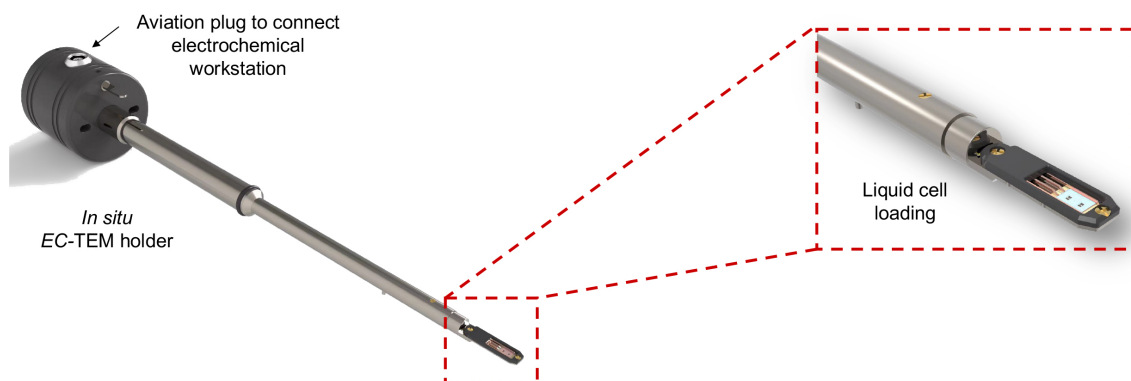
6.2 XRD patterns: Following the deposition of Li_2S in coin-type cells, the XRD patterns of Ti mesh with and without the decoration of Mo NCs/N-G nanosheet were analyzed, using a Kapton-filmed coin-type cell to avoid air exposure. Both patterns displayed characteristic diffraction peaks at approximately 26.4°, corresponding to the (111) crystal plane of cubic Li_2S (Supplementary Fig. 32b). Notably, the Li_2S -Mo NCs/N-G pattern exhibited a stronger diffraction peak, indicating higher conversion activity from soluble Li_2S_6 to solid Li_2S . The size of the deposited Li_2S crystals was assessed using the Scherrer equation, $D = K\lambda/(\beta\cos\theta)$, where K is the Scherrer constant; λ is the X-ray wavelength; β is the full width at half maximum (FWHM); θ is the Bragg angle. As the crystalline size was inversely related to the β value, Li_2S -Mo NCs/N-G exhibited a smaller crystalline size compared to Li_2S -Ti.

6.3 UV-vis spectra: We conducted UV-vis spectra to investigate the adsorption effects of soluble Li_2S_6 on various surfaces, including Ti mesh and Mo NCs/N-G decorated Ti mesh (Supplementary Fig. 32c). After a static adsorption, the electrolyte in the Mo NCs/N-G decorated Ti mesh appeared clearer and more transparent, indicating a strong adsorption of soluble Li_2S_6 . By measuring and linearly fitting the absorbance of blank Li_2S_6 electrolyte with varying concentrations, we were able to quantitatively calculate the Li_2S_6 adsorption capacity, showing 58.4 wt% of Mo NCs/N-G nanosheet and 13.4 wt% of bare Ti mesh (Supplementary Fig. 32d, e).

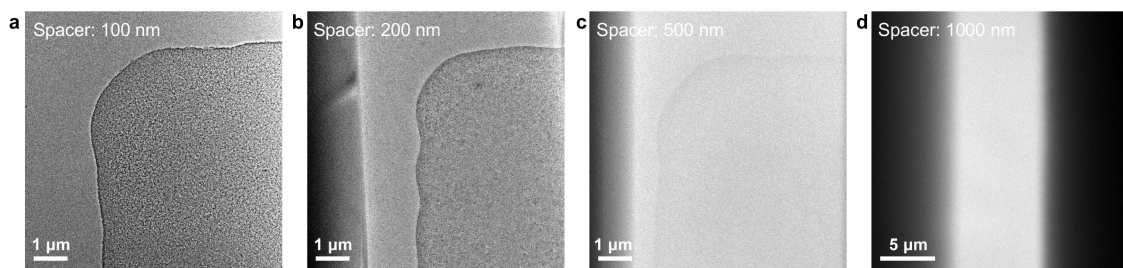
6.4 Ex situ SEM and TEM images: In *ex situ* SEM images, the bare Ti electrode exhibited a passivated layer covering the surface after Li_2S deposition, with sparse deposition of rod-like/plate-like Li_2S due to its limited nucleation sites (Supplementary Fig. 33a, b). By contrast, the presence of Mo NCs/N-G resulted in a thicker and rougher surface after Li_2S deposition, primarily in a particle-like structure (Supplementary Fig. 33c, d). The difference in surface morphology was further confirmed by *ex situ* (S)TEM images, EDS mappings, and SAED patterns. On the surface of Mo NCs/N-G nanosheet, Li_2S deposited as poly-crystalline nanoparticles, primarily exposing the (111), (200), and (220) crystal planes (Supplementary Fig. 34a-c), while on the bare Ti electrode, it was deposited as single-crystal rod-like/plate-like structures (Supplementary Fig. 34d-f). It is worth noting that while there may be variations in the size of Li_2S deposited in liquid cells and coin-type cells due to factors such as cell space, deposition time, and reactant amount, the reaction activity and deposition structure on different electrode surface remain highly consistent in both *in situ* and *ex situ* experiments.

Given that the same electrolyte was used in coin-type cells, the different deposition morphology and structure was attributed to the electrode surface with or without mediation of active centers. Mo NCs/N-G surface exhibited stronger adsorption, which induced the formation of soluble LiPSs dense phase (as evidenced by Raman spectra and UV-vis spectra). The fast charge transfer and reaction kinetics led to the deposition of Li_2S nanocrystalline (as evidenced by XRD, SEM, and TEM). Notably, even if the supplemented characterizations were highly consistent with the results obtained from *in situ* EC-TEM experiments, the details of gathering-induced collective charge transfer reaction, involving the gathering, conversion, and crystallization, could only be given by *in situ* EC-TEM due to its high spatial-temporal resolution. The irreplaceability of this method cannot be overemphasized.

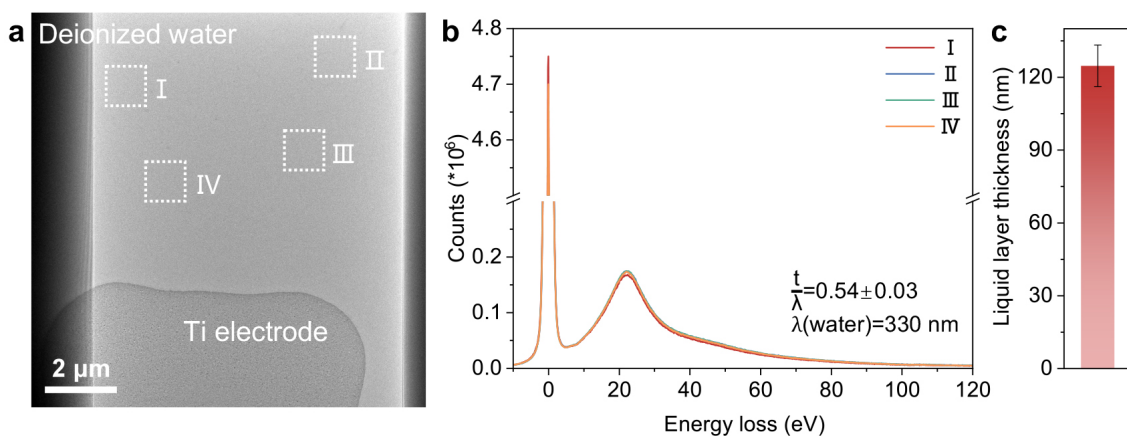
Supplementary Figures S1-S36



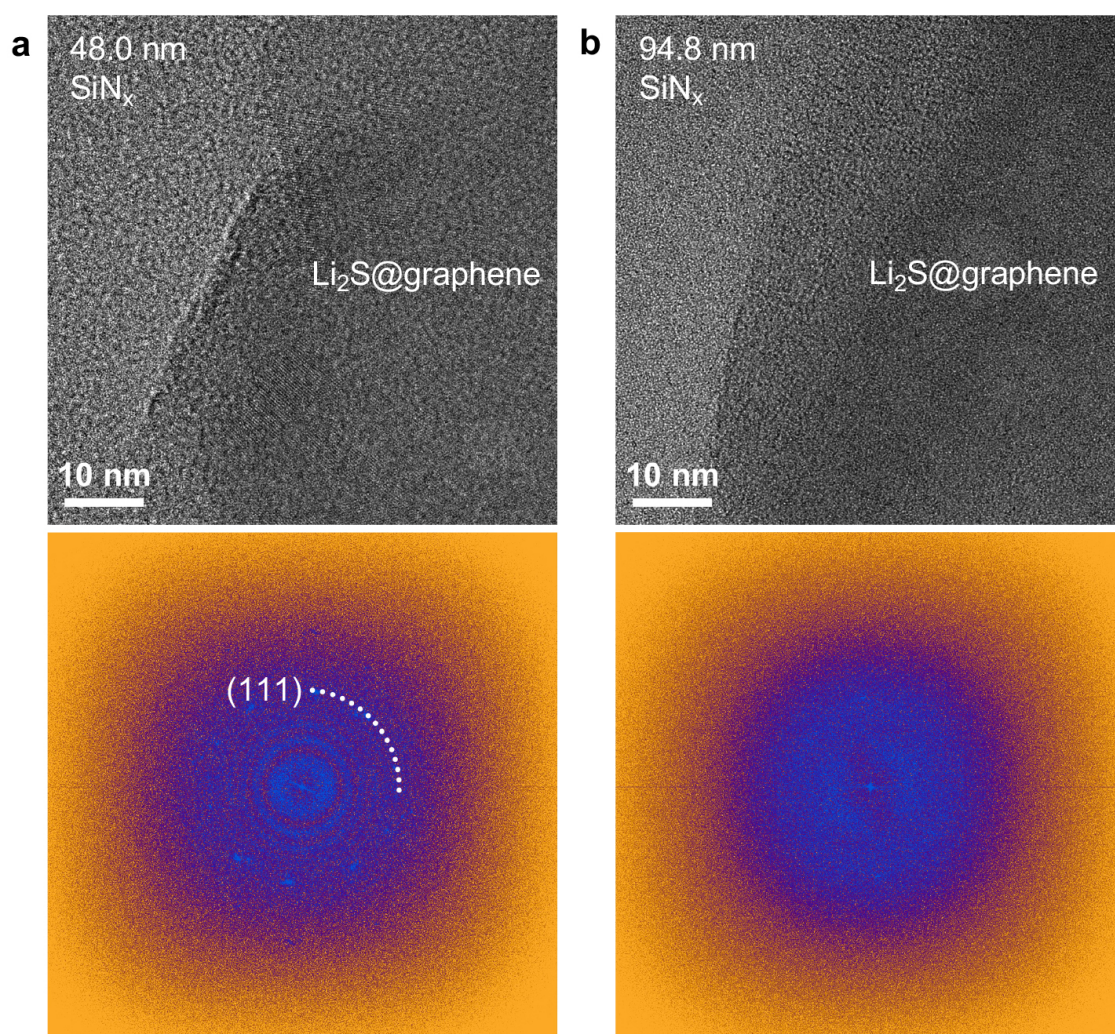
Supplementary Fig. 1 | Loading of the sealed liquid cell onto EC-TEM holder. It was connected to electrochemical workstation by an aviation plug after inserted into TEM column.



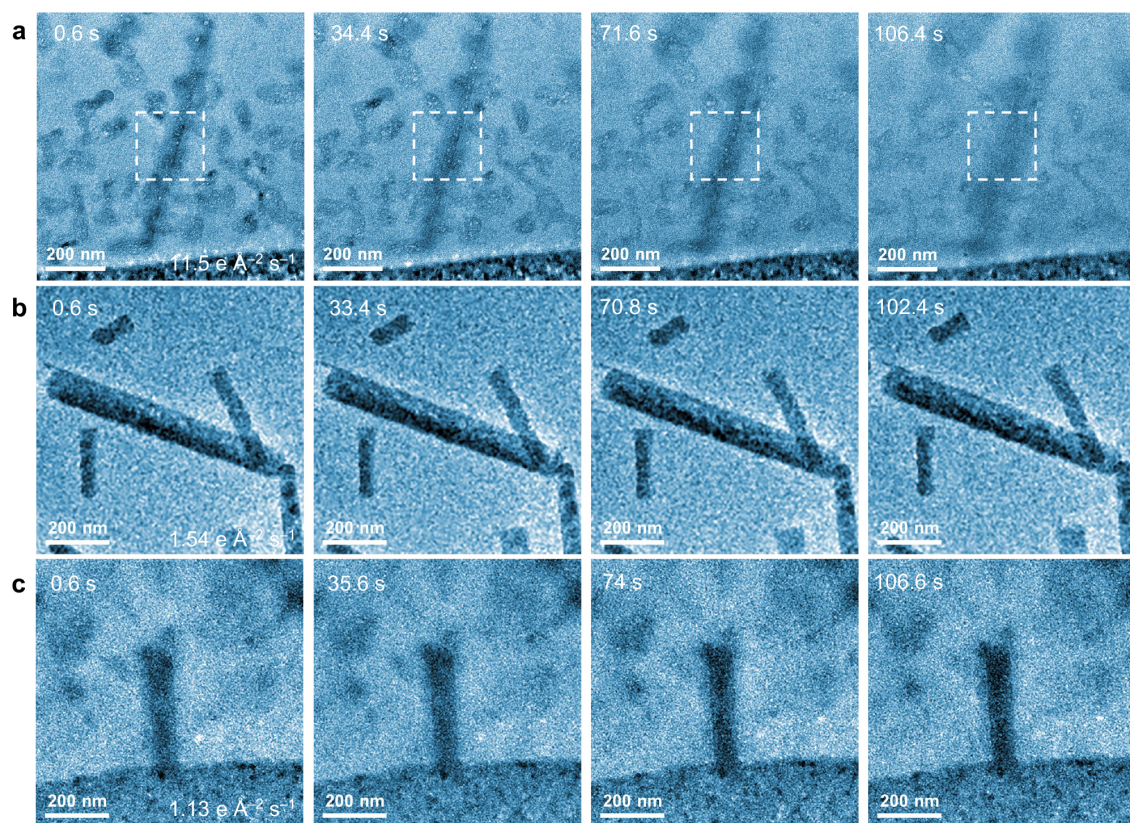
Supplementary Fig. 2 | Influence of spacer thickness on image resolution. (a-d) TEM images of electrochemical liquid cells assembled using spacers with varying thickness, including 100, 200, 500, and 1000 nm.



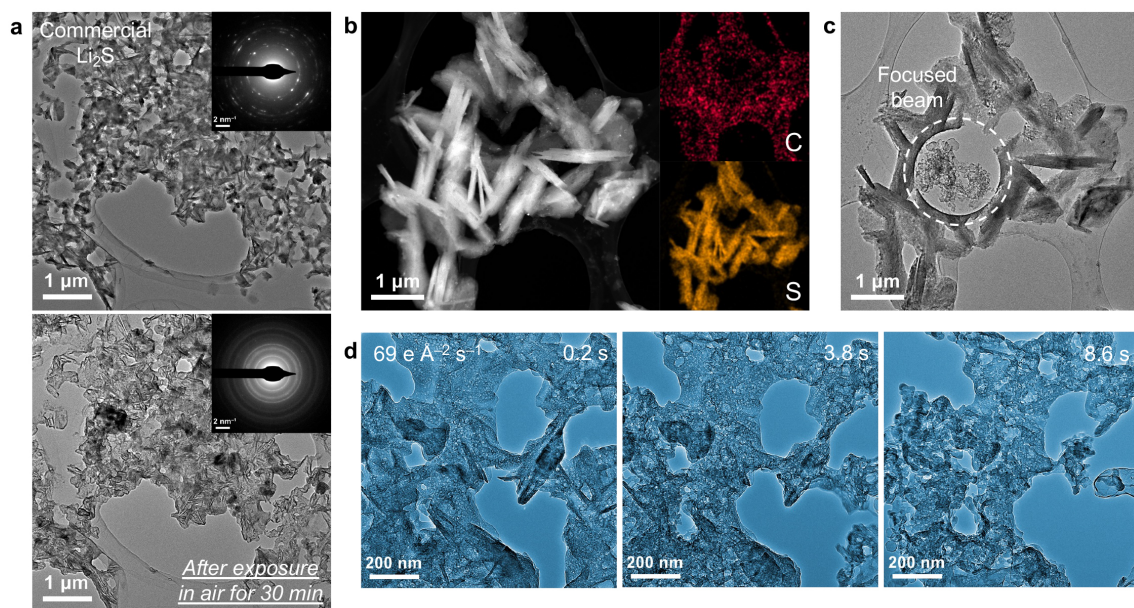
Supplementary Fig. 3 | Measurement of liquid layer thickness through EELS. (a) TEM image of an electrochemical liquid cell filled with deionized water. (b) Typical low-loss EELS of a liquid specimen sandwiched between two SiN_x membranes corresponding to the areas marked in Supplementary Fig. 3a. Relative thickness ($t_{\text{water}}/\lambda_{\text{water}}$) is obtained by the log-ratio method in Digital Micrograph software. (c) Average thickness of liquid layer. Error bars represent standard deviations from multiple EELS curves (I-IV).



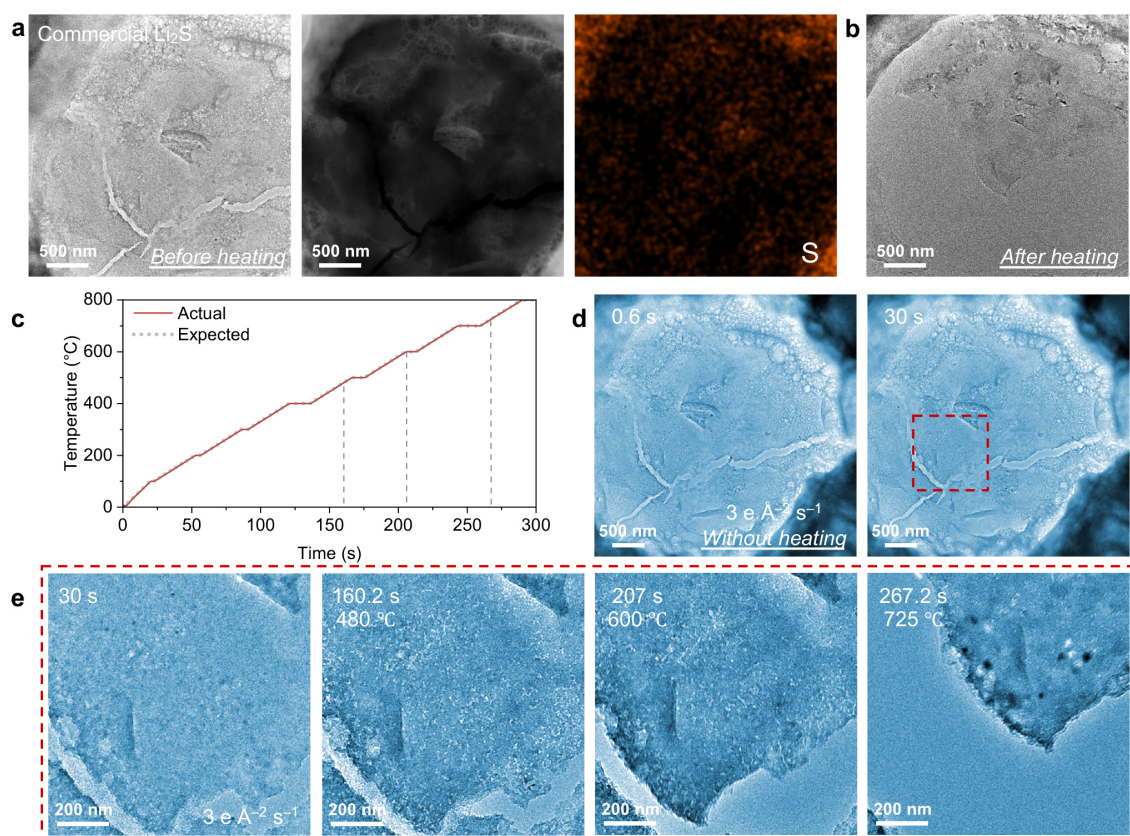
Supplementary Fig. 4 | HRTEM image resolution of $\text{Li}_2\text{S}@$ graphene at different SiN_x thickness. (a, b) HRTEM images and corresponding FFT patterns of $\text{Li}_2\text{S}@$ graphene loaded on single bottom chips with different thicknesses of SiN_x layers (48 and 94.8 nm). The thickness of the SiN_x layers was measured using a spectroscopic ellipsometer with a spectral range of 193–1000 nm. As the SiN_x layers increased in thickness, the spatial resolution of Li_2S nanocrystalline degraded due to the increased background noise.



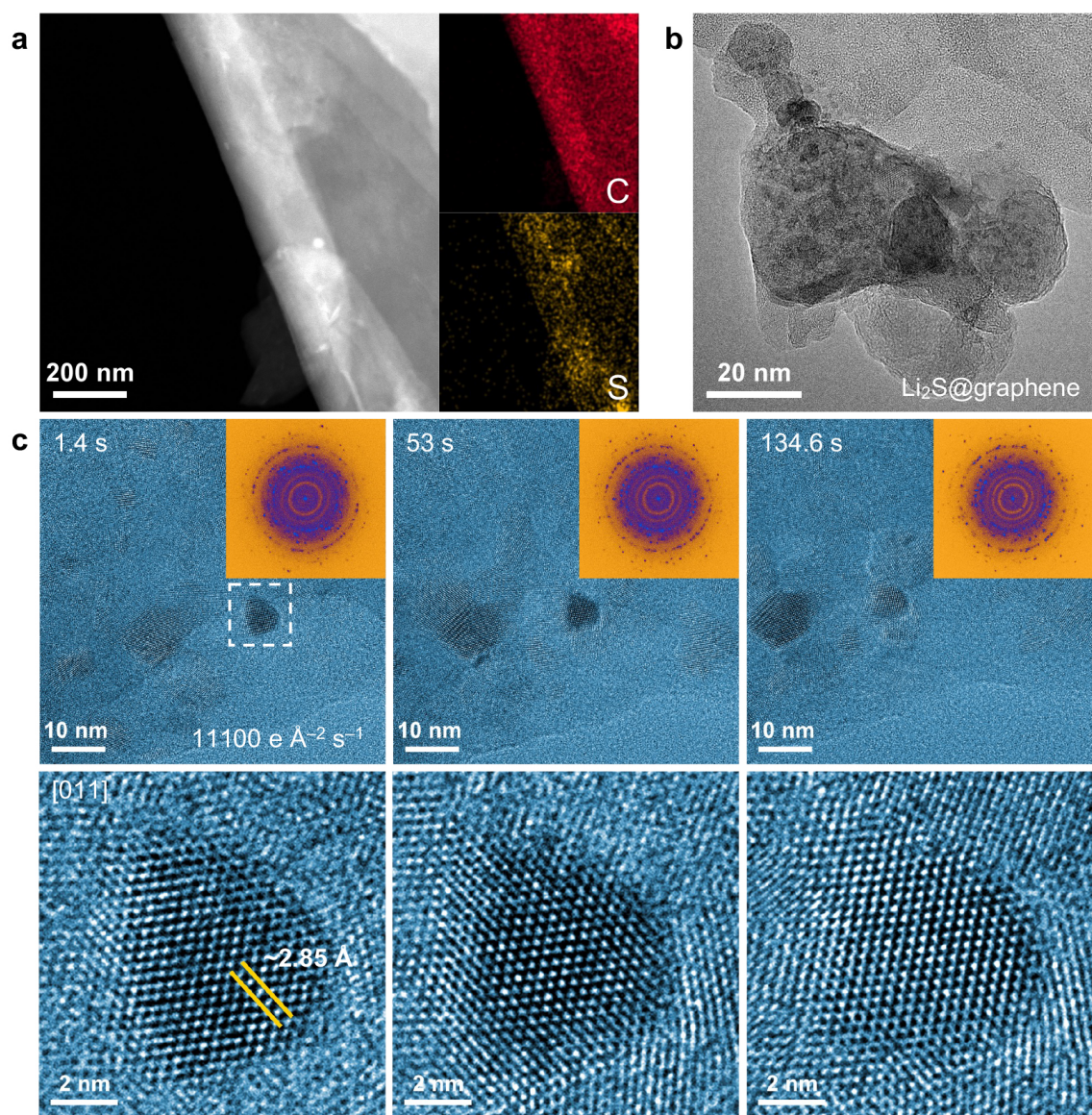
Supplementary Fig. 5 | E-beam effect on the electrochemically deposited Li_2S . (a-c) Time-series TEM images of Li_2S at the dose rates of 11.5, 1.54, and 1.13 $\text{e} \text{ \AA}^{-2} \text{ s}^{-1}$, respectively.



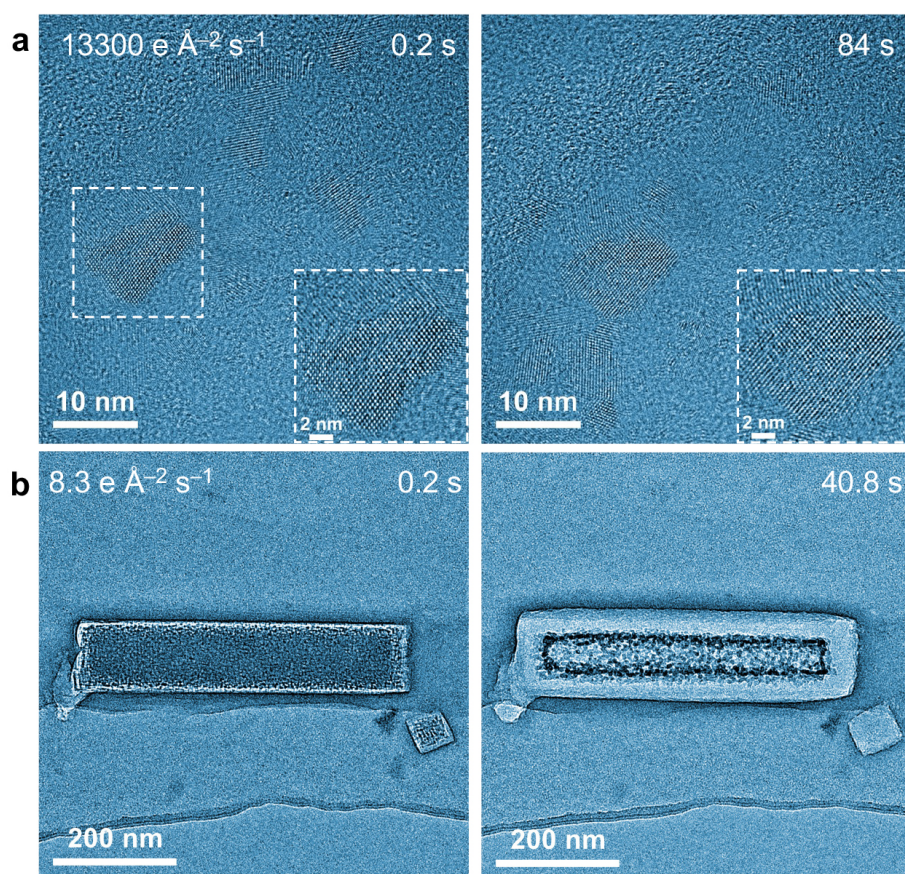
Supplementary Fig. 6 | E-beam effect on commercial Li_2S . (a) TEM images of commercial Li_2S before and after exposure in air. (b) STEM image and EDS mappings of the original commercial Li_2S . (c) TEM image of commercial Li_2S after focusing e-beam on the marked area. (d) Time-series TEM images of commercial Li_2S at a dose rate of $69 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$, showing severe structure damage due to the focused e-beam.



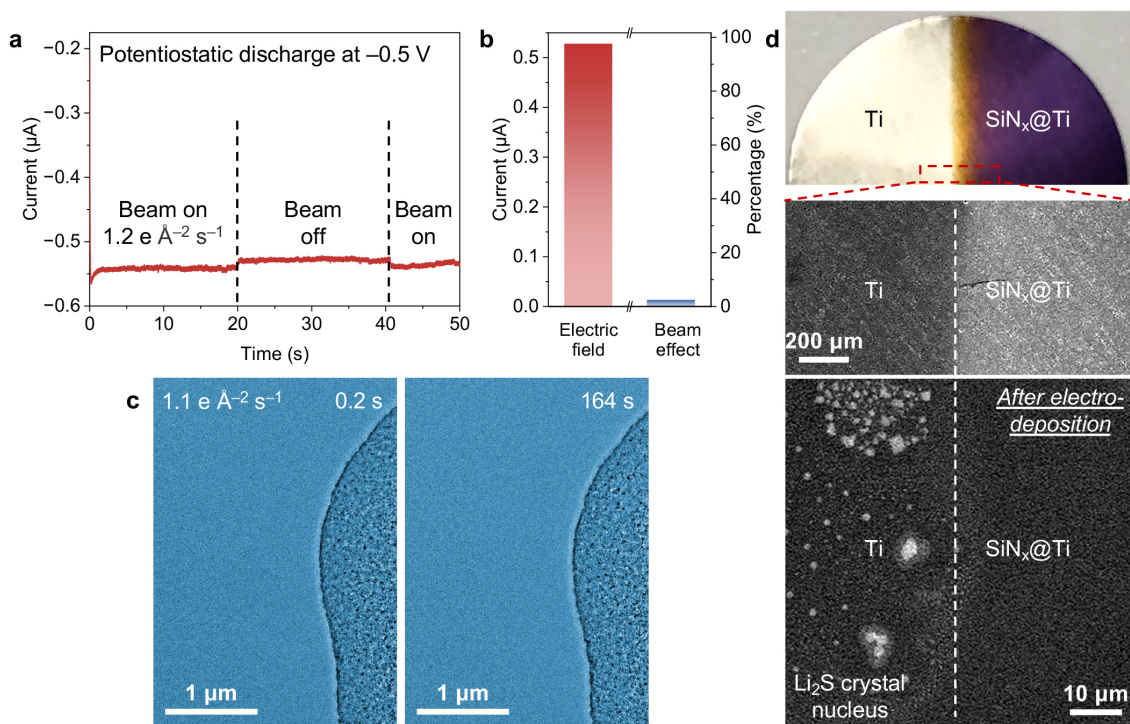
Supplementary Fig. 7 | *In situ* heating of commercial Li_2S in vacuum. (a) TEM and HAADF-STEM images, and EDS mapping of commercial Li_2S before heating. (b) TEM image of commercial Li_2S after heating in vacuum. (c) Heating time as a function of heating temperature (actual and expected). (d) Time-series TEM images of commercial Li_2S at a dose rate of $3 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$ without increasing temperature. (e) Time-series TEM images of commercial Li_2S at different temperature at the same dose rate of $3 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$. The commercial Li_2S was loaded onto the SiN_x observation window of a heating chip. The heating was carried out using a local Joule heating element integrated into the heating chip.



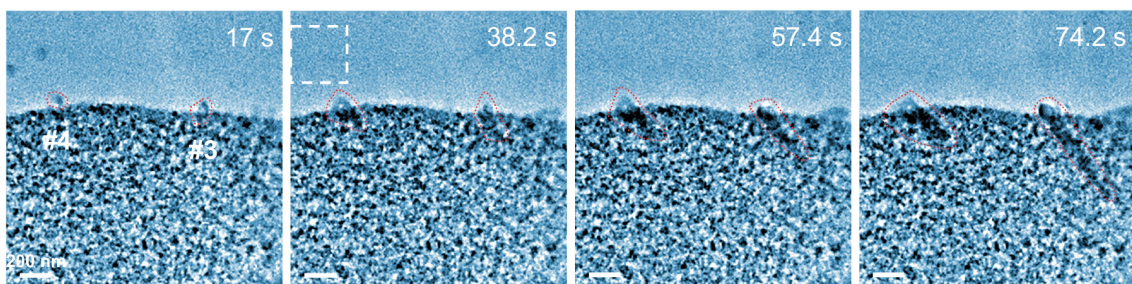
Supplementary Fig. 8 | E-beam effect on $\text{Li}_2\text{S}@$ graphene. (a, b) HAADF-STEM, HRTEM images, and EDS mappings of $\text{Li}_2\text{S}@$ graphene. $\text{Li}_2\text{S}@$ graphene was prepared by ultrasonically mixing commercial Li_2S with graphene in DME for 30 min. (c) Time-series HRTEM images, corresponding FFT patterns, and partial enlarged details of $\text{Li}_2\text{S}@$ graphene at a dose rate of $11000 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$, showing the alleviated e-beam damage and stable atomic structure of Li_2S nanocrystalline.



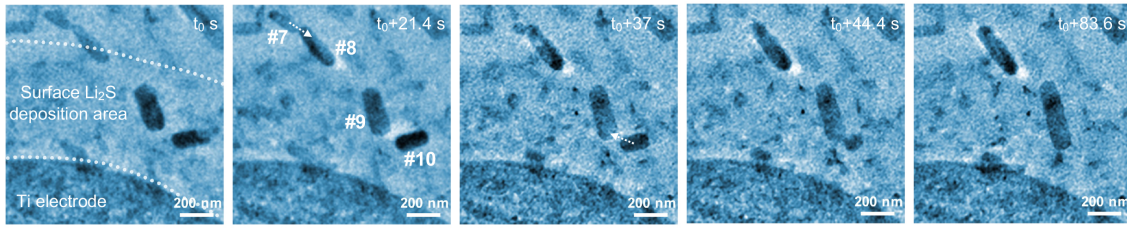
Supplementary Fig. 9 | E-beam effect on Li₂S deposited in coin-type cells. (a) Time-series HRTEM images of Li₂S nanocrystalline deposited on Mo NCs/N-G nanosheet. The inset is the partial enlarged details of the atomic structure. The e-beam dose rate was 13300 e Å⁻² s⁻¹. (b) Time-series TEM images of rod-like Li₂S deposited on bare Ti electrode. The e-beam dose rate was 8.3 e Å⁻² s⁻¹.



Supplementary Fig. 10 | E-beam effect on the electrochemical deposition of Li_2S . (a, b) Measured current during potentiostatic discharge at -0.5 V with e-beam on ($1.2 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$)/off. (c) Exclusion of e-beam effect on heterogeneous deposition of Li_2S . (d) The digital photograph and SEM images of Ti and $\text{SiN}_x@\text{Ti}$ surfaces before and after Li_2S deposition in coin-type cells. SiN_x layer on Ti current collector was constructed by PECVD. Li_2S deposition was conducted by galvanostatic discharge at $16 \mu\text{A cm}^{-2}$ with $100 \text{ mM Li}_2\text{S}_6$ electrolyte in coin-type cells from OCP to 1.7 V.



Supplementary Fig. 11 | Li_2S deposition on Ti electrode via a single-step pathway. Time-series TEM images from Supplementary Video 2 of single-step deposition of Li_2S (particles #3 and #4) in an electrochemical liquid cell. The electrochemical liquid cell was potentiostatically discharged at -0.5 V.

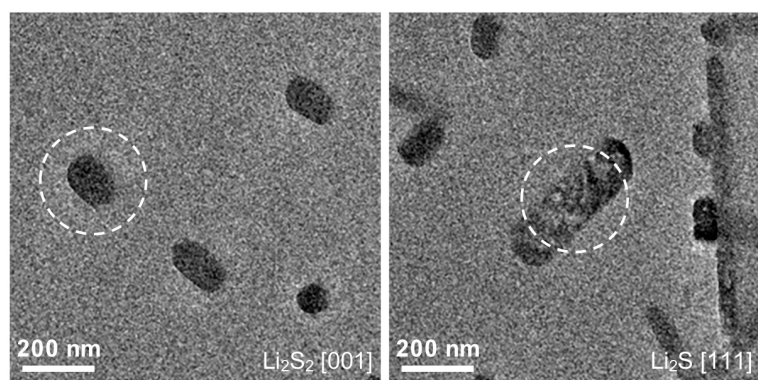


Supplementary Fig. 12 | Li₂S deposition on Ti electrode via a two-step pathway. Time-series TEM images showing two-step Li₂S deposition in an electrochemical liquid cell. TEM image (t_0 s) revealed solid Li₂S deposited on the surface of Ti electrode. The electrochemical liquid cell was potentiostatically discharged at -0.5 V. The moving direction of inter-particle mass-transfer (particles #7, #8, #9, and #10) is indicated by the arrows ($t_0+21.4$ s).

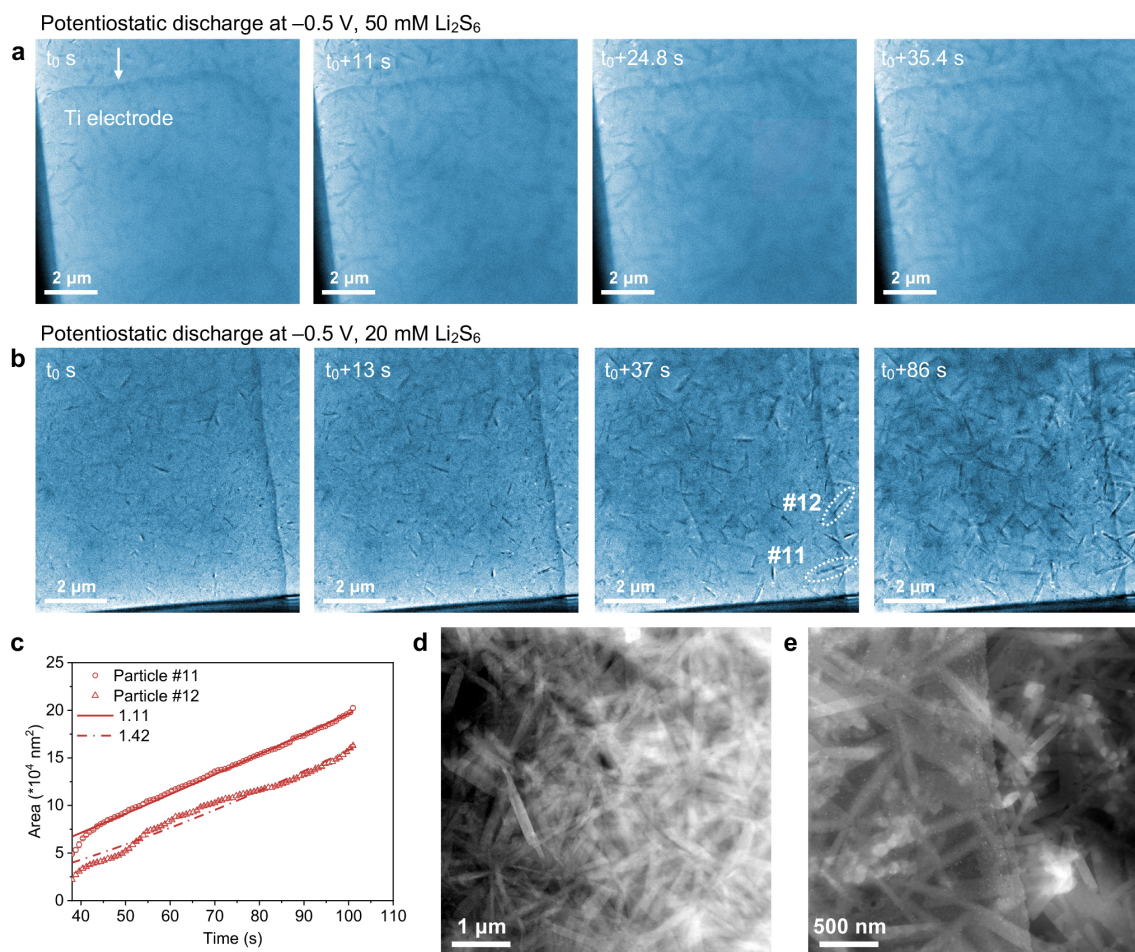
Explanation for the formation and dissolution of small nanoparticles: The conversion from soluble Li₂S₆ to solid Li₂S₂/Li₂S occurred through the electrochemical reduction at the electrode surface ($n/6\text{S}_6^{2-} + (2-n/3)e^- \rightarrow \text{S}_n^{2-}$, $n \leq 2$). During this process, some of the reduced $\text{S}_2^{2-}/\text{S}^{2-}$ ions diffused away from the electrode and caused the precipitation of solid Li₂S_n in the electrolyte ($\text{S}_n^{2-} + \text{Li}^+ \rightarrow \text{Li}_2\text{S}_n\downarrow$, $n \leq 2$), as revealed in Supplementary Figs. 11 and 12. However, these solid discharge products were thermodynamically unstable and were prone to undergo disproportionation reactions or chemically react with soluble/long-chain LiPSs intermediates,²⁸ thus leading to their spontaneous decomposition and dissolution. As a result, the formation and dissolution of solid discharge products in the electrolyte was observed during the potentiostatic discharge.

Impact of dissolved particles on the deposition of micro-rods: The impact on the deposition of larger rod-like structures can be understood according to the statistics of projection area variation in Fig. 2a. It revealed that the decrease of metastable particle #2 (smaller size) was accompanied by an increase of particle #1 (larger size), and the projection area of particle #1 underwent an acceleration after 116.2 s. Time-series TEM images (Fig. 2b), especially at 116.2 s, and Supplementary Video 1 showed the direct observation of mass transfer from particle #2 (smaller size) to particle #1 (larger size). This should be attributed to the large surface energy of small particles, which tended to dissolve and re-crystallize on the larger particles to lower the system energy and stabilize crystal structures. The inter-particle mass-transfer was confirmed by particles #7/#8 and particles #9/#10 (Supplementary Fig. 12).

Therefore, the above investigation indicates that reduced S_n^{2-} ($n \leq 2$) ions are diffusible and can result in the precipitation of solid Li₂S_n ($n \leq 2$) near the electrode surface. The thermodynamic instability and chemical reactivity of these solid discharge products can lead to their spontaneous dissolution or decomposition, thereby supplying LiPSs species for the growth of larger particles.



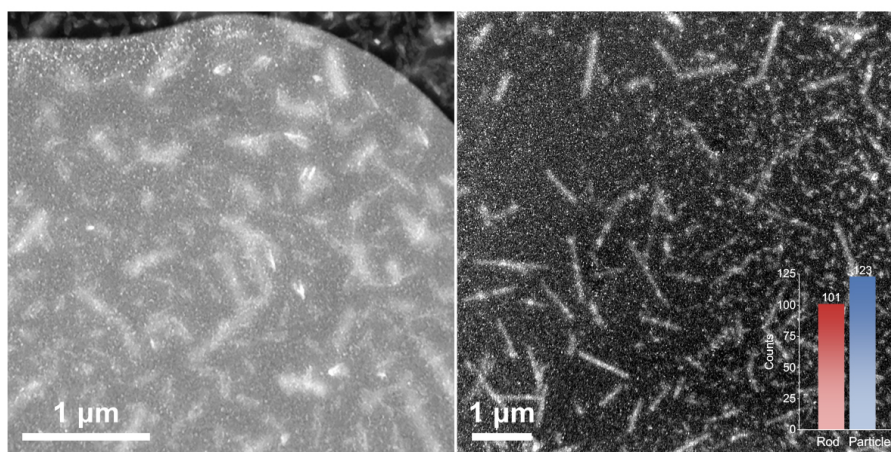
Supplementary Fig. 13 | TEM images of SAED patterns of Li₂S₂ and Li₂S. TEM images of SAED patterns of granular Li₂S₂ and rod-like/plate-like Li₂S in Fig. 2d, e.



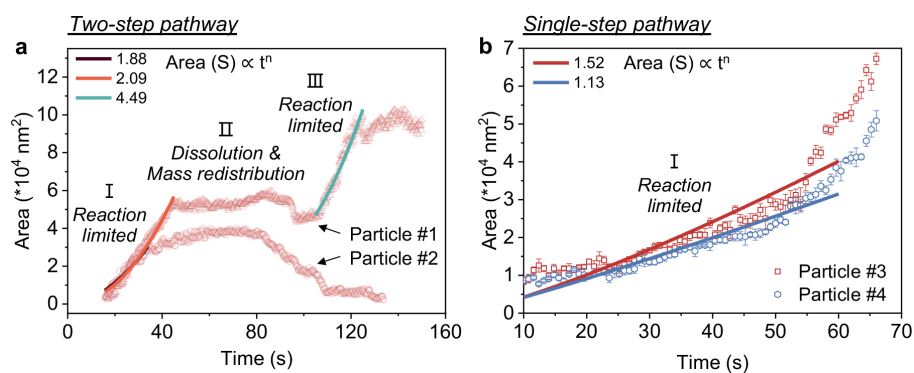
Supplementary Fig. 14 | Deposition of Li_2S at -0.5 V with various Li_2S_6 concentrations. (a) Time-series TEM images using 50 mM Li_2S_6 electrolyte for Li_2S deposition. Ti electrode edge is marked by a white arrow. (b) Time-series TEM images using 20 mM Li_2S_6 electrolyte for Li_2S deposition. (c) The projection area variation as a function of time of particles #11 and #12 in Supplementary Fig. 14b. Error bars represent standard deviations of the measurement. (d, e) HAADF-STEM images after Li_2S deposition on the surface of Ti electrode using 20 mM Li_2S_6 electrolyte.

Li_2S deposition using 20 and 50 mM Li_2S_6 as electrolyte: We investigated the effect of higher concentrations of Li_2S_6 electrolyte on the deposition of Li_2S . Our results showed that 50 mM Li_2S_6 (Supplementary Fig. 14a) yielded similar deposition of rod-like/plate-like Li_2S on the electrode surface, but the spatial resolution was significantly reduced. On the other hand, with 20 mM Li_2S_6 (Supplementary Fig. 14b), the electrode surface got clearer, and we observed both single-step and two-step deposition. Time-series TEM images and projection area variation indicated gradual deposition of Li_2S into rod-like/plate-like structures (Supplementary Fig. 14b, c). Statistical analysis of particles #11/#12 revealed similar reaction-limited stages in accordance with the Lifshitz-Slyozov-Wagner model (LSW, $\text{Area} \propto t^n$). Our findings suggest that the growth behavior remains largely unchanged compared to the lower concentration of Li_2S_6 electrolyte (10 mM) in the main text (Fig. 2). However, we did observe more solid discharge products, including both rod-like/plate-like and granular structures, on the electrode surface (Supplementary Fig. 14d, e). Additionally, the higher electrolyte concentration increased the non-elastic scattering of electrons, which further decreased the spatial resolution of the liquid cell. Our statistical analysis of particles deposited using different concentrations of Li_2S_6 electrolyte (10 and 20 mM) revealed a reaction-limited stage in both cases (Supplementary Figs. 14c and 16), indicating

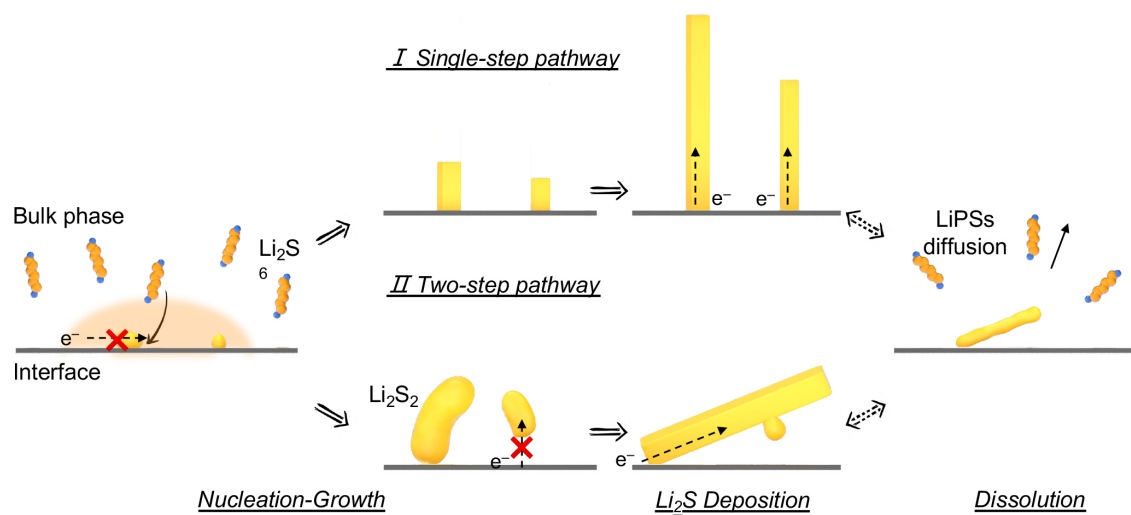
sufficient reactant at the electrode/electrolyte interface. As a result, increasing the Li_2S_6 concentration did not alter the nucleation-growth pathway, but rather decreased the image resolution. In contrast, when we changed the discharge potentials (Extended Data Fig. 3), we observed distinct variations in deposition pathways. These results suggest that the deposition of Li_2S is primarily controlled by charge transfer at the electrode surface rather than the concentration of Li_2S_6 electrolyte.



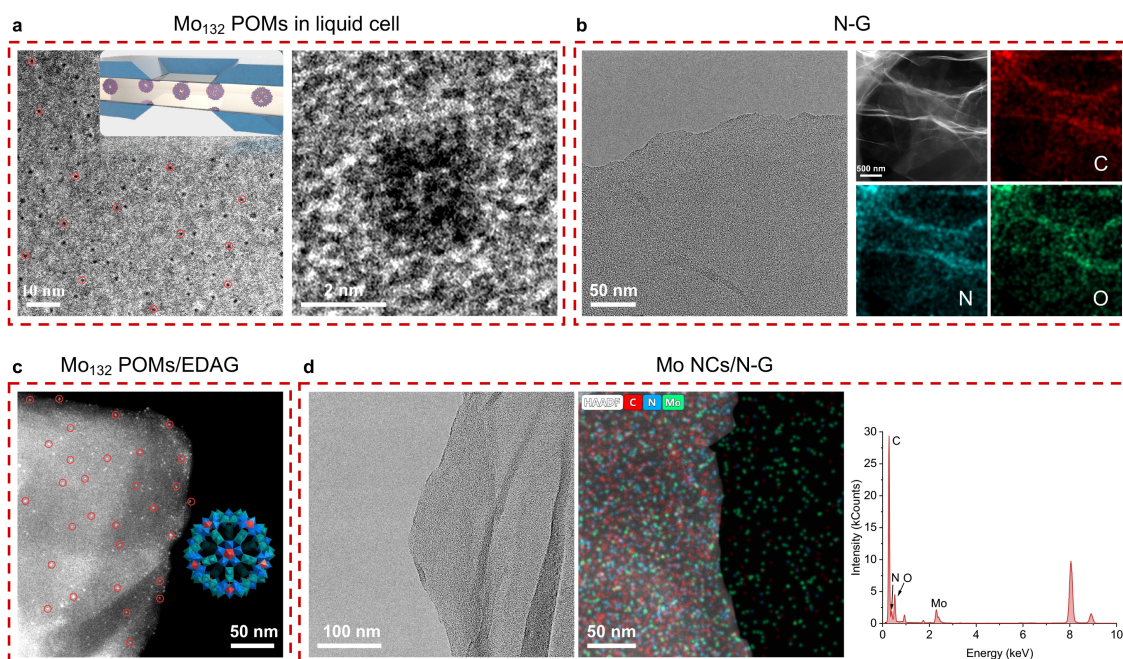
Supplementary Fig. 15 | Statistical analysis of deposited Li_2S at -0.5 V without mediation of active centers. STEM images and the corresponding statistics of granular and rod-like products after potentiostatic discharge at -0.5 V. It revealed the formation of both granular and rod-like structures, indicating that Li_2S deposition at -0.5 V underwent both single-step and two-step pathways simultaneously.



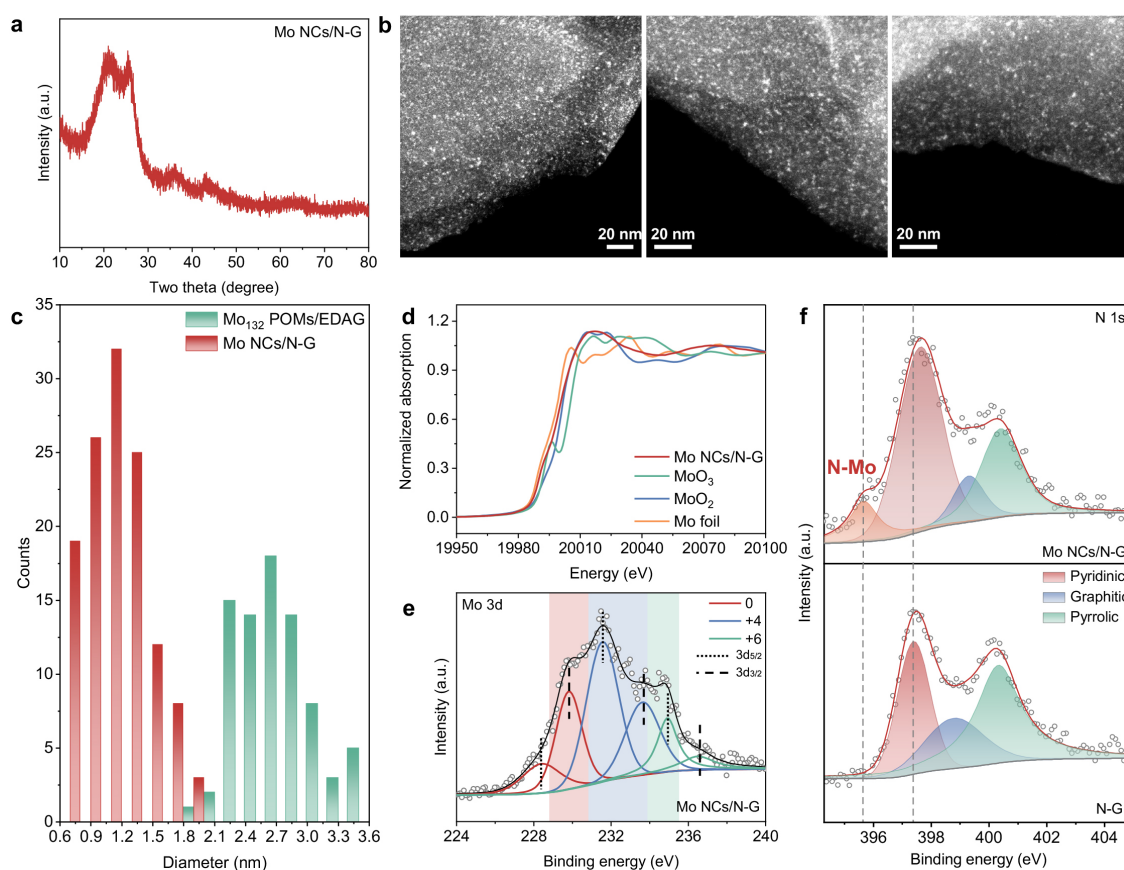
Supplementary Fig. 16 | Investigation of projection area variation. (a) Area variation of particles #1 and #2 in Fig. 2 as a function of time during potentiostatic discharge through a two-step pathway. (b) Area variation of particles #3 and #4 as in Supplementary Fig. 11 a function of time during potentiostatic discharge through a single-step pathway. A power function was used to fit the area variation over time ($\text{Area} \propto t^n$) according to LSW model, where $n \geq 1$ represents reaction-limited growth, and $n < 1$ represents diffusion-limited growth. Error bars represent standard deviations of the measurement.



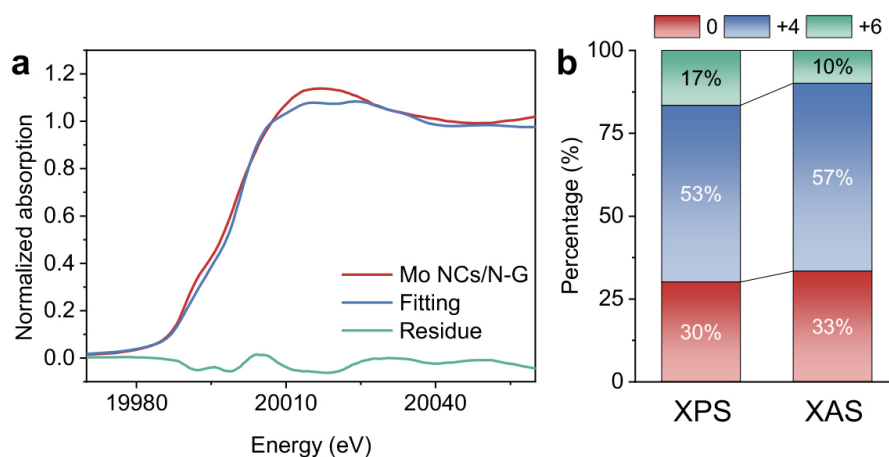
Supplementary Fig. 17 | Schematic illustration of interfacial reactions without mediation of active centers. The (I) single-step and (II) two-step pathways for rod-like/plate-like Li_2S deposition.



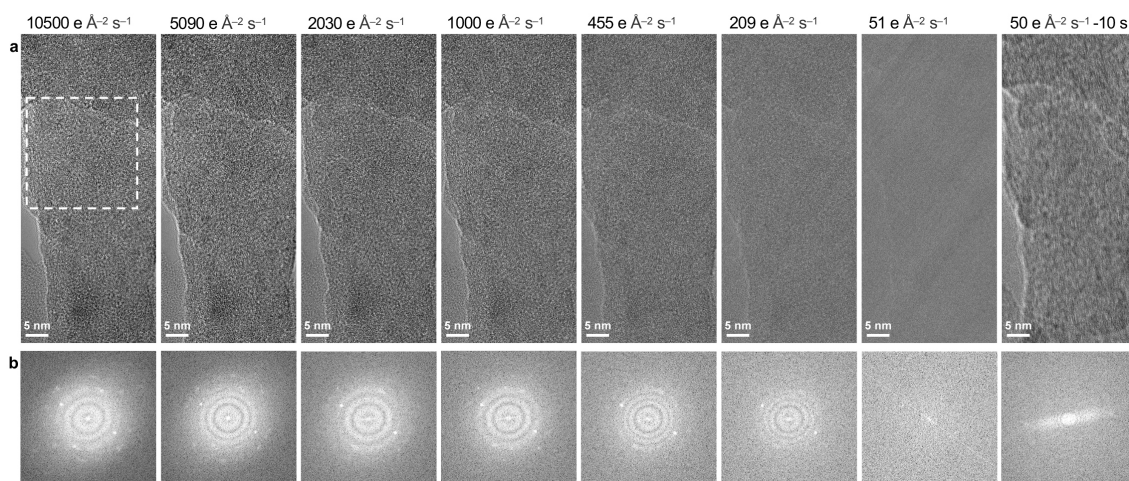
Supplementary Fig. 18 | Morphology characterization during the preparation of Mo NCs/N-G nanosheet. (a) HRTEM images of Mo₁₃₂ POMs observed in a liquid cell (aqueous solution of 1 mg mL⁻¹ POMs). (b) TEM, HAADF-STEM images, and element mappings (C, N, O) of N-G. (c) HAADF-STEM image of Mo₁₃₂ POMs/EDAG after electrostatic interaction assembly, showing a discrete distribution. The inset is the crystal structure of Mo₁₃₂ POMs. (d) TEM, overlapped HAADF-STEM image with element mappings (C, N, Mo), and EDS spectrum of Mo NCs/N-G.



Supplementary Fig. 19 | Morphology and structure characterization of Mo NCs/N-G nanosheet. (a) XRD pattern of Mo NCs/N-G, without the detection of crystallized Mo. (b) HAADF-STEM images of Mo NCs/N-G nanosheet, showing the monodispersed Mo nanoclusters. (c) Distribution statistics of Mo₁₃₂ POMs (~2.7 nm) on EDAG and Mo NCs (~1.1 nm) on N-G. (d) XANES of Mo NCs/N-G and reference samples of Mo-foil, MoO₂, and MoO₃. (e) Mo 3d XPS spectrum of Mo NCs/N-G. (f) Comparison of N 1s XPS spectra between Mo NCs/N-G and N-G. In the N 1s XPS spectrum of Mo NCs/N-G, the peaks at 400.5, 399.3, 397.7, and 395.7 eV indicated pyrrolic N, graphitic N, pyridinic N, and N-Mo bonds, respectively.

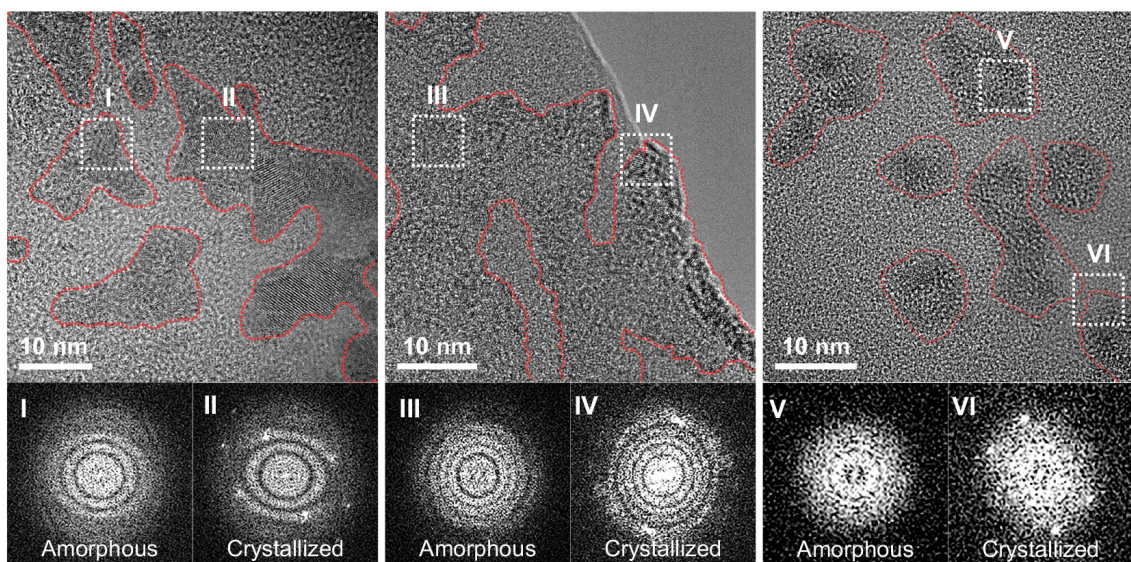


Supplementary Fig. 20 | Linear combination fitting. (a) XANES linear combination fitting of Mo NCs/N-G, using the reference samples of Mo-foil, MoO₂, and MoO₃. The fitting residual is expected due to the different coordination of Mo nanoclusters in Mo NCs/N-G compared to those in Mo foil, MoO₂, and MoO₃. (b) Percentage of Mo nanoclusters in Mo NCs/N-G with different valence of Mo⁰, Mo⁺⁴, and Mo⁺⁶, which were calculated based on Mo 3d XPS spectrum and XANES linear combination fitting. The valence distribution acquired through XANES linear combination fitting was verified by results obtained by the integrated areas of XPS peaks, and the slight difference should be attributed to the detection depth of characterization techniques.

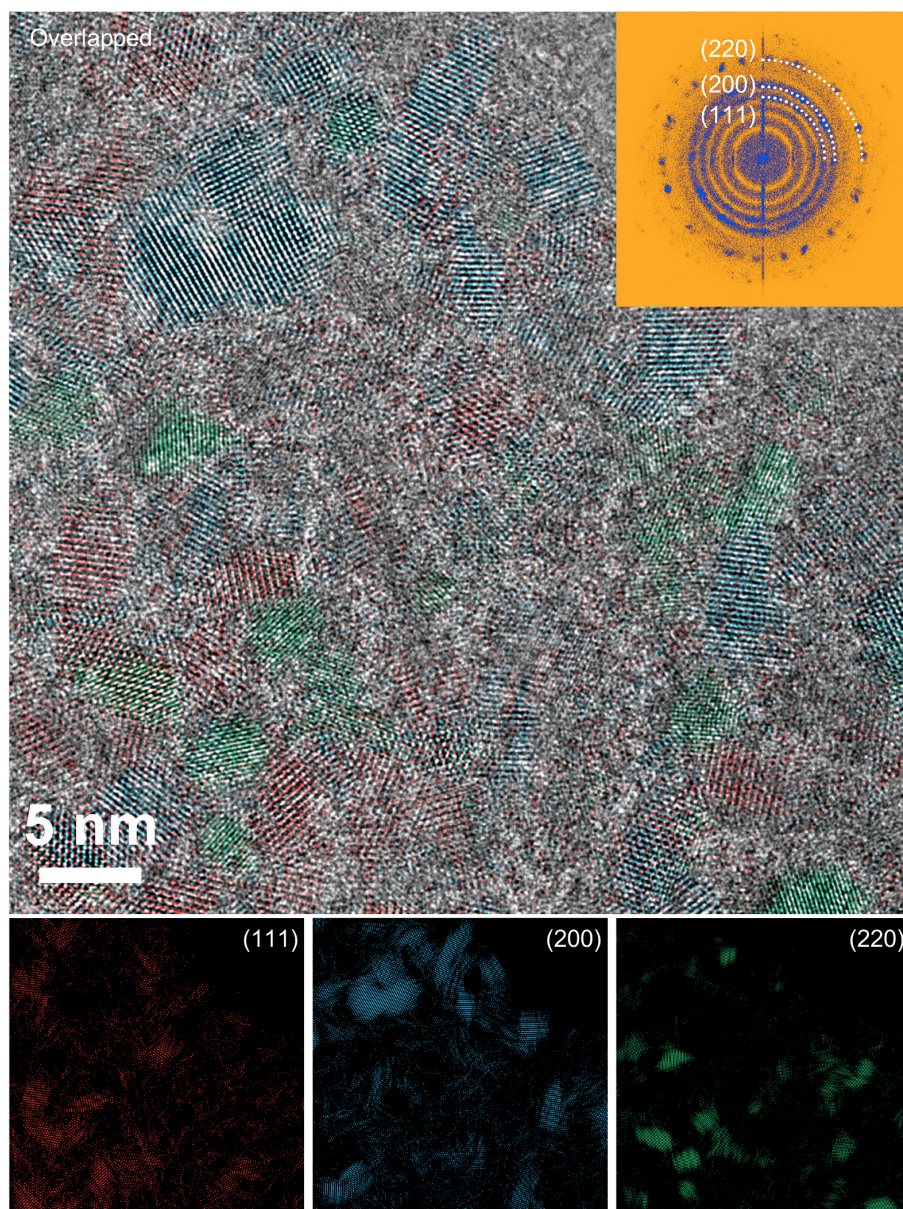


Supplementary Fig. 21 | Structures of $\text{Li}_2\text{S-Mo NCs/N-G}$ obtained at various e-beam dose rates. (a, b) HRTEM images and the corresponding FFT patterns of $\text{Li}_2\text{S-Mo NCs/N-G}$ after electrochemical deposition in a liquid cell. The HRTEM images were acquired by FEI Talos-F200s TEM operating at 200 kV, using Velox software at various e-beam dose rates, with a resolution of 4096×4096 pixels and an exposure time of 500 ms (from the first to the seventh columns) and 10 s (the eighth column).

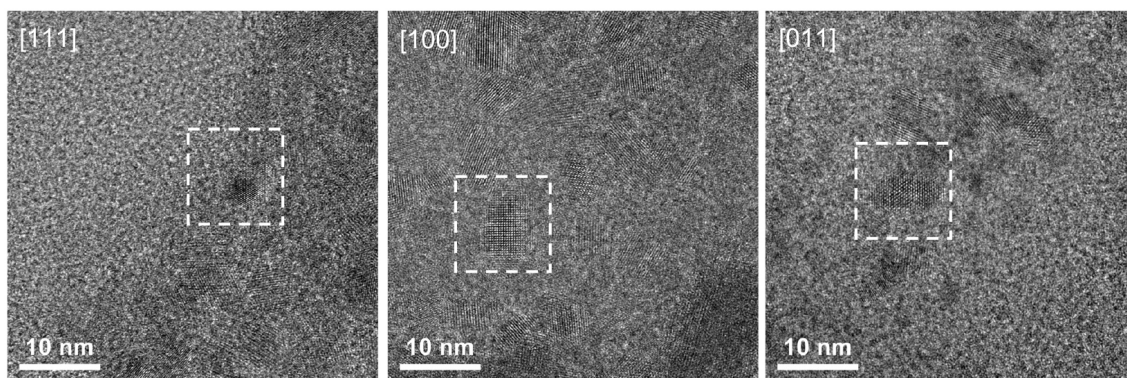
Influence of e-beam dose rates on HRTEM images: HRTEM images and the corresponding FFT patterns of $\text{Li}_2\text{S-Mo NCs/N-G}$ were obtained after the electrochemical deposition in a liquid cell. At a dose rate of $51 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$, using a resolution of 4096×4096 and 500 ms exposure time, the surface structures could not be observed. Even after extending the exposure time to 10 s, the sample drifting impeded high-resolution observation, although the outline of graphene was observable. However, by increasing the dose rate to approximately $200 \text{ e } \text{\AA}^{-2} \text{ s}^{-1}$, the crystal structure of Li_2S nanocrystalline become visible, as confirmed by the FFT patterns. With a further increase in the e-beam dose rate, the atomic structures became clearer. Therefore, it is crucial to note that achieving high-quality HRTEM images of Li_2S nanocrystalline requires a balance of the e-beam dose rate, exposure time, and image resolution.



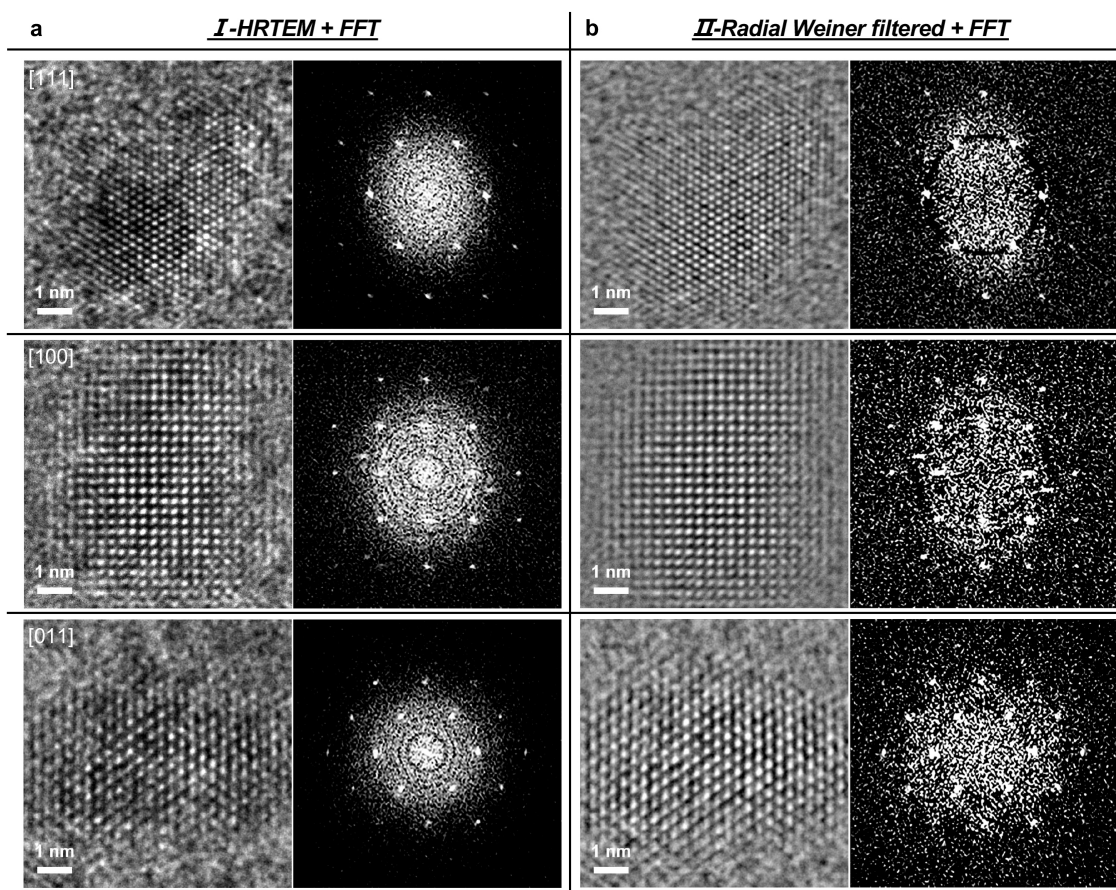
Supplementary Fig. 22 | Amorphous and crystallized Li_2S . HRTEM images and the corresponding FFT patterns showing the amorphous and poly-crystallized Li_2S deposited on Mo NCs/N-G.



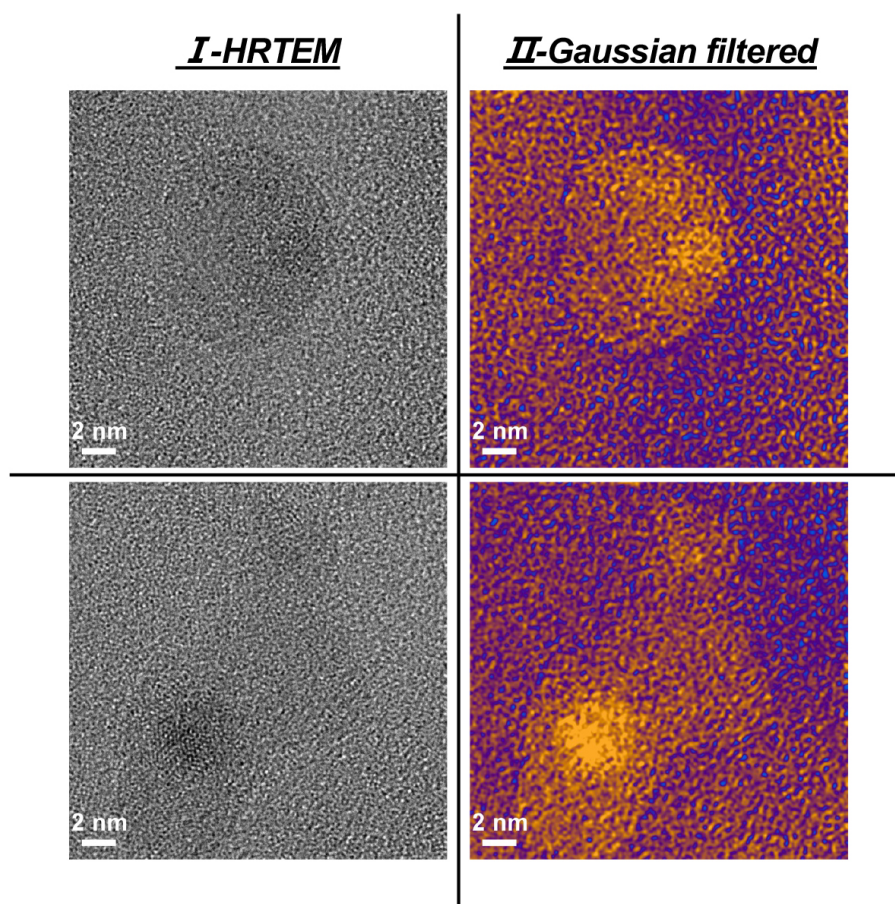
Supplementary Fig. 23 | HRTEM image and FFT patterns of Li_2S . HRTEM image, FFT pattern, and inversed FFT patterns filtered in specific frequencies, corresponding to the inversed FFT patterns in Fig. 3g. The (111), (200), and (220) crystal planes are overlapped in red, blue and green colours, respectively.



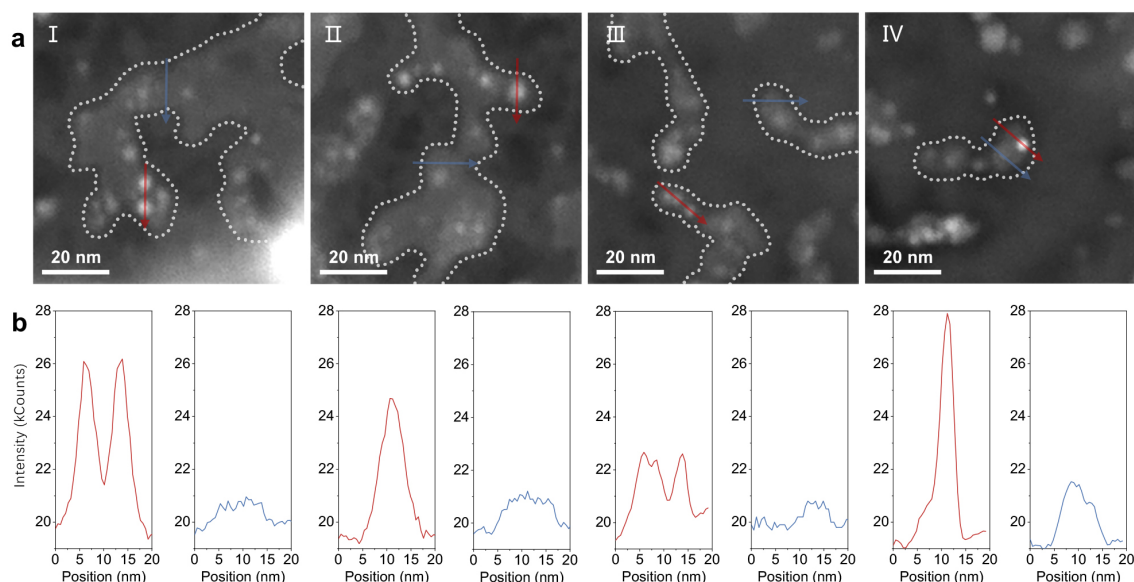
Supplementary Fig. 24 | HRTEM images at a lower magnification. HRTEM images of Li_2S nanocrystalline deposited on Mo NCs/N-G in a liquid cell, along [111], [100], and [011] directions, corresponding to Fig. 3i and Supplementary Fig. 25.



Supplementary Fig. 25 | Post-image processing of Li₂S atomic structure by radial Wiener filter. The raw data of HRTEM images in Fig. 3i before and after radial Wiener filtering, as well as the corresponding FFT patterns.

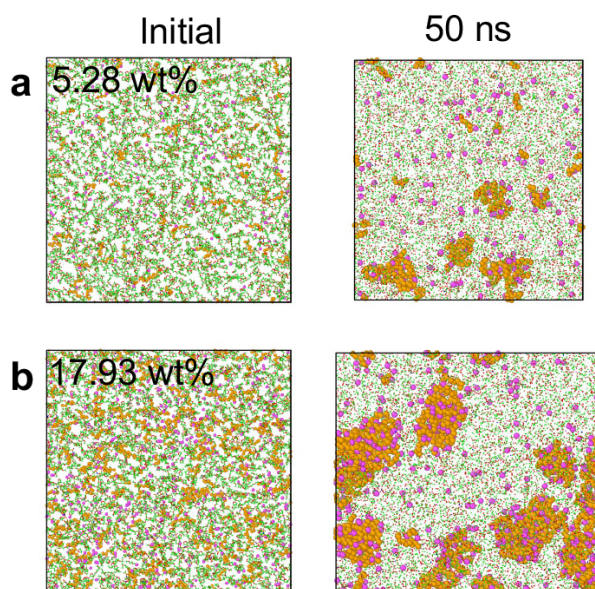


Supplementary Fig. 26 | Characterization of LiPSs dense phase from HRTEM images. Raw and post-processed HRTEM images using a Gaussian filter. To solve the scattering and artifacts in HRTEM images resulting from amorphous SiN_x windows, disordered electrolyte, and the contrast transfer function of the electron microscope, a Gaussian filter was applied to suppress high-spatial frequency noise and enhance the boundary of dense phase areas.

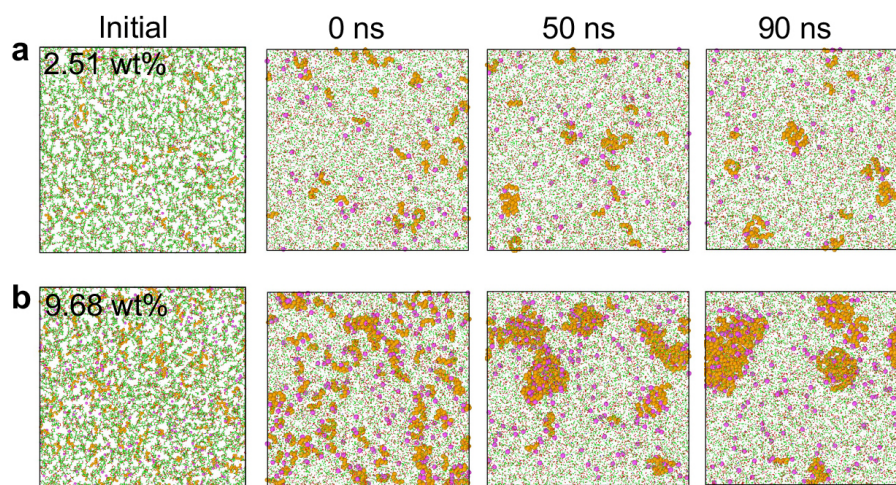


Supplementary Fig. 27 | Confirmation of LiPSs dense phase from HAADF intensity. (a, b) Partial enlarged details of HAADF-STEM images and the corresponding linear HAADF intensity analysis. The areas of LiPSs dense phase were marked by the white dotted lines. The particles with brighter contrast in the dense phase areas were Li₂S nanocrystalline. The red and blue arrows/curves corresponded to Li₂S nanocrystalline and LiPSs dense phase, respectively.

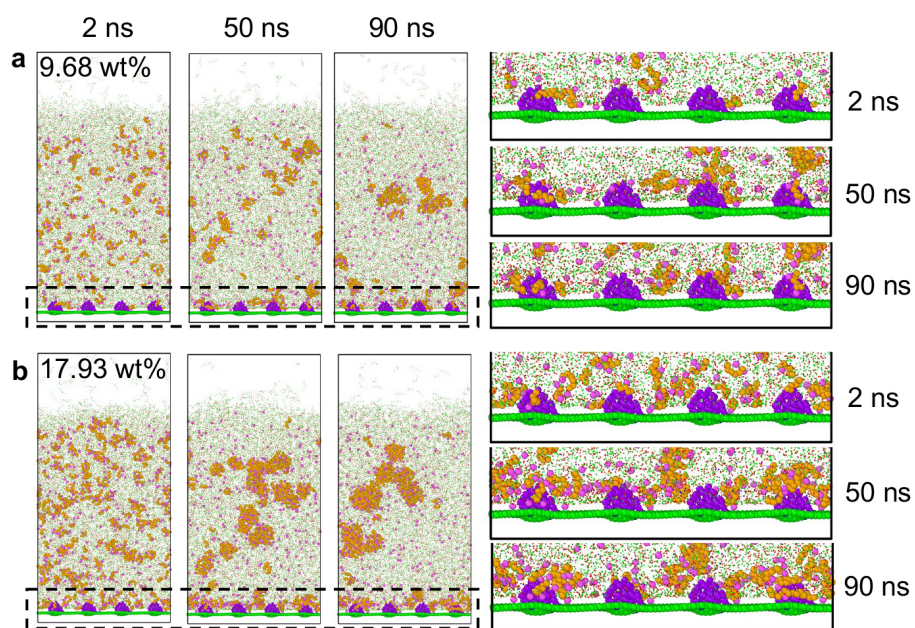
Z-contrast analysis: The contrast of the HAADF-STEM image, which is positively correlated with atomic number (Z), is determined by the elastically scattered electrons reaching the HAADF detector. In our analysis, we found that Li₂S nanocrystalline exhibited a higher contrast compared to the dense phase, as the former was the FCC close-packed structure of Li⁺ and S²⁻ ions, while the later was the mixed structure of ions and solvent molecules. From the linear analysis of HAADF intensity, the contrast contribution can be attributed to Li₂S nanocrystalline, LiPSs dense phase, electrolyte, and the background, respectively (Extended Data Fig. 7e–g). This was further confirmed in multiple areas and the linear HAADF intensity analysis. The results revealed that Li₂S nanocrystalline had a sharper and higher intensity, while LiPSs dense phase exhibited a more fluctuant and weaker intensity (Supplementary Fig. 27).



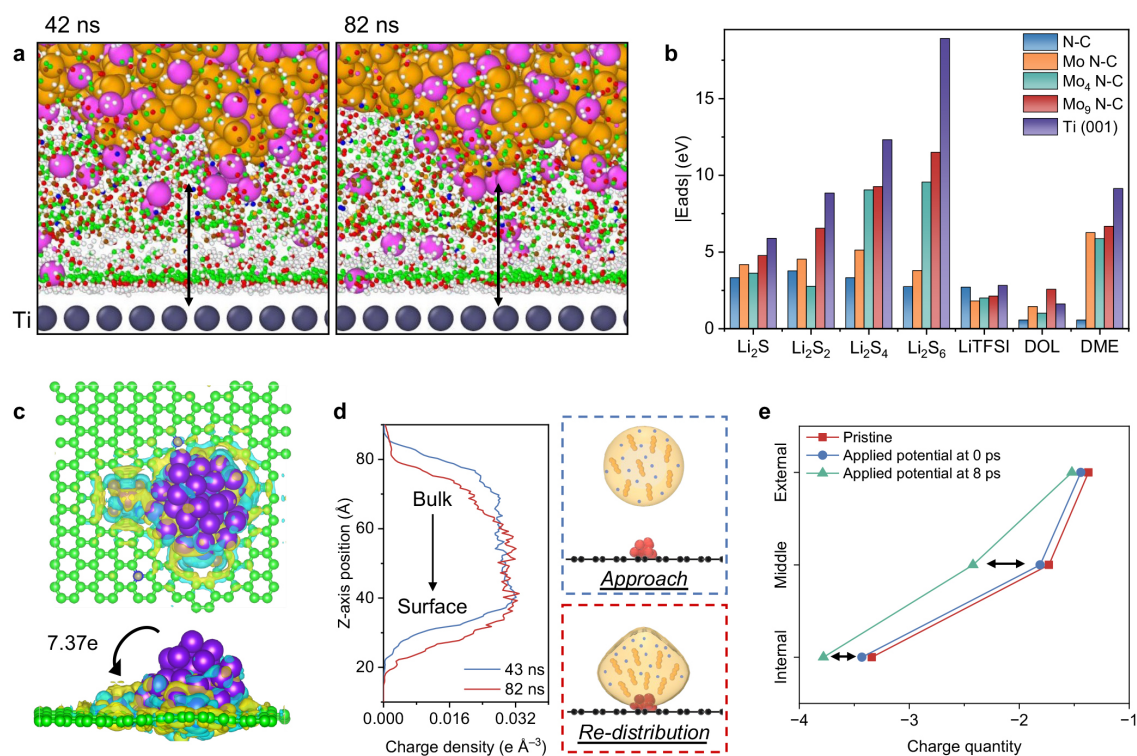
Supplementary Fig. 28 | Time-series MD simulations of spontaneous aggregation of Li_2S_6 without electrode surfaces. Snapshots of MD simulations with different Li_2S_6 concentrations of (a) 5.28 wt% and (b) 17.93 wt%, respectively. Snapshots of 0 and 90 ns at these concentrations are presented in Extended Data Fig. 8a. The first row is the initial structures of MD simulations, where S_6^{2-} and Li^+ ions are randomly dispersed in the electrolyte. After 2 ns of 1 bar NPT simulation, the NVT simulation sampling is carried out. The simulation results reveal that the aggregation degree of Li_2S_6 molecular increases with an increase in Li_2S_6 concentration.



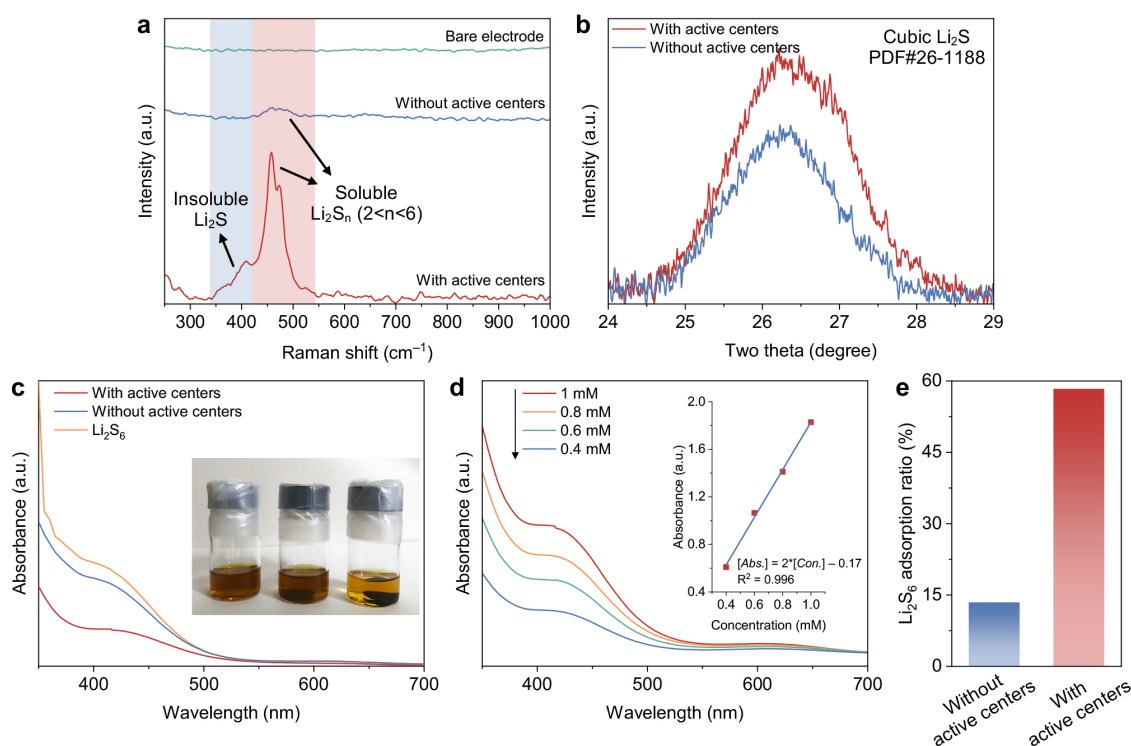
Supplementary Fig. 29 | Time-series MD simulations of spontaneous aggregation of Li_2S_6 without electrode surfaces. Snapshots of MD simulations with different Li_2S_6 concentrations of (a) 2.51 wt% and (b) 9.68 wt%, respectively. The initial structures are the models before NPT simulations, and the 0 ns structures are the models after NPT relaxations.



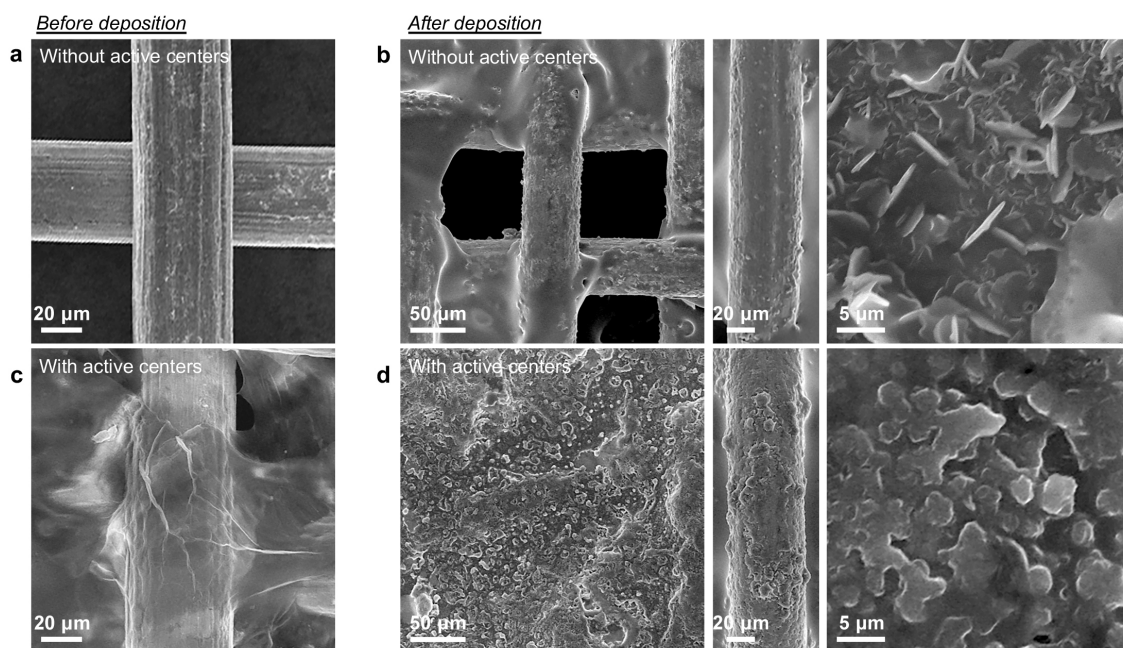
Supplementary Fig. 30 | Time-series MD simulations of Li_2S_6 movement on the surface of Mo NCs/N-G and Ti. Snapshots of MD simulations on the surface of Mo NCs/N-G with different Li_2S_6 concentrations of (a) 9.68 wt% and (b) 17.93 wt%. The right row is the enlarged view of the interface details, and the initial S_6^{2-} and Li^+ ions are randomly dispersed in the electrolyte. After the NVT relaxation of 2 ns, the sampling results indicate that Mo NCs/N-G has a strong long-range attraction with S_6^{2-} ions.



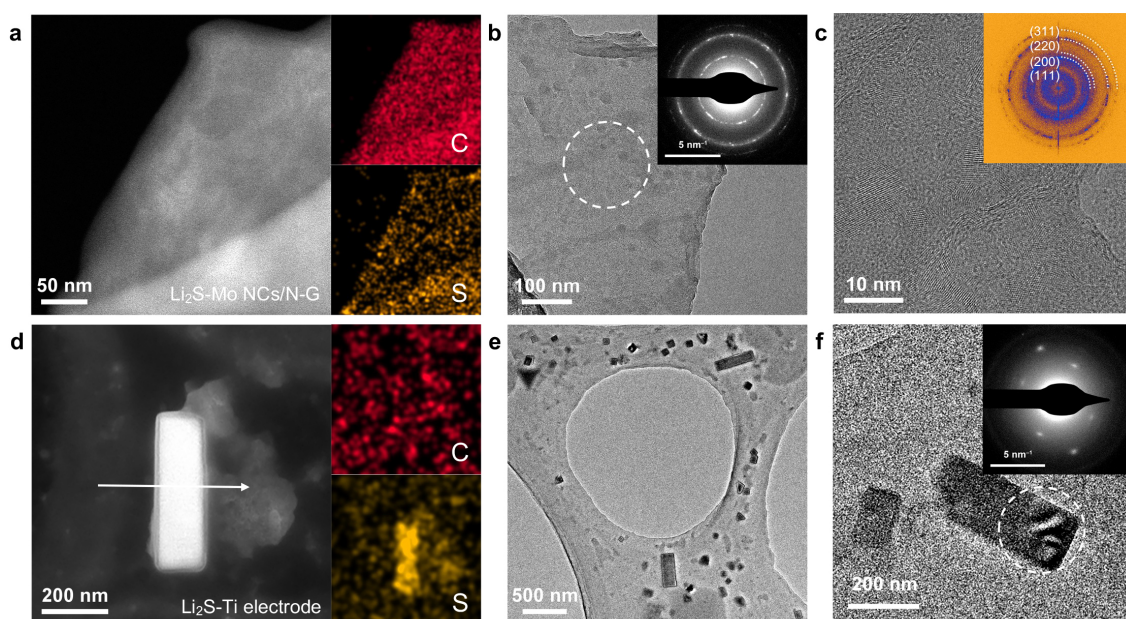
Supplementary Fig. 31 | Simulations and calculations. (a) Time-series MD simulations, showing that the LiPSs was not adsorbed by Ti surfaces after 82 ns. The pink, orange, purple, blue, and green balls represent Li, S, Mo, N, and C atoms, respectively. (b) DFT calculation of adsorption energy of N-C, Mo N-C, Mo₄ N-C, Mo₉ N-C, and Ti (001) towards Li₂S_n (n = 1, 2, 4, 6), LiTFSI, DOL, and DME. (c) DFT calculation of charge quantity of Mo active centers. (d) Comparison of charge density variation curves between 43 and 82 ns of S₆²⁻ ions in dense ion-complex phase, corresponding to Fig. 4f, and the schematic illustration. The fluctuations in the curves and their movement along the Z-axis position should be attributed to the re-distribution of Li⁺ and S₆²⁻ ions and the continuous approach of dense ion-complex phase towards the Mo NCs/N-G surface, as illustrated schematically. The orange chains and blue balls in schematic illustration represent S₆²⁻ and Li⁺ ions, respectively. (e) Statistics of charge variation of S₆ ions in the internal, middle, and external layers, corresponding to AIMD simulations in Extended Data Fig. 8g.



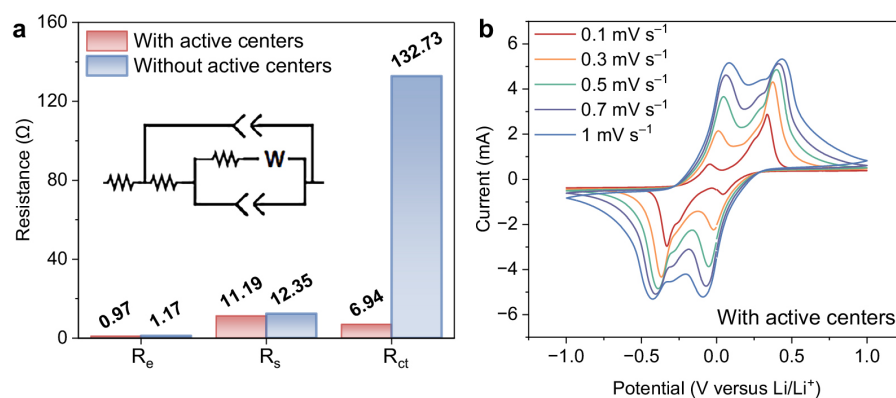
Supplementary Fig. 32 | *Ex situ* Raman spectra, XRD patterns, and UV-vis spectra characterizations. (a) *Ex situ* Raman spectra of Ti mesh with/without the decoration of Mo NCs/N-G after galvanostatic discharge in coin-type cells from OCP to 1.7 V. To prevent air exposure to the cycled electrodes, a specialized stainless steel Raman device was utilized with a 0.5 mm thick quartz window on its upper surface. (b) *Ex situ* XRD patterns of Ti mesh with/without the decoration of Mo NCs/N-G after galvanostatic discharge in coin-type cells from OCP to 1.7 V. To avoid air exposure, the deposited cells were dis-assembled in argon-filled glovebox and re-assembled into Kapton-filmed coin-type cells. (c) UV-vis spectra and digital photograph after a 12-hour static Li₂S₆ adsorption of Ti mesh with/without the decoration of Mo NCs/N-G. 0.02 M Li₂S₆ was used the electrolyte. (d) UV-vis spectra of blank Li₂S₆ electrolyte with different concentrations of 1, 0.8, 0.6, and 0.4 mM, as well as the corresponding linear fitting of absorbance and concentration. (e) The calculated Li₂S₆ adsorption ratio of Ti mesh with/without the decoration of Mo NCs/N-G based the absorbance and linear fitting. For the above *ex situ* characterizations, the areal loading of Mo NCs/N-G was controlled at around 0.5 mg cm⁻² (16 mm in diameter), prepared by ball milling the mixture of 80 wt% active materials and 20 wt% LA133 aqueous binder.



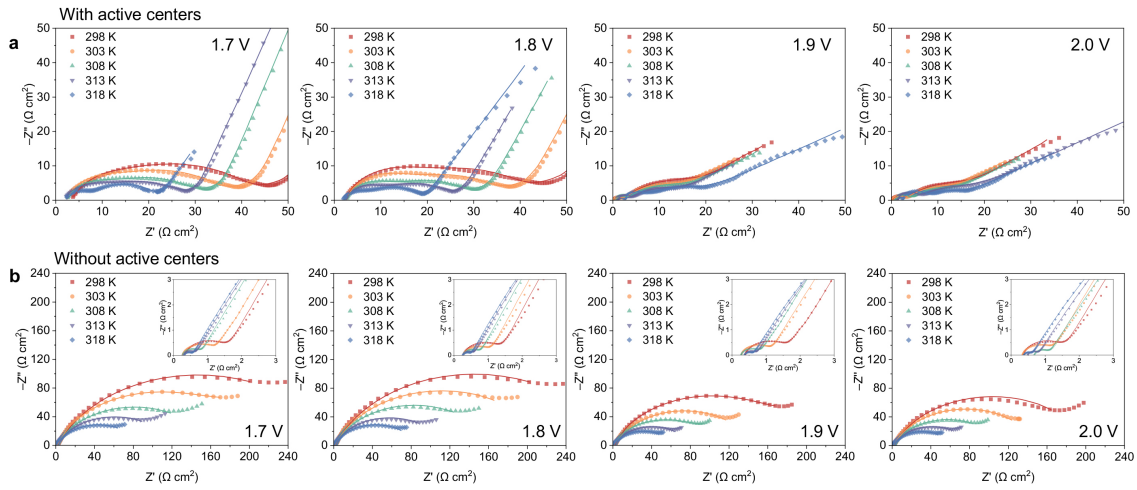
Supplementary Fig. 33 | *Ex situ* SEM characterization. (a, b) SEM images of Ti mesh without and with the decoration of Mo NCs/N-G before Li_2S deposition. (c, d) SEM images of Ti mesh without and with the decoration of Mo NCs/N-G after Li_2S deposition. Li_2S deposition was conducted by galvanostatic discharge at $16 \mu\text{A cm}^{-2}$ with 100 mM Li_2S_6 electrolyte in coin-type cells from OCP to 1.7 V.



Supplementary Fig. 34 | *Ex situ* (S)TEM characterization of deposited Li_2S with/without active centers. (a) *Ex situ* STEM and EDS mappings of Mo NCs/N-G nanosheet after Li_2S deposition in coin-type cells. (b, c) (HR)TEM images and the corresponding SAED and FFT patterns of Li_2S nanocrystalline deposited on Mo NCs/N-G nanosheet. (d) *Ex situ* STEM images and EDS mappings of rod-like/plate-like Li_2S deposited on bare Ti electrode in coin-type cells. (e, f) TEM images and the corresponding SAED pattern of Li_2S micro-rods. Li_2S deposition was conducted by the same galvanostatic discharge. Li_2S deposition was conducted by galvanostatic discharge at $16 \mu\text{A cm}^{-2}$ with 100 mM Li_2S_6 electrolyte in coin-type cells from OCP to 1.7 V.



Supplementary Fig. 35 | Electrochemical behaviors. (a) Resistance values from Nyquist profiles after potentiostatic discharge, corresponding to Extended Data Fig. 9b. The inset is the equivalent circuits for fitting. (b) CV profiles of the symmetric cell with active centers at different scan rates of 0.1, 0.3, 0.5, 0.7, and 1 mV s^{-1} .



Supplementary Fig. 36 | Calculation of activation energy. (a, b) Nyquist profiles of EIS including the measured (symbols) and fitting (lines) impedance data with/without the decoration of Mo NCs/N-G after galvanostatic discharge at 1.7, 1.8, 1.9, and 2.0 V. The insets are the local magnification profiles. The intercept of the first semicircle with the horizontal axis corresponds to the resistance of electrode and electrolyte (R_e). The first semicircle forms due to the surface deposition of solid $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ (R_s). The second semicircle is induced by the charge transfer process occurring at the surface of active centers (R_{ct}). The straight line represents the resistance of Li^+ diffusion inside Mo NCs/N-G nanosheet (Z_w).

Supplementary Videos 1-10

Supplementary Video 1 | Two-step deposition of rod-like Li_2S via metastable Li_2S_2 and its following dissolution without mediation of active centers. For the two-step pathway, the reactions on bare electrode surface involved the initial nucleation of metastable granular Li_2S_2 and further growth of rod-like Li_2S . (Displayed with a speed 25× of a real time process)

Supplementary Video 2 | Single-step deposition of rod-like Li_2S without mediation of active centers. For the single-step pathway, rod-like Li_2S was deposited directly on bare electrode surface. (Displayed with a speed 25× of a real time process)

Supplementary Video 3 | Two-step deposition of rod-like/plate-like Li_2S without mediation of active centers at -0.1 V. When reducing the discharge potential to -0.1 V, solid discharge products primarily nucleated in granular structures during the early stage of deposition, which gradually transformed into rod-like/plate-like Li_2S as the deposition continued. (Displayed with a speed 25× of a real time process)

Supplementary Video 4 | Deposition of Li_2S with mediation of active centers. During potentiostatic discharge, Mo NCs/N-G nanosheet continuously spread with an increase in projection area possibly due to the deposition of Li_2S . By contrast, no nucleation-growth of rod-like/plate-like Li_2S was observed on the Ti electrode. (Displayed with a speed 50× of a real time process)

Supplementary Video 5 | Deposition of Li_2S following Supplementary Video 4 with mediation of active centers. Further observation at a higher magnification during discharge revealed that the spreading of Mo NCs/N-G nanosheet in Supplementary Video 4 should be attributed to the deposition of Li_2S nanocrystalline on the edge and surface. (Displayed with a speed 10× of a real time process)

Supplementary Video 6 | Deposition of Li_2S from 100 mM Li_2S_6 electrolyte with mediation of active centers. In Li_2S_6 electrolyte with a higher concentration, distinct contrast variation was observed on the electron-accessible areas of Mo NCs/N-G nanosheet (right bottom) due to the deposition of Li_2S , in comparison with the electron-inaccessible Mo NCs/N-G nanosheet (left bottom) and bare Ti electrode surface (right top). (Displayed with a speed 50× of a real time process)

Supplementary Video 7 | Reversible deposition of Li_2S via droplet-like dense phase with mediation of active centers. With mediation of active centers, multiple droplets (#1, #2, and #3) were observed on the surface of Mo NCs/N-G nanosheet before the instantaneous deposition of Li_2S . Droplet #1 was marked with red square and locally zoomed. It indicated a gathering-induced crystallization pathway, involving the collective reaction behaviour of gathering, conversion, and crystallization. Active centers also enabled the reversible solid-liquid phase transformation of LiPSs, revealed by the surface of Mo NCs/N-G nanosheet periodically getting clear and blurry. (Displayed with a speed 10× of a real time process in the first deposition, and 20× of a real time process in the following dissolution/deposition)

Supplementary Video 8 | MD simulation of LiPSs diffusion at Mo NCs/N-G surface with different electrolyte concentrations. Mo NCs/N-G gathered the S_6^{2-} and Li^+ ions with different concentrations (5.28 wt%, 9.68 wt%, and 17.93 wt%) from bulk solution to the electrode surface. The pink, orange, purple, blue, and green balls represent Li, S, Mo, N, and C atoms, respectively.

Supplementary Video 9 | MD simulation of LiPSs diffusion at Mo NCs/N-G surface. S_6^{2-} and Li^+ ion-complex was continuously attracted and gathered by Mo NCs/N-G surface to form a droplet-like dense phase. The pink, orange, purple, blue, and green balls represent Li, S, Mo, N, and C atoms, respectively.

Supplementary Video 10 | MD simulation of LiPSs diffusion at Ti surface. Ti surface revealed no interaction with LiPSs. The pink, orange, purple, blue, and green balls represent Li, S, Mo, N, and C atoms, respectively.

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