

# Regulating Polysulfide Transformation and Stabilizing Lithium Anode Using $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ Cluster@Carbon Nanotube-Modified Separator for Lithium-Sulfur Batteries

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Lithium-sulfur (Li-S) batteries emerge as compelling contenders for next-generation energy-storage devices, boasting a noteworthy mass-specific energy of 2600 Wh kg<sup>-1</sup>. However, the cycle stability and commercialization of Li-S batteries encounter challenges because of polysulfide shuttle and uncontrolled lithium dendrite growth. In this study, we present a polyoxometalates-based dual-function  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  cluster@carbon nanotube modified polypropylene (PP) separator ( $\text{PMo}_{12}\text{O}_{40}$ @CNT/PP) to regulate polysulfide transformation and safeguard the lithium anode in Li-S batteries. Leveraging its multi-electron redox properties and stable cluster structure, the  $\text{PMo}_{12}$  cluster acts as a polysulfide mediator, effectively capturing and

promoting electrochemical polysulfide transformation. The incorporation of CNT fosters consistent Li-ion nucleation, stabilizes the lithium anode, and impedes dendrite formation throughout cycling. Hence, Li-S cells equipped with the  $\text{PMo}_{12}\text{O}_{40}$ @CNT/PP separator display higher capacity and better stability (675 mAh g<sup>-1</sup> at 3.0 C and 0.02% capacity decay per cycle over 700 cycles). The pouch cells with a sulfur loading 4.5 mg cm<sup>-2</sup> exhibit an initial discharge specific capacity of 925 mAh g<sup>-1</sup> at 0.1 C, and remain 849 mAh g<sup>-1</sup> after 40 cycles, underscoring the significant potential for practical applications of Li-S batteries.

## Introduction

Lithium-sulfur (Li-S) batteries have garnered considerable attention owing to their high theoretical capacity (1675 mAh g<sup>-1</sup>), environmental friendliness, nontoxicity, and low cost of sulfur.<sup>[1-4]</sup> The theoretical energy density of Li-S batteries is 2600 Wh kg<sup>-1</sup>, three to five times greater than that of commercial Li-ion batteries.<sup>[5]</sup> Nevertheless, enduring challenges persist, rapid capacity fading, and the insulating property of sulfur, impeding electron/ion transfer. Additionally, the shuttle of lithium polysulfides (LiPSs) during charge/discharge processes results in low sulfur utilization and continuous threats from unrestrained lithium dendrites, significantly slowing their commercialization.<sup>[6-10]</sup> In the multi-step discharge process, dissolved LiPSs diffuse from the cathode side to the anode side through the electrolyte due to different concentrations on either side of the separator.<sup>[11-13]</sup> The shuttle effect damages Li-S batteries by reducing positive active material content and limiting sulfur utilization. The decrease in cycle stability and Coulomb efficiency results in a more pronounced self-

discharge.<sup>[14,15]</sup> Separator properties play a crucial role in redox reaction kinetics and the interfacial behavior between electrodes and electrolytes. However, conventional polypropylene (PP) separators, with oversized pores, fail to effectively restrict the shuttle effect.<sup>[16-18]</sup> The imperative need arises to design a functional separator capable of regulating polysulfide transformation and controlling dendrite growth. The distinctive characteristics of carbon materials, such as their expansive specific surface area, robust physical adsorption capacity, and exceptional mechanical strength, render them a compelling choice for the electrochemical field.<sup>[19-27]</sup> Earlier investigations, involving the application of carbon films like carbon nanotube (CNT)<sup>[28,29]</sup> and graphene oxide (GO)<sup>[30,31]</sup> onto PP, have demonstrated efficacy in managing LiPSs. However, carbon materials cannot regulate the transformation of polysulfide. The incorporation of catalysts, including metal oxides,<sup>[32]</sup> metal sulfides,<sup>[33]</sup> MXenes,<sup>[34]</sup> and MOFs,<sup>[35]</sup> into the barrier separator is essential for capturing LiPSs and accelerating their transformation to Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S by enhancing redox kinetics.

Polyoxometalates (POMs) represent a category of metal-oxygen cluster compounds, predominantly composed of cations and polyanions, with preferred elements being Mo, W, V, Nb, and Ta. These compounds exhibit an impressive open nanocluster structure, multi-electron redox properties, and stability in their cluster structure throughout reduction-oxidation processes. These characteristics make them highly promising for a range of applications in various catalytic reactions<sup>[36-37]</sup> and electrocatalysis,<sup>[38-39]</sup> and other electrochemical reactions.<sup>[40-58]</sup> In 2018, Dong, Cronin, and their co-workers developed a dual-function Lewis acid and base catalyst for Li-S batteries in the form of an Ag(I)-substituted Keggin

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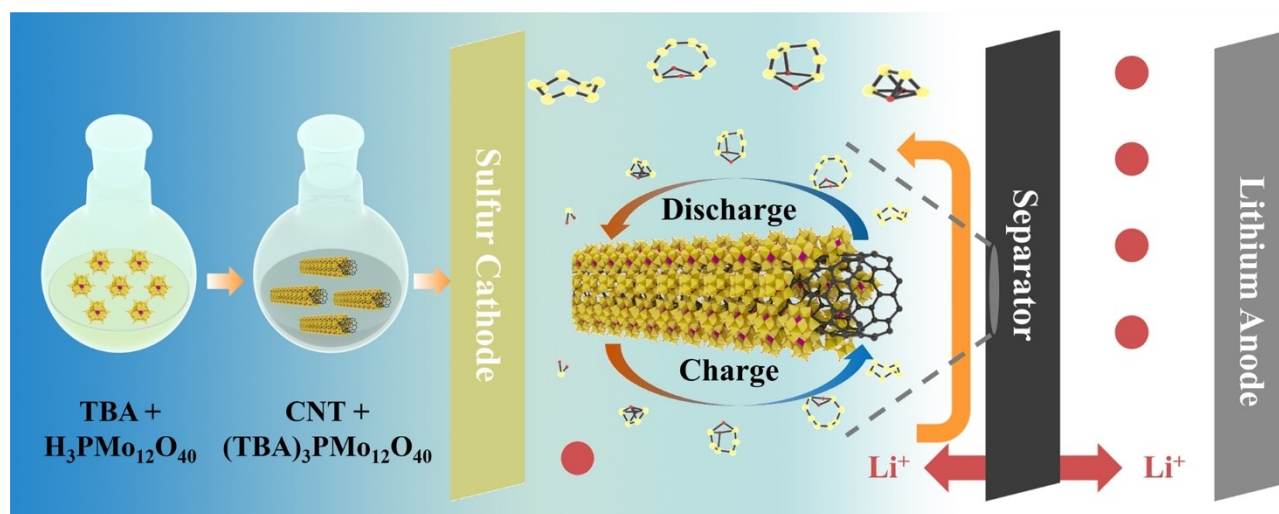
$K_3[H_3AgIPW_{11}O_{39}]$  cluster. LiPSs can be strongly adsorbed on the  $\{AgIPW_{11}O_{39}\}$  cluster. This interaction serves to enhance the chemical affinity between LiPSs and the POMs.<sup>[59]</sup> Then, Wei, Diao, Ni, and their co-workers introduced a POMs-based sulfur host material incorporating a Keggin-type  $H_3PW_{12}O_{40}$  embedded into a 3D reduced graphene oxide-CNT (rGO-CNT) conductive matrix.  $H_3PW_{12}O_{40}$  catalyzed the reduction of long-chain LiPSs ( $Li_2S_n$ ,  $4 \leq n \leq 8$ ) and the oxidation of short-chain LiPSs ( $Li_2S_2/Li_2S$ ), thus enhancing the redox kinetics of Li-S batteries. However,  $H_3PW_{12}O_{40}$  experienced partial lithiation, increasing its solubility in electrolytes and consequently leading to the loss of the catalyst.<sup>[60]</sup> To tackle this challenge, Chen, Dong, and co-workers designed an innovative composite by combining POMs with rGO, forming a bifunctional electrocatalyst in 2022. This novel POMs/rGO composite utilized a positively charged polymer to link  $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$  clusters to the rGO. The exposed unsaturated cobalt (Co) atoms within  $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$  clusters played a pivotal role, enhancing the adsorption of LiPSs and concurrently lowering the activation energy associated with the conversion of LiPSs.<sup>[61]</sup> Although the use of POMs-based composites as sulfur hosts increased polarization due to the poor conductivity of POMs, it acted as a bidirectional molecular catalyst and accelerated interfacial charge transfer. Other studies focused on modifying commercial PP separators using POMs. In 2018, Su, Qin, and their collaborators innovatively crafted a bifunctional composite separator,  $[PW_{12}O_{40}]^{3-}$ /Super P, strategically harnessing Coulombic repulsion between  $[PW_{12}O_{40}]^{3-}$  and LiPSs to effectively hinder the shuttle effect.<sup>[62]</sup> Recently, Diao, Wei, Ni, and their collaborators introduced an innovative crystalline material, comprising  $[Zn_2(H_2O)_3(WO_2)_2(SbW_9O_{33})_2]^{10-}$  and two  $\beta$ -cyclodextrin ( $Zn_2W_2@2CD$ ), for the modification of the separator in Li-S batteries. It has been demonstrated that POMs exhibit a bidirectional catalytic effect on LiPSs. Additionally, the distinctive structure of CD facilitates the transport channel for Li-ions. This molecular-level assembly facilitates the controlled immobilization of POM and effectively captures LiPSs.<sup>[63]</sup> While the aforementioned research has delved into understanding the

catalytic mechanism of POMs and successfully addressed the issue of POMs loss, as well as effectively mitigated the shuttle effect, the persistent challenge of dendrite formation remains unresolved.

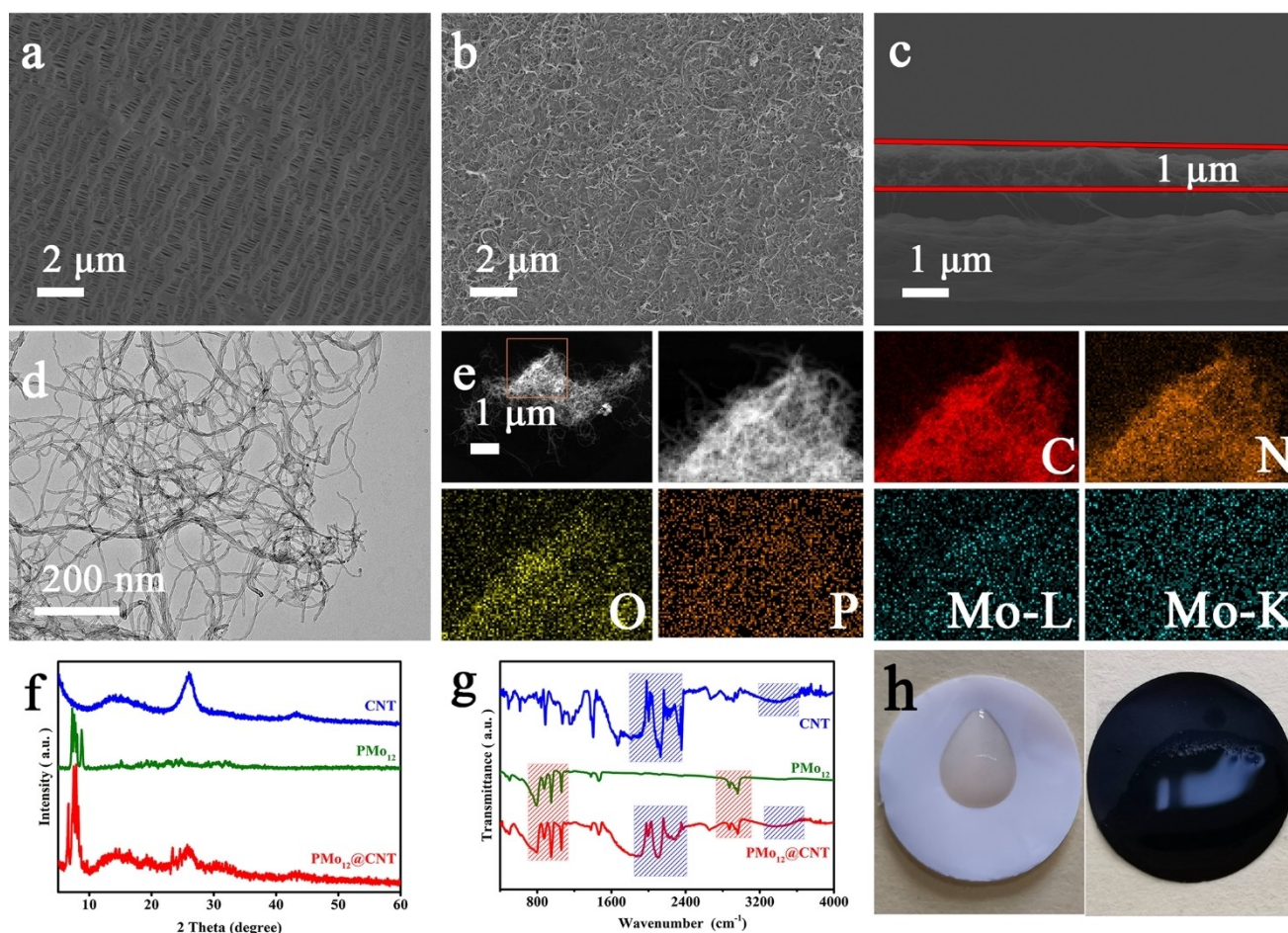
In this work, we present a bifunctional separator utilizing a Keggin-type  $[PMo_{12}O_{40}]^{3-}$  cluster@CNT modified PP separator ( $PMo_{12}@CNT/PP$ ) for Li-S batteries, effectively curtailing the shuttle of polysulfides and impeding the growth of lithium dendrites (Figure 1). The  $[PMo_{12}O_{40}]^{3-}$  cluster, bearing a negative charge, electrostatically interacts with CNT coated with positively charged conducting polymer (TBA) ultra-thin layers. The  $PMo_{12}$  cluster, with its bi-directional catalytic performance, facilitates the conversion of long-chain LiPSs to short-chain LiPSs during discharging and actively catalyzes the production of long-chain LiPSs during charging. Additionally, the CNT enhances the swift transfer of Li-ion and exhibits excellent physical adsorption to LiPSs. The utilization of the  $PMo_{12}@CNT/PP$  separator in Li-S batteries resulted in commendable rate performance and stability ( $675 \text{ mAh g}^{-1}$  at 3.0 C and 0.02% capacity decay per cycle over 700 cycles). The pouch cell underwent cycling at a sulfur load of  $4.5 \text{ mg cm}^{-2}$ , achieving a discharge-specific capacity of  $925 \text{ mAh g}^{-1}$ . Even after 40 cycles, the battery retained a substantial capacity of  $849 \text{ mAh g}^{-1}$ . Continued investigation and optimization of POMs integration into Li-S batteries hold great promise for enhancing overall performance, reliability, and battery lifespan.

## Results and Discussion

Scanning Electron Microscopy (SEM), High-resolution Transmission electron microscopy (HRTEM), and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) were applied to scope the structure and morphology of PP, and the  $PMo_{12}@CNT/PP$  separator. The SEM image illustrates the flat surface of a conventional PP separator (Figure 2a). While the PP separator facilitates Li-ion diffusion channels, it fails to impede the shuttling of polysulfides, resulting in continual



**Figure 1.** Schematic illustration of the fabrication of functional  $PMo_{12}@CNT/PP$ .



**Figure 2.** Top-view SEM images of a) PP and b)  $\text{PMo}_{12}\text{@CNT/PP}$  separator. c) Cross-section SEM image of  $\text{PMo}_{12}\text{@CNT/PP}$  separator. d) TEM and e) STEM image and EDX elemental mapping images of  $\text{PMo}_{12}\text{@CNT}$ . f) XRD patterns of CNT,  $\text{PMo}_{12}$ , and  $\text{PMo}_{12}\text{@CNT}$ . g) FT-IR spectra of CNT,  $\text{PMo}_{12}$ , and  $\text{PMo}_{12}\text{@CNT}$ . h) Contact angle measurements with the electrolyte for PP and  $\text{PMo}_{12}\text{@CNT/PP}$  separator.

sulfur loss and a decline in battery life. Figure 2b shows that the incorporation of  $\text{PMo}_{12}\text{@CNT}$  into the PP separator eradicates visible macropores in the resulting composite separator. To corroborate this, Brunauer-Emmett-Teller analysis (BET) was employed to characterize the surface state of PP and  $\text{PMo}_{12}\text{@CNT/PP}$  separator. The  $\text{PMo}_{12}\text{@CNT}$  effectively covers the large pores in the PP separator, providing a hindrance to the passage of LiPSs while ensuring the migration of Li-ion. The incorporation of CNT amplifies the adsorption capacity of the  $\text{PMo}_{12}\text{@CNT/PP}$  separator, thereby strengthening its affinity to LiPSs. The surface area of  $\text{PMo}_{12}\text{@CNT/PP}$  is  $46.072 \text{ m}^2 \text{ g}^{-1}$ , while PP is  $59.650 \text{ m}^2 \text{ g}^{-1}$  (Figure S1a and Figure S1b). In Figure 2c, a cross-sectional view of the composite separator reveals an approximately  $1 \mu\text{m}$  loading of  $\text{PMo}_{12}\text{@CNT}$  on PP. Although the Thermogravimetric Analysis (TGA) reveals a  $\text{PMo}_{12}$  cluster content as high as 20.5% in  $\text{PMo}_{12}\text{@CNT}$  (Figure S2), their small size prevents substantial aggregation, as evidenced by transmission electron microscope images (Figure 2d). Energy-dispersive X-ray Spectrometer (EDX) elemental mapping of C, N, O, P, and Mo in Figure 2e distinctly illustrates the even dispersion of the  $\text{PMo}_{12}$  cluster on the surface of the CNT.

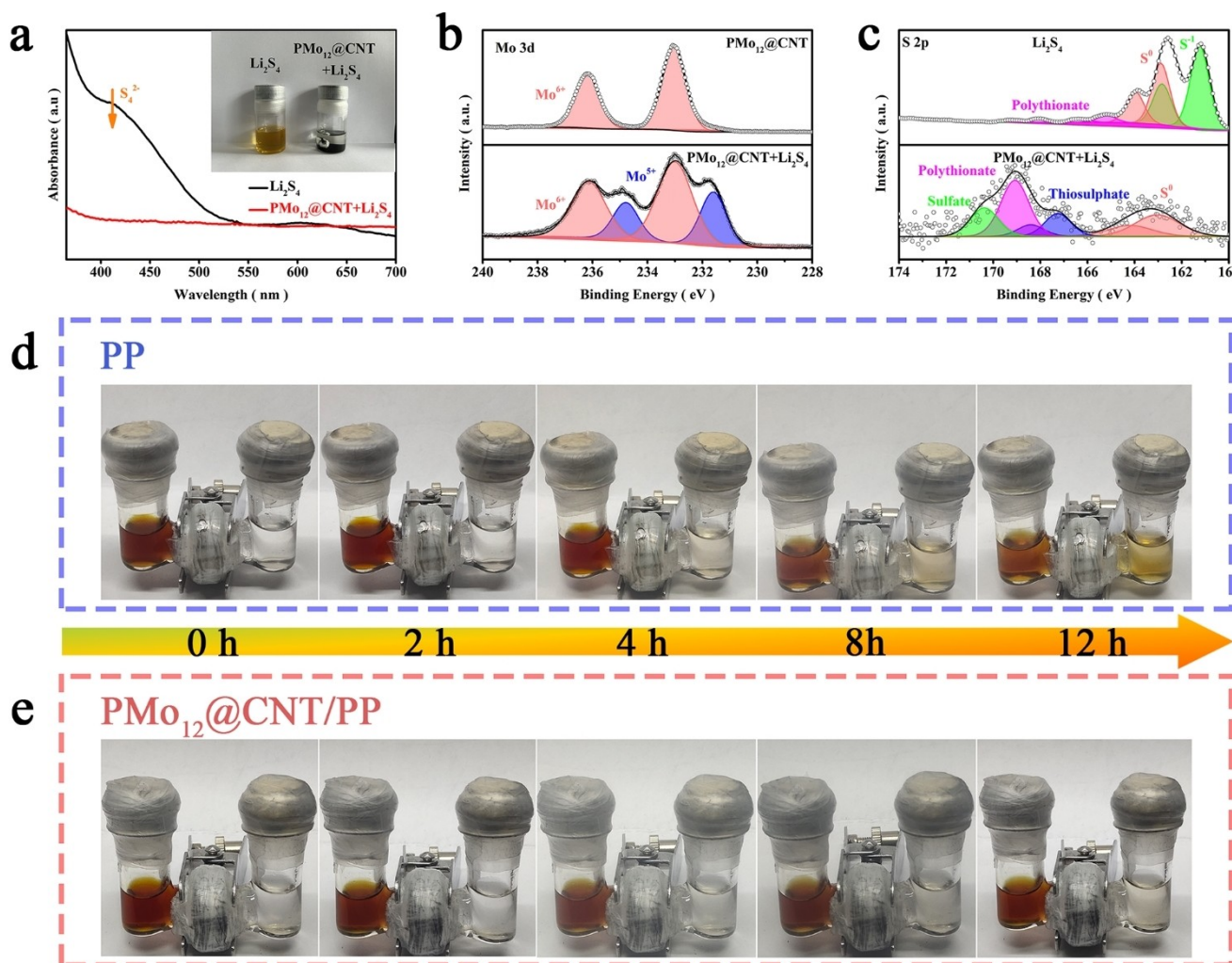
The crystallinity and composition of the  $\text{PMo}_{12}$  cluster, CNT, and  $\text{PMo}_{12}\text{@CNT}$  were analyzed using Powder X-ray diffraction (PXRD) (Figure 2f). On the  $\text{PMo}_{12}\text{@CNT}$  curve, a distinct peak at  $26.6^\circ$ , attributed to the (002) crystallographic planes of CNT, is observable.<sup>[64]</sup> Characteristic peaks of the  $\text{PMo}_{12}$  cluster around  $10^\circ$  are also discernible in the  $\text{PMo}_{12}\text{@CNT}$  curve.<sup>[65]</sup> Fourier Transform Infrared (FT-IR) spectra (Figure 2g) of  $\text{PMo}_{12}\text{@CNT}$  reveal four distinctive absorption peaks at 1069, 953, 871, and  $789 \text{ cm}^{-1}$ . These peaks belong to the bending vibration of P–O, the anti-symmetric telescopic vibration of Mo–O<sub>d</sub>, the telescopic vibration of Mo–O<sub>c</sub>–Mo, and the telescopic vibration of Mo–O<sub>b</sub>–Mo, respectively, in the  $\text{PMo}_{12}$  cluster.<sup>[66]</sup> The Raman spectra of CNT,  $\text{PMo}_{12}$  cluster, and  $\text{PMo}_{12}\text{@CNT}$  are presented in Figure S3. The peak around  $1000 \text{ cm}^{-1}$  belongs to the  $\text{PMo}_{12}$  cluster. Two typical peaks, D peak (around  $1360 \text{ cm}^{-1}$ ) and G peak (around  $1560 \text{ cm}^{-1}$ ) occur at CNT and  $\text{PMo}_{12}\text{@CNT}$  curves. The  $I_D/I_G$  value increases from 0.766 for CNT to 1.002 for  $\text{PMo}_{12}\text{@CNT}$ , indicating the removal of functional groups and the formation of defects resulting from the partial reduction of CNT. In contrast to pure PP, the  $\text{PMo}_{12}\text{@CNT/PP}$  separator exhibits improved wettability with electrolyte and lower surface tension (Figure 2h), facilitating enhanced Li-ion flow and trans-



fer. To explore the adsorption capacity of  $\text{PMo}_{12}/\text{CNT}$  for  $\text{LiPSs}$ , a predetermined quantity of  $\text{PMo}_{12}/\text{CNT}$  was introduced into a  $\text{Li}_2\text{S}_4$  solution (Figure 3a). After reacting for 0.5 h, the solution became nearly colorless and transparent, indicating the robust adsorption capability of  $\text{PMo}_{12}/\text{CNT}$  for  $\text{Li}_2\text{S}_4$ . UV-visible spectrophotometry (UV) analysis of the sample liquid, after the 0.5 h treatment, revealed a prominent absorption peak at 417 nm in the blank  $\text{Li}_2\text{S}_4$  solution. Contrastingly, the  $\text{Li}_2\text{S}_4$  solution with added  $\text{PMo}_{12}/\text{CNT}$  exhibited no discernible absorption peaks, affirming the vigorous adsorption capacity of  $\text{PMo}_{12}/\text{CNT}$  for  $\text{Li}_2\text{S}_4$ . For a more profound understanding of the interaction mechanism between the  $\text{PMo}_{12}$  cluster and  $\text{LiPSs}$ , X-ray photoelectron spectroscopy analysis (XPS) was employed. The Mo  $3d_{3/2}$  spectrum of the pristine  $\text{PMo}_{12}$  cluster displayed characteristic double peaks at 236.2 eV and 233.1 eV, consistent with  $\text{Mo}^{6+}$ . After a 0.5 h  $\text{Li}_2\text{S}_4$  treatment,  $\text{Mo}^{6+}$  underwent reduction to  $\text{Mo}^{5+}$ , leading to a Mo 3d spectrum with relative concentrations of 66.8% for  $\text{Mo}^{6+}$  and 33.2% for  $\text{Mo}^{5+}$  (Figure 3b).<sup>[67]</sup> Simultaneously, the S 2p XPS spectrum of pristine  $\text{Li}_2\text{S}_4$  (Figure 3c) exhibited double peaks at 163.2 eV and 161.7 eV,

corresponding to bridging sulfur ( $\text{S}^0$ ) and terminal sulfur ( $\text{S}^{-1}$ ). Following a 0.5 h treatment with the  $\text{PMo}_{12}$  cluster, the S 2p spectrum revealed three distinct sulfur states, indicating redox interactions with polysulfides. The oxidation process of  $\text{Li}_2\text{S}_4$  induced by its reaction with the  $\text{PMo}_{12}$  cluster led to the formation of polythionate and thiosulfate, accompanied by the conversion of  $\text{Mo}^{6+}$  to  $\text{Mo}^{5+}$ . These findings affirm a robust interaction between the  $\text{PMo}_{12}$  cluster and  $\text{LiPSs}$ .<sup>[68]</sup> To better understand the reduced  $\text{PMo}_{12}$  cluster species, a visual beaker battery equipped with a  $\text{PMo}_{12}/\text{CNT}$  electrode in a Li-S electrolyte was conducted, as illustrated in Figure S4a. Throughout the initial discharge cycle, the electrolyte in the beaker battery undergoes a transition from its initial transparency to a dark blue color. The UV vis spectra of the electrolyte reveal a prominent absorption band at 760 nm, signifying the gradual reduction of the  $\text{PMo}_{12}$  cluster to heteropoly blue, as depicted in Figure S4b.

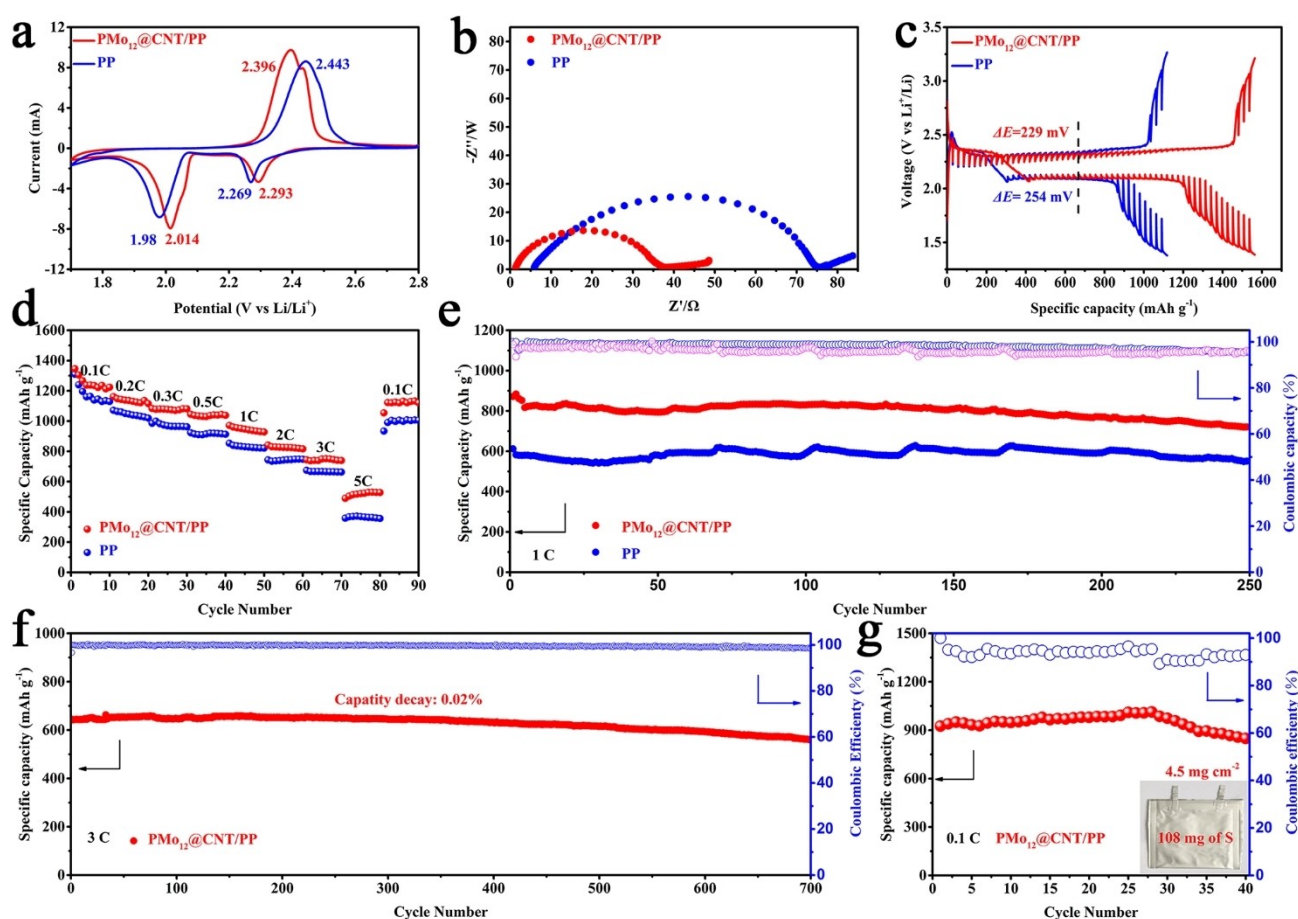
To estimate the effectiveness of the  $\text{PMo}_{12}/\text{CNT}/\text{PP}$  separator in regulating polysulfide transformation, H-type glass cells were utilized to assess the permeation of  $\text{LiPSs}$  under different



**Figure 3.** a) Digital pictures and UV vis spectra of  $\text{Li}_2\text{S}_4/\text{DME}$  solution upon contact with blank and  $\text{PMo}_{12}/\text{CNT}$ ; b) Mo 3d XPS spectrum of  $\text{PMo}_{12}/\text{CNT}$  clusters and the  $\text{PMo}_{12}/\text{CNT}$  clusters after  $\text{Li}_2\text{S}_4$  treatment; c) S 2p XPS spectrum of  $\text{Li}_2\text{S}_4$  and the  $\text{Li}_2\text{S}_4$  after  $\text{PMo}_{12}/\text{CNT}$  treatment; d) Digital photograph of a polysulfide diffusion test with a PP and  $\text{PMo}_{12}/\text{CNT}/\text{PP}$  separator.

separators. The left cell contained a  $\text{Li}_2\text{S}_6$  solution, while the right cell contained a standard electrolyte. A PP separator (Figure 3d) and a  $\text{PMo}_{12}\text{@CNT/PP}$  separator (Figure 3e) separated the two cells. Due to distinct  $\text{Li}_2\text{S}_6$  concentrations on both sides,  $\text{Li}_2\text{S}_6$  spontaneously permeated into the right cell, driven by a high concentration gradient. Upon employing a PP separator, the right side rapidly transitioned from transparency to brown, indicating the penetration of  $\text{Li}_2\text{S}_6$  through the PP separator. However, with the utilization of the  $\text{PMo}_{12}\text{@CNT/PP}$  separator, only a subtle change in color on the right side was observed after 12 h, suggesting a significant reduction in penetration compared to the PP separator. This substantiates the resilient anchoring and catalytic effectiveness of the  $\text{PMo}_{12}\text{@CNT/PP}$  separator on  $\text{Li}_2\text{S}_6$ , successfully hindering the infiltration of LiPSs and alleviating the shuttle effect. To assess the electrocatalytic performance of the  $\text{PMo}_{12}\text{@CNT/PP}$  separator in Li–S batteries, a series of electrochemical tests were conducted using both PP and  $\text{PMo}_{12}\text{@CNT/PP}$  separators on a dedicated electrochemical workstation. The cyclic voltammetry (CV) curves for the  $\text{PMo}_{12}\text{@CNT/PP}$  separator (Figure S5b) exhibit minimal deviation after the initial cycle, and there are no discernible alterations in current or peak positions, revealing better stability and reversibility compared to cells with a PP

separator (Figure S5a). Figure 4a demonstrates the CV curve of the first cycle for both Li–S cells with PP and  $\text{PMo}_{12}\text{@CNT/PP}$  separators. The reduction peak at 2.27 V is the reduction of sulfur to soluble intermediate products, whereas the reduction peak at 1.98 V signifies the transition from soluble intermediate products to  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  in the CV curve of PP separators. During this process, soluble intermediate products dissolve in the electrolyte, resulting in the reduction of cathode sulfur. The low density of solid  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  contributes to volume expansion during charge/discharge. The oxidation peak of the  $\text{PMo}_{12}\text{@CNT/PP}$  separator shifts positively by 0.05 V, while the reduction peak shifts negatively by 0.03 V compared to the PP separator, indicating accelerated reaction kinetics of LiPSs. The CV curve of the  $\text{PMo}_{12}\text{@CNT}$  electrode reveals multi-electron redox behavior, with a redox potential ( $E_{\text{eq}}$ ) of approximately 2.682 V and 2.753 V vs  $\text{Li/Li}^+$ . This voltage range surpasses the redox potential of polysulfides, thereby facilitating the conversion of LiPSs (Figure S6). Electrochemical impedance spectroscopy (EIS) conducted on Li–S cells with different separators reveals a diminished electrolyte/electrode interface resistance ( $R_s = 1.28 \Omega$ ) and charge transfer resistance ( $R_{\text{ct}} = 36.78 \Omega$ ) for the  $\text{PMo}_{12}\text{@CNT/PP}$  separator in contrast to the PP separator ( $R_s = 5.92 \Omega$ ,  $R_{\text{ct}} = 69.59 \Omega$ ), indicating a reduction in internal



**Figure 4.** a) CV curve of cell with PP and  $\text{PMo}_{12}\text{@CNT/PP}$  separator in the first cycle. b) Nyquist plot of cell with PP and  $\text{PMo}_{12}\text{@CNT/PP}$  separator. c) GITT profiles at 0.1 C. d) Rate performance of cell with  $\text{PMo}_{12}\text{@CNT/PP}$  and PP separator from 0.1 to 5.0 C. e) Cycling performance and Coulombic efficiency of cell with  $\text{PMo}_{12}\text{@CNT/PP}$  and PP separator at 1.0 C. f) Long cycle performance of the cells with  $\text{PMo}_{12}\text{@CNT/PP}$  at 3.0 C for 700 cycles. g) Cycling performance of Li–S pouch cell with  $\text{PMo}_{12}\text{@CNT/PP}$  separator at 0.1 C.

energy consumption (Figure 4b). The galvanostatic intermittent titration technique (GITT) of Li–S cells with different separators was performed at 0.1 C to investigate the impact of PMo<sub>12</sub>@CNT/PP on the kinetics of the system throughout the discharge/charging process (Figure 4c). The PMo<sub>12</sub>@CNT/PP separator consistently demonstrated a smaller overpotential than the PP separator, indicating an enhancement in redox kinetics and a reduction in interfacial reaction barriers. The enhancement observed can be ascribed to the robust catalytic capability of the PMo<sub>12</sub> cluster. Furthermore, the PMo<sub>12</sub>@CNT/PP separator is evaluated using the potentiostatic intermittent titration technique (PITT) to augment Li-ion diffusion in comparison to the PP separator (Figure S7), aligning with the findings from CV.

Galvanostatic charge/discharge at various current rates (Figure 4d) illustrates the superior rate performance of the PMo<sub>12</sub>@CNT/PP separator, maintaining a high discharge-specific capacity even under elevated current densities. The Li–S cells utilizing the PMo<sub>12</sub>@CNT/PP separator demonstrated exceptional rate performance, yielding specific capacities of 1346, 1148, 1077, 1037, 960, 830, 737, and 503 mAh g<sup>−1</sup> at low rates of 0.1, 0.2, 0.3, 0.5 C, and high rate of 1.0, 2.0, 3.0, and 5.0 C, respectively (Figure S8a, and Figure S8b). This highlights the effectiveness of the PMo<sub>12</sub>@CNT/PP separator in controlling polysulfide transformation and improving sulfur utilization. In contrast, the PP separator experiences a significant reduction in discharge-specific capacity, especially at high current densities (1.0 C to 5.0 C), attributable to the pronounced shuttle effect of LiPSs. Li–S cells equipped with a PMo<sub>12</sub>@CNT/PP separator demonstrate a discharge-specific capacity of 852 mAh g<sup>−1</sup> at 1.0 C and maintain 715 mAh g<sup>−1</sup> after 250 cycles (Figure 4e). The application of the PMo<sub>12</sub>@CNT/PP separator in Li–S cells yielded notable rate performance and stability (675 mAh g<sup>−1</sup> at 3.0 C and 0.02% capacity decay per cycle over 700 cycles), showcasing exceptional capacity retention (Figure 4f). The pouch cell (S: 4.5 mg cm<sup>−2</sup>) provides a discharge-specific capacity of 925 mAh g<sup>−1</sup> and remains at 849 mAh g<sup>−1</sup> after 40 cycles (Figure 4g). Table S1 presents the performance of batteries utilizing the PMo<sub>12</sub>@CNT/PP separator, offering a comparative analysis with various modified separators.

In a comprehensive investigation of morphological changes in PP, the PMo<sub>12</sub>@CNT/PP separator, and the lithium metal are characterized using SEM after 250 cycles at 1.0 C. Figure 5a and Figure 5d depict PP and the PMo<sub>12</sub>@CNT/PP separator after cycling. Relative to their initial states, the uniform holes on the PP separator are predominantly obstructed by lithium LiPSs (Figure 5a). The surface of the PMo<sub>12</sub>@CNT/PP separator (Figure 5d) exhibits increased roughness and size. Upon removing functional materials from the PMo<sub>12</sub>@CNT/PP separator, the pores on the PP become visible, and the deposited material does not hinder normal functionality (Figure S9). The initial surface of the lithium metal appears smooth (Figure S10). Nonetheless, in the absence of a barrier, LiPSs traverse the separator, eventually reaching the anode and depositing on the lithium surface after cycling. In contrast, the battery utilizing the PMo<sub>12</sub>@CNT/PP separator preserves a comparatively smooth lithium metal surface. Furthermore, EDX analysis validates a

reduction in LiPSs shuttling to the anode in batteries equipped with the PMo<sub>12</sub>@CNT/PP separator (Figure 5b and Figure 5e). The introduction of CNT facilitates the uniform nucleation of Li-ion, stabilizes the lithium anode, and inhibits dendrite formation throughout the entire cycling process. Consequently, the deposited layer of lithium metal in batteries utilizing the PMo<sub>12</sub>@CNT/PP separator appears thinner after cycling (Figure 5c and Figure 5f). To further validate the protection of the lithium anode by the composite separator, PP and PMo<sub>12</sub>@CNT/PP separator were employed to assemble a symmetric battery (Li/separator/Li) (Figure 5g). In comparison with the battery equipped with a PP separator, batteries featuring the PMo<sub>12</sub>@CNT/PP separator exhibit lower overpotential, persisting at only 44 mV after 600 hours of cycles, while the battery with the PP separator is rapidly damaged by dendrites penetrating the separator.

## Conclusions

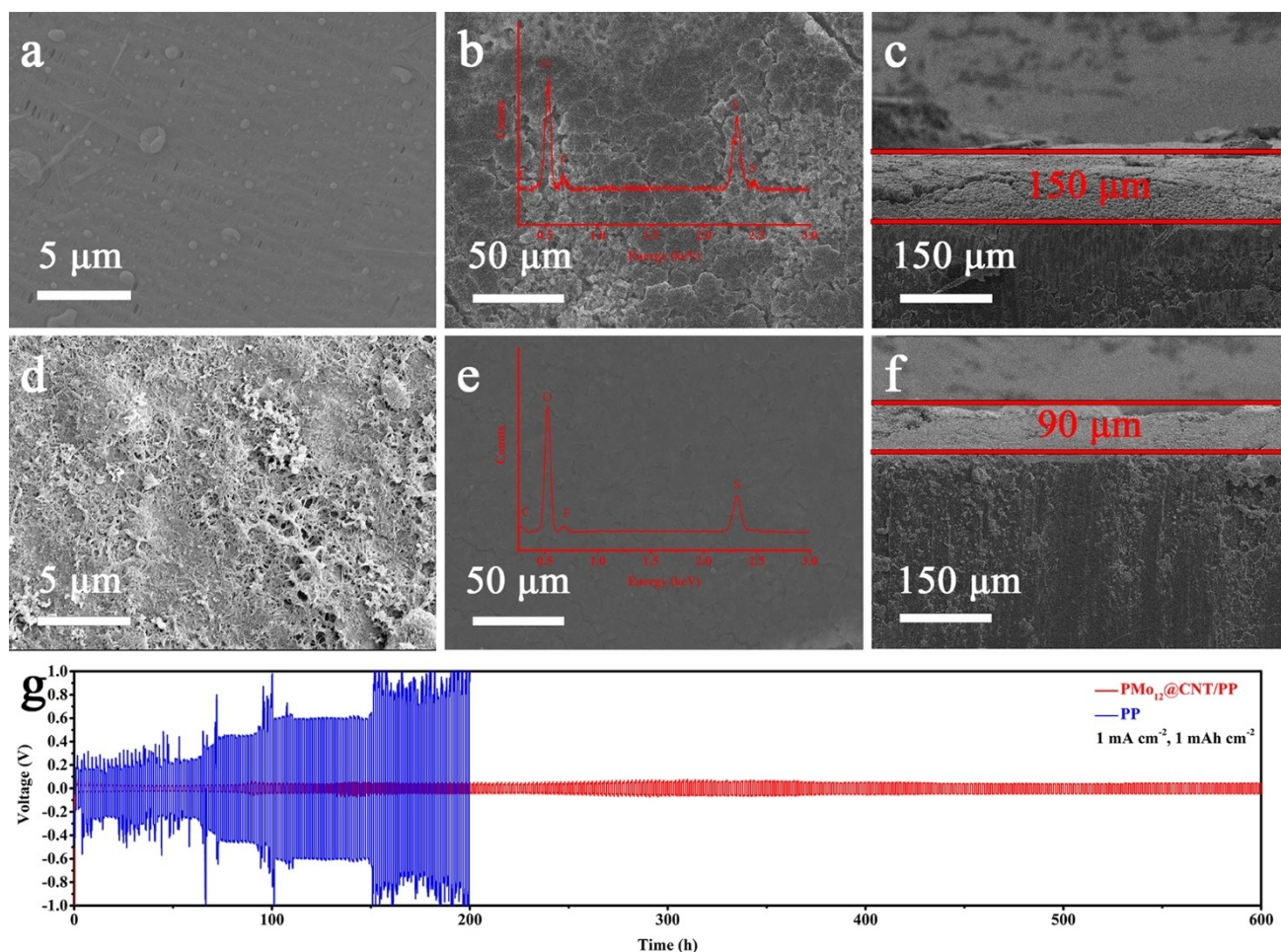
As demonstrated, we devised an innovative bifunctional PMo<sub>12</sub>@CNT/PP separator to address the challenges of regulating polysulfide transformation and protecting lithium metal in Li–S batteries. The active catalytic properties of PMo<sub>12</sub> clusters and the satisfactory physical adsorption capacity of CNT collaboratively capture LiPSs. Leveraging the abundant active sites provided by PMo<sub>12</sub> clusters at the electrode/separator interface, LiPSs undergo rapid conversion into the final discharge product, enhancing sulfur utilization and impeding the shuttle effect. Moreover, owing to the commendable electrical conductivity of PMo<sub>12</sub>@CNT and swift Li-ion conductivity, the PMo<sub>12</sub>@CNT/PP separator can modulate the Li-ion flux to facilitate Li nucleation. Consequently, the initial battery capacity employing the PMo<sub>12</sub>@CNT/PP separator was 675 mAh g<sup>−1</sup>, maintaining 559 mAh g<sup>−1</sup> after 700 cycles. The pouch cell (S: 4.5 mg cm<sup>−2</sup>) cycled at 0.1 C exhibited a discharge-specific capacity of 925 mAh g<sup>−1</sup> and maintained 849 mAh g<sup>−1</sup> after 40 cycles. Additionally, symmetric batteries incorporating the PMo<sub>12</sub>@CNT/PP separator demonstrate reduced overpotential, maintaining only 44 mV even after 600 hours of cycling. This study investigates the utilization of POMs in lithium-sulfur batteries, anticipating that POMs and their derivatives will find broader applications in Li–S batteries in the future.

## Experimental Section

### CNT purification

The as-received CNT (Sinopharm, >95%) was purified with a procedure reported by Nakashima et al.<sup>[69]</sup> The CNT was placed in a crucible and heated in a tubular furnace at 225 °C for 18 h. The treated CNT was ultrasonic 15 min in hydrochloric acid, then washed with deionized water until pH = 7. The solid material was washed several times with sodium bicarbonate and heated at 50 °C.





**Figure 5.** a) SEM images of the PP separator at 1.0 C after 250 cycles. SEM images of the surface b) and cross-section c) of Li metal anode with PP. d) SEM images of PMo<sub>12</sub>@CNT/PP separator after 250 cycles. Front view e) and cross-section f) of Li metal anode with PMo<sub>12</sub>@CNT/PP separator; g) Galvanostatic cycling of PP (blue) and PMo<sub>12</sub>@CNT/PP symmetric battery (red) at 1.0 mA cm<sup>-2</sup>.

### Synthesis of TBA<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>]

Phosphomolybdic acid (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, Sinopharm, AR) and Tetrabutylammonium bromide (TBA, C<sub>16</sub>H<sub>36</sub>NBr, Sinopharm, AR) were dissolved in DI water at a molar ratio of 1:3 and reacted in a water bath for 1 h. The yellow precipitate was TBA<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>].

### Synthesis of PMo<sub>12</sub>@CNT

An acetonitrile solution (5 mL) of TBA<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] (40 mg) was added in CNT (40 mg)-toluene dispersion (50 mL). After stirring the mixture violently at room temperature for 10 minutes and standing for 1 h, the supernatant fluid became colorless, and black precipitation was obtained. The sediment was washed with toluene and dried in a vacuum. The collected material is PMo<sub>12</sub>@CNT.

### Preparation of PMo<sub>12</sub>@CNT/PP

40 mg PMo<sub>12</sub>@CNT was uniformly dispersed in 8 mL (10 mg mL<sup>-1</sup>) PVDF solution, then 40 mL ethanol was added under continuous stirring at room temperature, and ultrasonic stirring for 1 h. 1 mL mixture was dripped on PP (Celgard 2500) via vacuum filtration

until the mixed solution was completely drained. The PMo<sub>12</sub>@CNT/PP separator was removed and vacuum-dried at 60 °C for 5 h.

### Preparation of Li<sub>2</sub>S<sub>4</sub>/Li<sub>2</sub>S<sub>6</sub> solution and polysulfide adsorption

For the synthesis of the Li<sub>2</sub>S<sub>4</sub> solution, n(Li<sub>2</sub>S):n(S)=1:3 were dissolved in a DOL/DME (1:1 by volume) mixture, and stirred at 80 °C for 7 days. The preparation of the Li<sub>2</sub>S<sub>6</sub> solution followed the same procedure as the Li<sub>2</sub>S<sub>4</sub> solution, n(Li<sub>2</sub>S):n(S)=1:5. Polysulfide adsorption experiments were conducted by adding 20 mg of PMo<sub>12</sub>@CNT to the Li<sub>2</sub>S<sub>4</sub> solution, stirring uniformly for 0.5 h, and standing for several minutes. All procedures were conducted in an argon-filled glovebox.

### Visualization of H-tube permeation experiment

A pre-prepared Li<sub>2</sub>S<sub>6</sub> solution was introduced to the one side of, and 12 mL of a clear electrolyte was added to the other side. Separate two chambers with PP and PMo<sub>12</sub>@CNT/PP separator, respectively.

## Synthesis of cathode

The cathode slurry comprised a mixture of sulfur/CNT, Super P Li, and polyvinylidene fluoride in a weight ratio of [(7:3);2;1] in N-methyl-pyrrolidone solvent. The cathode slurry was applied to a carbon paper (GDL 28 AA, SGL). The loading of S was  $\sim 1.2 \text{ mg cm}^{-2}$ . Furthermore, the ratio of electrolyte to sulfur (E/S) was standardized at  $12\text{--}15 \mu\text{L mg}^{-1}$ .

## Cell assembly

In the construction of CR2032 coin cells, a meticulously prepared cathode, lithium metal as the anode, and PP and  $\text{PMo}_{12}\text{@CNT/PP}$  as separators,  $0.5 \text{ M LiCF}_3\text{SO}_3$  and  $0.5 \text{ M LiNO}_3$  dissolved in a mixture of DOL/DME (1:1 by volume) as the electrolyte, were utilized. CR2032 coin cells were prepared under an argon atmosphere glove box.

## Supporting Information

Supporting Information is available from the Wiley Online Library or the author.

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Lithium-sulfur batteries • Separator • Polyoxometalates • Shuttle effect • Lithium dendrite

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