

Inorganic Mediator toward Organosulfide Active Material: Anchoring and Electrocatalysis

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Organosulfides are promising high-capacity cathode materials for rechargeable lithium batteries. However, they are hindered by several key challenges including the electronic/ionic insulation and solubility issues of the discharged products. Herein, TiS₂ nanosheets@carbon nanotubes (TiS₂ NSs@MWCNT) are proposed as a promoter and booster toward phenyl tetrasulfide (PTS). It serves as a bifunctional mediator, not only anchoring active materials in the cathode through chemical adsorption but also facilitating the reaction kinetics. The Li-organosulfide cell yields a reversible discharge capacity of 467.6 mAh g^{-1} and a high capacity retention of 81.9% after 200 cycles at 0.5 C rate. When the PTS areal mass loading is 5.8 mg cm⁻² and the electrolyte/PTS ratio is 3.8 μ L mg⁻¹, a high specific capacity of 444 mAh g^{-1} at 0.5 C rate can still be achieved. The strong anchoring and electrocatalysis effects of TiS₂ toward PhSLi and polysulfide are revealed using experimental and computational approaches. The study sheds light on metal sulfides as mediators to improve the cycling life of Li-organosulfide batteries and provides deep comprehension of the instinct interaction evolution at molecular level, which is invaluable for fabrication of electrode materials.

1. Introduction

Lithium-ion (Li-ion) batteries with high energy densities have quickly dominated the energy storage market for portable electronics and electric vehicles.^[1–3] However, Li-ion batteries based on transition metal oxide/phosphate cathodes have reached the limit of energy density due to the inherent low specific capacities, which cannot meet the ever-increasing demand of energy storage market.^[2] Hence, alternative electrode materials with higher capacities are needed.

Organosulfides (R- S_n -R, $n \ge 3$) with long sulfur chains in the structure are a class of promising high-capacity cathodes for rechargeable lithium batteries,^[4] such as dimethyl trisulfide,^[5] diphenyl trisulfide,^[6] phenyl tetrasulfide (PTS), phenyl pentasulfide (PPS), and phenyl hexasulfide (PHS).^[7] For example, they can reduce the formation of high-order lithium polysulfides (LiPSs) to a certain extent during charge-discharge processes, reducing the shuttle effect of LiPSs.^[5,8] High specific energies

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can be achieved due to the low electrolyte/ active material ratios. In addition, they can enhance the discharge voltage by flexibly adjusting the functional groups.^[9,10] However, many organosulfides have poor conductivity and unsatisfactory cycling stability mainly due to the high solubility of discharged product RSLi and intermediate LiPSs during the reduction of organosulfides with lithium.^[6,11] In particular, dissolved RSLi and LiPSs may increase the viscosity and lower the ionic conductivity of liquid electrolyte, and degrade the reversibility of the redox reactions of organosulfides in lithium batteries.

In regards to solving these issues, it is vital to anchor polysulfides within the cathode by using novel electrode configuration. Various chemical modifications on the electrode surfaces with oxides,^[12,13] sulfides,^[14,15] nitrides,^[16,17] or polymers^[18] have been applied to retain polysulfides in electrodes in Li-S batteries. However,

related studies on RSLi are still lacking. In addition, successful modification should not only show strong adsorption capability, but also allow favorable reduction reactions.^[19] As we know, two-dimensional layered transition metal disulfides (MS₂, M = Mo, Ti, V, Co, Fe) possess high conductivity, large polar surface and high catalytic activity.^[20-22] Among them, TiS₂ is promising^[23,24] as it displays high lithium diffusion rate and electrical conductivity $(5.24 \times 10^3 \text{ S} \text{ m}^{-1})$,^[25-27] which are ideal transport features for facilitating reaction kinetics. Recent studies also show that TiS_2 is able to adsorb polysulfides, which improves the stability of cathode. Attracted by the multifunctionality of TiS₂ for improving the performance of Li-S batteries, we construct a hybrid cathode of titanium disulfide nanosheets (TiS₂ NSs) embedded in multiwalled carbon nanotubes (TiS2 NSs@MWCNT) network with PTS to promote and boost electrochemical performance of battery. The self-woven TiS₂ NSs@MWCNT shows an effective physical confinement due to its highly porous structure.^[28] Meanwhile, TiS₂ can serve as a bifunctional mediator to adsorb the discharged product lithium thiophenolate (PhSLi) and intermediate LiPSs through weak binding and facilitate the reaction kinetics of PhSLi/LiPSs. The interactions between PhSLi and TiS₂ were probed and rationalized using X-ray photoelectron spectroscopy (XPS) analysis and density functional theory (DFT) computation. The TiS₂ NSs@MWCNT-PTS hybrid cathode delivers a reversible discharge capacity of 467.6 mAh g⁻¹ after 200 cycles at 0.5 C rate. With a high PTS loading of 5.8 mg cm^{-2} and a





Figure 1. a) Synthesis process of PTS along with a visual representation of the PTS liquid. b) Extract ion chromatogram and c) corresponding mass spectrum of phenyl tetrasulfide.

low electrolyte/PTS ratio of 3.8 μL mg^-1, PTS exhibits a high specific energy of 901 Wh kg^-1 at 0.5 C rate.

2. Results and Discussion

2.1. Synthesis of PTS

Figure 1a shows the synthesis process of PTS. The phenyl disulfide/sulfur (PDS/S) molar ratio is 1:2, therefore the target compound is PTS. The reaction proceeds without the need of any solvent and catalyst. The synthesized PTS turns out to be a yellow liquid. After the reaction, there is no solid precipitation in the PTS liquid indicating complete conversion of sulfur. In order to verify the success of forming PTS, Waters Xevo G2-XS OTof mass spectrometer was utilized. The synthesized liquid was tested in the atmospheric solids analysis probe (ASAP) positive mode with the first-order mass spectrometry model. Figure 1b displays the extract ion chromatogram of PTS, a strong peak appears at the retention time of 1.709 min, and the corresponding m/z of this peak (Figure 1c) is 281.9665, which can be assigned to the molar mass for the ionized [PTS]⁺. The synthesized liquid could be a mixture of phenyl polysulfides in which high-order polysulfides such as PPS and PHS may be present. Because the stoichiometric formula of the product is Ph-SSSS-Ph, PTS is used in the following discussion.

2.2. Synthesis and Structure of the ${\tt TiS}_2$ ${\tt NSs}@{\tt MWCNT}$ Composite Paper

The single-crystal TiS₂ nanosheets were synthesized via a colloidal chemistry method developed by Zhu et al.^[29] Briefly, appropriate amounts of TiCl₄ and CS₂ were mixed and heated at 300 °C for 5 h in the mixture solvent of oleylamine and octadecen. The as-prepared TiS₂ NSs have uniform hexagonal

morphology (Figure S1a, Supporting Information) with a thickness of tens of nanometers (Figure S1b, Supporting Information). The TiS₂ NSs@MWCNT composite paper was prepared through the vacuum filtration method, the detailed preparation processes are shown in the experimental section (Supporting information). MWCNTs were selected as conductive matrix due to their excellent electrical conductivity and long electron transport pathway.^[30] Based on the elemental analysis shown in Figure S2 in the Supporting Information, the mass ratio of MWCNT to TiS₂ is estimated to be about 7:1.

Figure 2a shows the photographs of the TiS₂ NSs@MWCNT composite paper. It can be seen that TiS₂ NSs@MWCNT is freestanding and flexible. To reveal the structure of TiS₂ NSs@ MWCNT, scanning electron microscopy (SEM) and high resolution-transmission electron microscopy (HR-TEM) of TiS2 NSs@MWCNT were performed. As shown in Figure 1b,c, TiS₂ NSs are uniformly embedded in the carbon nanotube network, which can significantly improve the conductivity of cathode and encapsulate the active materials during the battery cycling. Figure S3 in the Supporting Information also shows the high magnification SEM image of the TiS2 NSs@MWCNT to display its porous structure. The porous structure of TiS2 NSs@MWCNT can be further proven via Brunauer-Emmett-Teller (BET) method. The nitrogen adsorption/ desorption isotherms of TiS2 NSs@MWCNT are shown in Figure S4 in the Supporting Information, the TiS2 NSs@ MWCNT exhibits a BET surface area of 132 m² g⁻¹ and a pore volume of 0.79 cm³ g⁻¹, the pore size distribution is around 22.5 nm and centered at ≈0.38 nm. The large surface area, high pore volume, and abundant porous structure of the TiS₂ NSs@MWCNT can not only facilitate Li⁺ diffusion, but also are favorable for increasing the electrode/electrolyte contact and physical confinement for soluble active materials. The energydispersive X-ray spectroscopy (EDS) elemental mapping images shown in Figure 2d-g reveal that TiS2 NSs are intertwined with MWCNTs uniformly.







Figure 2. a) Photograph of the TiS₂ NSs@MWCNT composite paper showing its free-standing and flexible features. b) SEM image of TiS₂ NSs@ MWCNT composite apper. c) HR-TEM image of TiS₂ NSs@MWCNT composite. d) EDS images of e) carbon, f) titanium, and g) sulfur. h) XRD patterns of MWCNTs, TiS₂ NSs, and TiS₂ NSs@MWCNT composite. i) Raman spectra of TiS₂ NSs and TiS₂ NSs@MWCNT composite.

The X-ray diffraction (XRD) pattern of the TiS₂ NSs@ MWCNT is compared with those of TiS₂ NSs and MWCNTs in Figure 2h. All the diffraction peaks of the synthesized TiS₂ NSs can be perfectly matched with hexagonal TiS₂ (JCPDS No. 15-0853),^[29] indicating that the obtained TiS₂ NSs are pure without any oxide by-products. Furthermore, the XRD pattern of the TiS₂ NSs@MWCNT exhibits the same peaks as TiS₂ NSs except the peak at 26° assigned to the (002) plane peak of MWCNTs. However, the peak intensities of TiS₂ NSs in the composite are reduced because the MWCNTs coated on TiS₂ NSs block the peak signal of TiS₂. In addition, the Raman spectra of TiS₂ NSs and TiS₂ NSs@MWCNT are displayed in Figure 2i. The Raman characteristic peaks of MWCNTs (D and G peaks) and TiS₂ NSs (A_{1g} 332 cm⁻¹ and E_g 219 cm⁻¹) peaks are clearly seen in the composite.^[19]

2.3. Dual Chemisorption of TiS₂ toward PhSLi and LiPSs

Although linear organic polysulfides can reduce the formation of high-order LiPSs to a certain extent,^[8] a small amount of LiPSs will inevitably be formed during the discharge process. To verify the dual chemisorption ability of TiS₂ toward PhSLi and LiPSs, visual adsorption experiments and UV–vis analysis were performed. An equivalent mass of MWCNTs and TiS₂ NSs was added into 5×10^{-3} M PhSLi (**Figure 3**a) or 5×10^{-3} M Li₂S₆ (Figure 3b) solution. After prolonged interaction, the yellow PhSLi and Li₂S₆ solutions containing TiS₂ NSs become much lighter, whereas the PhSLi and Li₂S₆ solutions containing MWCNTs still remain yellow. In addition, the UV absorbance of PhSLi and Li₂S₆ solutions exposed to TiS₂ NSs become much lower than those of solutions exposed to MWCNTs, which indicates the TiS₂ NSs has strong ability to adsorb both PhSLi and LiPSs.

To directly validate the chemical interaction between TiS₂ and PhSLi, XPS analyses of the TiS2 NSs before and after the PhSLi adsorption experiments were performed. As shown in Figure 3c, the Ti 2p spectra of the pristine TiS₂ shows two peaks located at binding energies of 456.0 and 462.0 eV with an energy separation of 6.0 eV, which are attributed to the Ti 2p_{3/2} and Ti 2p_{1/2} spin-orbit levels of TiS₂, respectively.^[31] Upon contact with PhSLi, the characteristic Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks of TiS₂-PhSLi both shift toward higher binding energies of +0.3 eV compared with pristine TiS₂. The obvious upshifts for Ti $2p_{3/2}$ and $2p_{1/2}$ evidence the polarization of electrons away from Ti to PhSLi, and the decrease of the electron cloud density around Ti atoms. The two peaks of Ti 2p at higher binding energies in the TiS₂-PhSLi sample are ascribed to Ti in TiO₂. The presence of Ti in TiO₂ environment probably derives from hydrolysis/oxidation process of TiS2 when it is exposed to ambience.^[32] On the other hand, the upshifts of S 2p_{3/2} (160.8 eV) and S 2p_{1/2} (162.0 eV) peaks of TiS₂ in contact with PhSLi are observed as well. The S $2p_{3/2}$ peak at ≈ 161.6 eV belongs to the S in PhSLi.^[9] Because of the occurrence of electron transfer **ADVANCED** SCIENCE NEWS_

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Figure 3. UV–vis absorption spectra of the a) PhSLi, b) Li_2S_6 solutions before and after the addition of MWCNT and TiS_2 , the insets in (a) and (b) show the color changes of the PhSLi and Li_2S_6 solutions in the adsorption tests. XPS spectra of c) Ti 2p and d) S 2p of TiS_2 before and after contacting with the PhSLi solution. The fully optimized adsorption configurations of e) PhSLi and f) Li_2S_6 on TiS_2 with 3D differential charge contour surfaces. The carbon, hydrogen, lithium, sulfur, and titanium elements are shown in gray, white, purple, yellow and blue, respectively. The electronic attachment and detachment densities are shown in blue and green surfaces, respectively.

from Ti to PhSLi and the lower electronegativity of S in TiS_2 than S in PhSLi as phenyl is an electron-withdrawing group, the S atoms in TiS_2 also lose electron inducing an obvious shift to the higher binding energy.^[33] To further verify the

strong chemical adsorption of $\rm TiS_2$ toward PhSLi and $\rm Li_2S_6,$ the binding features were studied by first-principles calculations with the density-functional theory (DFT). Figure 3e,f shows the final optimized structures of PhSLi and $\rm Li_2S_6$



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compounds on the surface of TiS₂. It is worth to note the adsorption elongate the S-Li bond of PhSLi from 2.20 to 2.39 Å. Meanwhile, the S-Li distance between TiS₂ and PhSLi is in the range of 2.56–2.64 Å, which is close to bonding distance, indicating the existence of chemical interaction. The binding energy, $E_{\rm b}$, is computed to measure the binding strength.^[34] The binding energy between PhSLi and TiS₂ is 2.18 eV, which is much larger than that (1.24 eV) between Li₂S₆ and TiS₂. The large binding energy indicates the adsorption interaction is favored. The larger the value is, the stronger the anchoring effect occurs.^[22] It is believed that the adsorption interaction does not only exist between TiS₂ and PhSLi/Li₂S₆, but also exist between TiS₂ and other possible intermediate and discharged products such as PhS_xLi (x > 1), Li₂S₄, Li₂S₃, Li₂S₂, and Li₂S.

The strong chemical adsorption of TiS₂ NSs toward LiPSs/ PhSLi can be further probed through UV–vis spectroscopy measurements of the cycled cathodes. The pure PTS and PTS/TiS₂ NSs electrodes were both discharged to 1.8 V after 5 cycles at 0.1 C rate, therefore the discharge product PhSLi was formed. The cycled electrodes were soaked in electrolyte solvent. The UV–vis spectra are shown in Figure S5a in the Supporting Information. According to the inset spectrum of the commercial PhSLi, the peak in the 220–280 cm⁻¹ region belongs to the characteristic adsorption of PhSLi. For the PTS/ TiS₂ NSs electrode, the UV–vis absorbance of PhSLi is higher than that of pure PTS, suggesting a strong chemical interaction between TiS₂ and PhSLi, retaining PhSLi in the carbon paper. When pure PTS and PTS/TiS₂ NSs cathodes were discharged to 2.2 V, PhS_xLi ($x \ge 1$) were formed.^[7] As shown in Figure S5b in the Supporting Information, only the UV–vis adsorption peak of PhS_xLi can be seen, which indicates that the formation of higher-order polysulfides during cycling is suppressed. Moreover, the UV–vis absorbance of PhS_xLi in PTS/TiS₂ NSs cathode is higher than that of pure PTS cathode, indicating a strong retention of PhS_xLi in the electrode. In addition, the morphology of the cycled Li foil extracted after 250 cycles is shown in Figure S6 in the Supporting Information. It can be seen that the surface of the Li anode paired with pure PTS cathode is covered with a layer of black material, which could be PTS' discharged products migrated to the Li anode. In contrast, the surface of the Li anode paired with PTS/TiS₂ cathode is smooth, implying the strong affinity and retention of TiS₂ NSs for PTS' discharge products.

2.4. Electrocatalytic Effect of TiS_2 NSs toward the Redox Reaction of PTS Cathode

To confirm the electrocatalytic properties of TiS_2 NSs toward redox processes of PhSLi and LiPSs, cyclic voltammetry (CVs) of symmetric cells were conducted in 0.2 M PhSLi (**Figure 4a**) or 0.2 M Li₂S₆ (Figure 4b) electrolyte. Figure 4a shows that TiS₂ NSs@MWCNT has a pair of distinct redox peaks at -0.55 and 0.55 V, which are more obvious than pure MWCNTs. It indicates that the TiS₂ NSs is beneficial for accelerating the conversion reaction of PhSLi. The peak at 0.55 V in the anodic scan can be assigned to the formation of PDS by the oxidation of PhSLi on the working electrode, the peak at -0.55 V in cathodic



Figure 4. CV curves of the symmetric cells with TiS₂ NSs@MWCNT or pure MWCNTs as electrodes in a) 0.2 M PhSLi or b) 0.2 Li₂S₆ electrolyte at 3 mV s⁻¹. c) CV curves of PTS/TiS₂ NSs cathodes in Li cells at different scan rates. d) Plots of CV peak current of PTS/TiS₂ electrodes for the cathodic reduction processes (I_{C1} , I_{C2}) and the anodic oxidation process (I_A) versus the square root of the scan rate.



scan arises from the reduction of PDS. Similarly, Figure 4b shows that TiS₂ NSs exhibits a better electrocatalytic effect than pure MWCNTs for Li₂S₆. The TiS₂ NSs@MWCNT symmetric cell with 0.2 \mbox{M} Li₂S₆ exhibits two pronounced reduction and oxidation peaks located at -0.38 and 0.48 V, respectively. The peak at 0.48 V in anodic scan is due to the oxidation of Li₂S₆ to generate elemental S on the working electrode, the peak at -0.38 V is accompanied by the reduction of S to Li₂S₆ then maybe Li₂S. A single broad peak is observed in each scan direction, which could be due to the catalytic effect of TiS₂ on the charge transfer, which could suppress their redox features in the narrow voltage range.

To reveal the improvement in electrode kinetics, the lithium ion diffusion coefficient (DLi+) of PTS/TiS2 NSs@MWCNT composite (denoted as PTS/TiS2 NSs) (Figure 4c) and pure PTS (Figure S7, Supporting Information) electrodes were calculated by a series of CV at different scan rates. As shown in Figure 4d, the anodic (I_A) and cathodic (I_{C1}, I_{C2}) current peaks of PTS/TiS₂ NSs and pure PTS electrodes both have a linear relationship with the square root of the scan rates ($\nu^{0.5}$), indicating a diffusion-limited process. Therefore, the diffusion coefficient of Li ions can be described by the Randles-Sevcik equation: $^{[34]}I_p = (2.69 \times 10^5) n^{1.5} S D^{0.5} C_{Li} v^{0.5}$, where I_p is the peak current, n is the charge transfer number, S is the area of the electrode, D is the Li⁺ diffusion coefficient, C_{1i} is the concentration of lithium ions in the cathode, and v is the scan rate. As *n*, *S*, and C_{Li} are unchanged, lithium ion diffusion rate can be correlated positively to the slope of the curve $(I_p/\nu^{0.5})$. It is worth noting that the slopes for the redox peaks of the PTS/TiS₂ NSs cathode are higher than those of pure PTS electrode, indicating that TiS₂ NSs facilitates fast Li⁺ transport and reaction kinetics of PTS/TiS2 NSs cathode. The electrocatalytic effect of TiS₂ could enhance the charge transfer kinetics and diffusion of lithium ions, thus promote the conversion of PhSLi/LiPSs. Electrochemical impedance spectroscopy (EIS) was also used to measure charge transfer resistance R_{ct} of both symmetric cells (Figure S8, Supporting Information). TiS2 NSs@MWCNT exhibits lower R_{ct} than pure MWCNTs, either with PhSLi or Li_2S_6 . Therefore, Higher D_{Li+} along with lower charge transfer resistance in EIS verify the accelerated redox kinetics of TiS₂ NSs in PTS cathode.^[35]

2.5. Electrochemical Performance of the $PTS/TiS_2 NSs$ Composite Cathode

Constructing an "anchoring and electrocatalysis" mediator toward PTS can serve as an effective strategy to promote and boost electrochemical performance. To reveal the roles of the TiS₂ NSs mediator on the actual Li-organosulfide batteries, the electrochemical performances were collected on coin cells with the PTS/TiS₂ NSs@MWCNT composite cathode. Figure S9 in the Supporting Information displays the CV profiles of TiS₂ NSs@MWCNT, pure PTS, and PTS/TiS₂ NSs cathodes in the 1st cycle at 0.02 mV s⁻¹. TiS₂ NSs@MWCNT exhibits only one cathodic peak at ~2.3 V and one anodic peak at ~2.4 V, which are related to the lithium intercalation (Li_xTiS₂, 0 < *x* < 1) and de-intercalation process of TiS₂ NSs,^[36] respectively. The total areas of the anodic and cathodic peaks of TiS₂ NSs@MWCNT are very small, indicating the negligible capacity contribution of TiS₂ NSs itself when the cell is cycled between 1.8 and 3.0 V. Pure PTS shows three cathodic peaks. The first peak at ≈2.4 V corresponds to the breakage of the central S-S bond of PTS, the second cathodic peak at ≈2.1 V corresponds to the reduction of LiPSs. Finally, lithium sulfide (Li2S) and PhSLi are formed at \approx 1.9 V. In the anodic scan, there are two anodic peaks indicating two-step reactions during the charging process. The main conversion occurs at about 2.5 V, and then the PTS was reformed at 2.56 V.^[7] Compared to pure PTS cathode, the PTS/ TiS₂ NSs cathode displays more negative anodic peaks and more positive cathodic peaks, indicating smaller polarization and improved kinetics of the PTS/TiS2 NSs cathode. Figure S10 in the Supporting Information shows the EIS spectra of pure PTS and PTS/TiS2 NSs electrodes before and after 50 discharge-charge cycles. As shown in Figure S10a in the Supporting Information, the fresh PTS/TiS2 NSs electrode delivers a smaller R_{ct} (115.9 Ω) than that (324.1 Ω) of pure PTS electrode, which is closely related to the excellent conductivity of TiS₂@MWCNT composite accelerating the electron transfer of PTS/TiS₂ NSs electrode. After 50 cycles, the R_{ct} (65.7 Ω) of the PTS/TiS2 NSs electrode decreases and is still much smaller than that of the pure PTS electrode (Figure S10b, Supporting Information). Figure 5a shows the galvanostatic voltage profiles of pure PTS and PTS/TiS2 NSs electrodes at 0.2 C rate. Both cells display three discharge plateaus, which are consistent with the CV result in Figure S9 in the Supporting Information. The PTS/TiS₂ NSs electrode exhibits a higher discharge capacity of 527.4 mAh g^{-1} (1 C = 570 mA g^{-1}) than that (438.1 mAh g^{-1}) of the pure PTS electrode. Furthermore, the polarization potential (ΔE) between the charge plateau and discharge plateau of the PTS/TiS₂ NSs electrode is much lower than that of the pure PTS electrode (0.178 vs 0.348 V, respectively). These improved performances show that the superior catalytic capability of TiS₂ NSs boosts the redox reaction kinetics during the discharge/ charge processes in Li-PTS cells.

The rate performances of cells at higher cycling rates of 1 C, 2 C, 3 C, and 4 C are displayed in Figure 5b. The PTS/TiS₂ NSs cathode delivers reversible discharge capacities of 570, 512, 451, 438, and 486 mAh g⁻¹, respectively, which are all higher than those of the pure PTS electrode, indicating the improved rate performance of PTS/TiS2 NSs cathode. Figure 5c shows the cycling performance of the pure PTS and PTS/TiS₂ NSs cathodes at 0.5 C rate with PTS loading of 1.4 mg cm⁻² (1 C = 570 mA g^{-1}). The PTS/TiS₂ NSs cathode delivers a discharge capacity of 467.6 mAh g⁻¹ with high Coulombic efficiency of ≈99.9% after 200 cycles at 0.5 C rate, accounting for 81.9% of the capacity of the 5th cycle, which is much higher than that (66.1%) of the pure PTS cathode. Because TiS₂ is electrochemically active and lithium intercalation reaction occurs when the discharge cut-off voltage is higher than 1.45 V.^[24] The MWCNTs also contribute irreversible capacity during the first few cycles. Both cause the discharge capacity of the PTS/TiS2 NSs cathode exceeds the theoretical capacity (570 mAh g⁻¹) of PTS in the first 5 cycles at 0.5 C rate. The voltage profiles of TiS₂@MWCNT composite current collector are presented in Figure S11a, Supporting Information. It appears two discharge voltage plateaus at ≈2.3 and ≈1.8 V (Figure S9a, Supporting Information) in the first cycle,







Figure 5. a) Discharge–charge profiles of pure PTS and PTS/TiS₂ NSs electrodes of the 10th cycle at 0.2 C rate. The theoretical capacity of PTS is 570 mAh g^{-1} . b) Rate performances of pure PTS and PTS/TiS₂ NSs electrodes. c,d) Cycling performances of pure PTS and PTS/TiS₂ NSs electrodes with PTS areal loadings of 1.4 and 5.8 mg cm⁻², respectively, at 0.5 C rate. e) Long cycling stability of PTS/TiS₂ NSs electrode at 2 C rate.

which are related to the lithium intercalation (Li_xTiS₂, 0 < x < 1) process of TiS₂ NSs and irreversible capacity contribution of MWCNT, respectively. In the following cycles, it significantly decreases. The corresponding absolute capacities of TiS₂ NSs, pure PTS, and PTS/TiS2 NSs electrodes at same current are shown in Figure S11b in the Supporting Information. The PTS/ TiS₂ NSs electrode displays higher discharge capacities than the sum of the capacities of the TiS₂ and pure PTS electrodes except the first cycle, which can verify the improved capacity of the PTS/TiS2 NSs cathode is ascribed to the chemical adsorption and electrocatalysis of TiS2 on PhSLi/LiPSs rather than the contributed capacity of TiS₂ itself. Figure S12 in the Supporting Information presents some selected charge/discharge voltage profiles of the pure PTS and PTS/TiS2 NSs cathodes for different cycles at 0.5 C rate. It can be seen that the PTS/TiS2 NSs cathode displays lower voltage hysteresis and longer discharge voltage plateaus compared with the pure PTS cathode.

To show the feasibility of PTS/TiS₂ NSs in practical application, Figure 5d displays the cycling performance of a high loading PTS/TiS₂ NSs cell. The PTS/TiS₂ NSs cell delivers a specific capacity of 444 mAh g⁻¹ at 0.5 C of the 1st cycle, corresponding to a high areal capacity of 3.0 mAh cm⁻² (Figure S13, Supporting Information) and a high specific energy of 901 Wh kg⁻¹ of PTS. Furthermore, the cell utilizes an electrolyte to PTS ratio of 3.8 μ L mg⁻¹ when the loading of PTS is 5.8 mg cm⁻². Such a low electrolyte/PTS ratio can help to increase the energy density of PTS batteries. The cell is stable during 120 cycles with a capacity retention of 83.5%. In addition, even at 2 C rate, the PTS/TiS₂ NSs cathode still exhibits considerably higher cycling stability with 75.5% of the initial capacity after 300 cycles than that (60.9%) of the pure PTS cathode after 200 cycles (Figure 5e). The improved cycling performance of the PTS/TiS₂ NSs cathode is attributed to the immobilization of soluble PhSLi and LiPSs via an anchoring effect through strong chemical absorption and accelerated reaction kinetics promoted by TiS₂ NSs.

2.6. The Redox Mechanism Analysis of the $\mathsf{PTS}/\mathsf{TiS}_2$ NSs Composite Cathode

As a promising organosulfide cathode material, PTS exhibits a high capacity in Li batteries. Therefore, understanding its redox

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Figure 6. a) XPS analysis of the discharge products of PTS/TiS₂ electrode. b) The mass spectrum of the recharged PTS/TiS₂ electrode. c) The proposed redox reactions of the PTS/TiS₂ NSs electrode in rechargeable lithium batteries.

mechanism will be helpful for further optimization of its electrochemical performance. The discharged PTS/TiS2 electrode was characterized by UPLC-QTof-MS in the APCI positive mode and the mass spectrum is shown in Figure S14 in the Supporting Information. An ion peak at m/z of 110.0206 can be seen corresponding to the protonated thiophenol, which is the form of PhSLi in the MS analysis. The discharge products of PTS/TiS2 cathode were also analyzed by XPS as shown in Figure 6a. The S 2p_{3/2} peak at binding energy of 169.0 eV belongs to the S in LiTFSI.^[37] The S $2p_{3/2}$ peak located at \approx 167.4 eV is assigned to the S of S₂O₃²⁻/SO₃²⁻, which mainly results from the oxidization of sulfur species during sample transfer.^{[38]} The S $2p_{3/2}$ peaks at ${\approx}161.6$ and ${\approx}160.6$ eV are assigned to the S in PhSLi and lithiated TiS2, respectively, and the S $2p_{3/2}$ peak at ${\approx}160.1$ eV could be assigned to $\rm Li_2S.^{[37,39]}$ The recharged PTS/TiS₂ electrode sample was analyzed by QTof-MS ASAP probe. As shown in Figure 6b, the m/z of PTS (281.9667) can be clearly detected in the mass spectrum, indicating that PTS can be re-formed after recharge.

According to the above analysis, we can propose the redox reactions of PTS/TiS₂ NSs electrode in rechargeable Li batteries, as shown in Figure 6c. The first-half discharge region corresponds to the cleavage and lithiation of S-S bonds in PTS to form PhS_xLi ($1 \le x$). At the same time, a small amount of LiPSs are formed which are due to the possible high-order phenyl polysulfide (e.g., PPS and PHS) in the starting material. These intermediate species are adsorbed on the surface of lithiated titanium disulfide (Li_xTiS₂, 0 < x < 1). In the following region, these materials are converted to Li₂S and PhSLi which can also

be firmly adsorbed on the surface of Li_xTiS_2 .^[40] In following charge process, there is a sloping plateau with two regions. The first one corresponds to the delithiation of Li_2S and PhSLi, which could form S•, SLi•, and PhS• radicals. These radicals are bonded together to form PhS_xLi and LiPSs, which again are adsorbed on the surface of Li_xTiS_2 . In the following region, they are bonded to form PTS as the primary recharged product. In the whole process, TiS₂ also facilitates the conversion of these intermediate species via the electrocatalytic effect.

3. Conclusion

In summary, PTS as a promising organosulfide cathode material is synthesized by a scalable method through the melting reaction of PDS and S8 without any solvent and catalyst. The PTS/TiS2 NSs@MWCNT cathode provides a facile and practical solution for promoting and boosting the electrochemical performance of Li-PTS cell, as well as circumventing the inappropriate fabrication parameters, such as low amounts of active material and excessive electrolyte. The PTS/TiS₂ NSs@MWCNT cathode features TiS₂ functioning as an anchor toward LiPS and PhS_xLi, so as to enhance the electrochemical efficiency and stability of the cell. The catalytic effect of TiS₂ leads to high lithium ion diffusion coefficient, relatively low polarization, and fast reaction kinetics, which in turn suppresses the dissolution of polysulfide intermediates in ether. The resulting PTS/TiS2 NSs@MWCNT cathode delivers a reversible discharge capacity of 467.6 mAh g⁻¹ after 200 cycles at 0.5 C rate. Moreover, with a high PTS loading

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of 5.8 mg cm⁻² and a low electrolyte/PTS ratio of 3.8 μ L mg⁻¹, PTS delivers a high specific energy of 901 Wh kg⁻¹ at 0.5 C rate. This work opens up a new prospect toward the design of high performance lithium battery through the effective combination of the organosulfides and inorganic mediators.

4. Experimental Section

Materials: Phenyl disulfide (PDS, $C_{12}H_{10}S_2$, 99%, Sigma-Aldrich), lithium thiophenolate (PhSLi, C_6H_5Li , 1 M in THF, Sigma-Aldrich), sulfur (S_8 , \geq 99.5%, Aladdin-reagent), titanium chloride (TiCl₄, 99.99%, Aladdin-reagent), carbon disulfide (CS_2 , 99%, J&K chemical), oleylamine (80–90%, Aladdin-reagent), octadecene (>90%(GC), Aladdin-reagent), lithium bis (trifluoromethanesulfonimide) (LiTFSI, LiN(CF₃SO₂)₂, 99.95%, Sigma-Aldrich), lithium nitrate (LiNO₃, 99.99%, Canrd), 1,2-dimethoxyethane (DME, 99.5%, Sigma Aldrich), 1,3-dioxolane (DOL, 99.8%, Sigma Aldrich), multiwalled carbon nanotubes (MWCNTs, Nanostructure and Amorphous Materials, Inc.).

Synthesis of Phenyl Tetrasulfide: Appropriate amounts of PDS and sulfur powder (the molar ratio of PDS to sulfur was 1:2) were added into a quartz tube and sealed by a MRVS-1002 single station vacuum sealing machine, then heated for about 8 h at 170 °C. The obtained product was a clear yellow liquid. There was no sulfur powder precipitation.

Synthesis of TiS_2 NSs: TiS_2 NSs were synthesized by the procedure of the synthesis published by Zeng and coworkers^[29] 2 mmol $TiCl_4$ was mixed with 8 mL oleylamine and 30 mL octadecene in a 250 mL three-neck flask with strong magnetic stirring. The mixture was heated to 120 °C and then 220 °C under argon atmosphere. Subsequently, CS_2 was injected into the mixture and reaction temperature was increased to 300 °C. After 3 h, the reaction was quenched and cooled down to room temperature. At end, TiS_2 nanoplates were collected by centrifugation, and washed sequentially with cyclohexane/ethanol (1:1 v/v) and pure ethanol. Finally, the product was dried at 80 °C in a vacuum oven.

Preparation of TiS₂ NSs@MWCNT Composite Paper: The TiS₂ NSs@ MWCNT composite paper was prepared through a vacuum filtration method. TiS₂ NSs and MWCNT were mixed in 500 mL ethanol with a mass ratio of 7:1, and the mixture was ultrasonicated for 15 min in order to interweave MWCNT with TiS₂ NSs. Before mixing the TiS₂ with MWCNT, the TiS₂ was fully dispersed in 300 mL ethanol by ultrasonication for about 10 min. The TiS₂-MWCNT mixture was vacuum filtered onto a 7 cm filter paper to render a free-standing TiS₂ NSs@MWCNT composite paper. The composite paper was dried under vacuum at 80 °C for 24 h before being peeled off and punched out into circular disks with a diameter of 1.2 cm (1.13 cm², 3.7–3.8 mg each).

Adsorption of Lithium Polysulfide and Lithium Thiophenolate: Li₂S₆ solution was prepared by chemically reacting sulfur and an appropriate amount of Li₂S in DME/DOL solution (1:1 v/v). The solution was then stirred at 60 °C in an Ar-filled glove box for 12 h to produce a brownish-red Li₂S₆ solution (1.0 M). The lithium thiophenolate (PhSLi) powder was obtained by removing THF solvent in the commercial PhSLi solution in an Ar-filled glove box at 60 °C. The obtained PhSLi powder was dissolved in DME/DOL solvent (1:1 v/v) to form 0.2 m PhSLi solution. The Li₂S₆ and PhSLi solutions were then diluted to 5×10^{-3} M for the adsorption test. TiS₂ or MWCNTs as adsorbents (10 mg) was added into 2 mL of Li₂S₆ and PhSLi solutions. After prolonged contact with Li₂S₆ and PhSLi, the supernatant separated by filtration was diluted to enable quantitative concentration measurements. Ultraviolet-visible (UV–vis) absorption spectra of these diluted solutions were collected using a UV-8453 spectrophotometer (Agilent) with baseline correction.

Catalytic Effect Evaluation: Symmetric cells were assembled with two TiS₂ NS@MWCNT composite or pure MWCNT electrodes. The electrolyte was 1.0 m LiTFSI in DME/DOL (1:1 v/v), 0.2 m Li₂S₆ or 0.2 m PhSLi solution. Cyclic voltammetry (CV) was performed on a Bio-Logic VMP-3 potentiostat between –1.0 and 1.0 V at the scan rate of 3 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was conducted at open

circuit potential of the cells with a Bio-Logic VMP-3 impedance analyzer in the frequency range of 100 kHz and 0.1 Hz with an amplitude of 5 mV.

Cell Fabrication and Electrochemical Evaluation: CR2032 type coin cells were fabricated inside the glove box with 1.0 м LiTFSI and 0.2 м LiNO₃ in the mixture solvent of DME and DOL (1:1 v/v) as the electrolyte. First, 1.6–1.7 mg PTS was added into the TiS₂ NSs@MWCNT composite paper as current collector (PTS/TiS2 NSs) followed by 25 µL of electrolyte. Then a Celgard 2400 separator was placed on the top of the electrode followed by adding 10 uL electrolyte on the top of the separator and lithium metal anode. Finally, the cell was crimped and taken out of the glove box for electrochemical evaluation. The mass ratio of PTS to TiS₂ was calculated to be about 3:1. The pure PTS cell was prepared by following the same procedure using the pure MWCNT paper as current collector. Cells were galvanostatically cycled on a LANHE battery cycler at different C rates $(1 \text{ C} = 570 \text{ mA g}^{-1})$, based on the mass of PTS in the cells). The pure PTS and PTS/TiS₂ NSs cells were cycled between 1.8-3.0 V at 0.1 C and 0.2 C rates, 1.75–3.0 V at 0.5 C and 1 C rate, 1.7–2.8 V at 2 C rate, and 1.65–2.8 V at 3 C and 4 C rates. For the pure PTS and PTS/TiS₂ NSs cells, the CV was performed with different scan rates between 1.8-3.0 V. EIS data were collected in the frequency range of 100 kHz-0.1 Hz.

Characterizations: The X-ray diffraction (XRD) data of the MWCNT, TiS₂ NSs, and TiS₂ NSs@MWCNT composite materials were collected on a Rigaku MiniFlex600 XRD Instrument equipped with Cu K α radiation. The scanning rate was 0.4° min⁻¹, and 2 θ was set between 10° and $80^\circ.$ Raman measurement was conducted on a HORIBA HR Evolution. N2 adsorption-desorption measurements were conducted on a Micrometrics ASAP2420-4MP instrument. The nitrogen adsorption and desorption were performed at 77 K. The morphology and microstructure of TiS2 NSs and TiS2 NSs@MWCNT composite materials were investigated by a Phenom FEG SEM and a JEM-2100-F HR-TEM. The elemental mapping was performed with energy-dispersive X-ray spectroscopy (EDS) attached to the HR-TEM. X-ray photoelectron spectroscopy (XPS) were analyzed with a 5000 VersaProbe II XPS spectrometer with monochromatic Al K α radiation. Element analysis was tested by Flash EA 1112 Automatic Element Analyzer. A Waters Xevo G2-XS QTof mass spectrometer was used to verify the synthesized PTS. The synthesized PTS and the recharge product of PTS/TiS₂ electrode samples were diluted and soaked in trichloromethane (CHCl₃), respectively, and the solutions were tested in atmospheric pressure solids analysis probe (ASAP) positive mode with the first-order mass spectrometry model. The discharge product was verified by a Waters ACQUITY UPLC I-Class PLUS liquid chromatogram coupled with a Waters Xevo G2-XS QTof mass spectrometer. The column was ACOUITY UPLC BEH C18 LC Column (2.1-100 mm, Waters). The discharged PTS/ TiS₂ cathode sample was soaked in chromatographic methanol and it was filtered. 1 μ L of the solution was tested in atmospheric pressure chemical ionization (APCI) positive mode.

Theoretical Computation: The density function theory (DFT) calculations were performed within generalized gradient approximation in the Perde-Burke-Ernzerh (PBE) scheme, as implemented in the Vienna ab initio simulation package (VASP) code.^[41-43] The valence electronic states were expanded in plane wave basis sets with energy cutoff of 400 eV. The energy optimization was completed with force convergence criterion of 10 meV Å⁻¹. The Monkhorst-Pack k-point mesh of 3 × 3 × 1 was used for surface structural relaxation and a vacuum slab of about 15 Å was employed. The TiS₂ (00-1) surface was chosen to calculate the adsorption energies. The adsorption energies (E_{ads}) for the PhSLi and Li₂S₆ compounds on the metal sulfide surfaces are defined as $E_{ads} = E_{total} - E_{comp} - E_{sufr}$ where E_{total} is the total energy of the adsorbed system, E_{comp} is the energy of the compound in vacuum and E_{suf} is the energy of the optimized clean surface slab. The binding energies (E_b) have a negative sign of the E_{ads} .

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

 ${\sf electrocatalysis},$ lithium batteries, nanosheets, organosulfides, titanium disulfides

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