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Two-dimensional layered transition metal disulphides for effective encapsulation of high-capacity lithium sulphide cathodes

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Fully lithiated lithium sulphide (Li₂S) is currently being explored as a promising cathode material for emerging energy storage applications. Like their sulphur counterparts, Li₂S cathodes require effective encapsulation to reduce the dissolution of intermediate lithium polysulphide (Li₂S_n, n = 4-8) species into the electrolyte. Here we report, the encapsulation of Li₂S cathodes using two-dimensional layered transition metal disulphides that possess a combination of high conductivity and strong binding with Li₂S/Li₂S_n species. In particular, using titanium disulphide as an encapsulation material, we demonstrate a high specific capacity of 503 mAh g $^{-1}$ Li₂S under high C-rate conditions (4C) as well as high areal capacity of 3.0 mAh cm $^{-2}$ under high mass-loading conditions (5.3 mg_{Li₂S} cm $^{-2}$). This work opens up the new prospect of using transition metal disulphides instead of conventional carbon-based materials for effective encapsulation of high-capacity electrode materials.

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echargeable lithium-ion batteries have revolutionized the world of consumer electronics by providing a lightweight means of powering small, portable electronic devices¹⁻⁷. However, the ever-increasing demand for large-scale energy storage and sustainable transport today has triggered the quest for alternative battery technologies with much higher specific energy. The main limiting factor in lithium-ion batteries today is the low theoretical specific capacity ($\sim 300 \,\mathrm{mAh \, g^{-1}}$) of conventional intercalation cathodes based on transition metal oxides and phosphates¹⁻⁷. Sulphur is a well-known, high-capacity cathode material that has been under active study $(S_8 + 16Li \leftrightarrow 8Li_2S)^{8-34}$, but further advancement is hindered by the need for pairing with a metallic lithium anode that is prone to dendrite formation and safety challenges. In this respect, fully lithiated lithium sulphide (Li₂S), with its high theoretical specific capacity of 1,166 mAh g^{-1} , represents a more attractive cathode material because of its compatibility with safer lithium metal-free anodes³⁵⁻⁵⁵. Moreover, since Li₂S is already in its fully lithiated and fully expanded state, it circumvents the volumetric expansion problem in sulphur cathodes, thus minimizing structural damage at the electrode level^{15,16}.

Similar to their sulphur counterparts, Li₂S cathodes are plagued with two main challenges: (1) the insulating nature of Li₂S, and (2) uncontrolled dissolution and loss of intermediate lithium polysulphide (Li₂S_n, n = 4-8) species into the electrolyte, leading to fast capacity decay and low Coulombic efficiency³⁵⁻⁵⁵. To address these challenges, the typical strategy is to encapsulate Li₂S cathodes with conductive coating materials in an attempt to improve their conductivity as well as physically entrap intermediate Li_2S_n species within the shell during cycling³⁵⁻⁵⁰. Besides acting as a physical barrier, an ideal encapsulation material should also possess strong chemical interaction with polar Li_2S and Li_2S_n species in order to further bind and confine these species within the shell during cycling. Out of the ~ 16 papers in the literature on encapsulating Li₂S cathodes thus far, the vast majority (15 of them) use electronically conductive carbon-based materials such as graphene and porous carbon for encapsulation $^{35-49}$ (the last paper uses Li₃PS₄, a lithium superionic conductor/solid electrolyte, which is a poor electronic conductor⁵⁰). Although carbon-based materials are conductive, their nonpolar nature leads to weak interaction with polar Li2S and Li₂S_n species¹⁷, which greatly reduces their ability to bind and confine these species within the shell during cycling. While it is possible to introduce polar oxygen-containing functional groups into carbon to improve its interaction with Li_2S/Li_2S_n species (for example, by using graphene oxide⁴²), such oxidation treatment decreases the conductivity of carbon drastically. In using carbonbased materials as encapsulation materials for Li2S cathodes, there is a major constraint involved: it is difficult to achieve both high conductivity and strong binding with Li_2S/Li_2S_n species simultaneously. This greatly limits the cycling performance of Li₂S cathodes so far, especially under high C-rate and high massloading conditions. Thus, there is an urgent need for a new class of encapsulation materials for Li₂S cathodes that can overcome this major constraint associated with conventional carbon-based materials.

Herein we demonstrate, for the first time, the use of titanium disulphide (TiS₂), a two-dimensional (2D) layered transition metal disulphide, as an effective encapsulation material for Li₂S cathodes to overcome this significant constraint. TiS₂ possesses a combination of high conductivity^{2,7} and polar Ti–S groups that can potentially interact strongly with Li₂S/Li₂S_n species. In this work, we synthesized Li₂S@TiS₂ core–shell nanostructures that exhibited 10 orders of magnitude higher electronic conductivity compared with pure Li₂S. The results of *ab initio* simulations also show strong binding between Li₂S and TiS₂, with a calculated

binding energy 10 times higher than that between Li_2S and carbon-based graphene, a very common encapsulation material used in the literature²⁹. Using the $Li_2S@TiS_2$ nanostructures as a cathode material, we achieve an unprecedented specific capacity of 503 mAh g⁻¹_{Li₂S} under high C-rate conditions (4C), as well as unprecedented areal capacity of 3.0 mAh cm⁻² under high mass-loading conditions (5.3 mg_{Li₂S} cm⁻²), both of which are the highest values reported to date for Li_2S cathodes on metal foil. Finally, using zirconium disulphide (ZrS₂) and vanadium disulphide (VS₂) as further examples, we open up the new concept of using 2D layered transition metal disulphides as a general class of effective encapsulation materials for achieving high performance in Li₂S cathodes.

Results

Synthesis and characterization. The $Li_2S@TiS_2$ core-shell nanostructures were synthesized as shown schematically in Fig. 1a (see Methods section for details). In brief, ball-milled commercial Li_2S particles were dispersed in anhydrous ethyl



Figure 1 | Synthesis and characterization of Li₂S@TiS₂ core-shell nanostructures. (a) Schematic of the synthesis process, (**b**) SEM image and (**c**) TEM image of Li₂S@TiS₂ structures. Scale bars, $5 \mu m$ (**b**) and 500 nm (**c**). (**d**) High-resolution TEM image of the TiS₂ shell, showing the interlayer spacing of 0.57 nm. Scale bar, 5 nm. (**e**) XRD spectrum of Li₂S@TiS₂ structures (JCPDS files 00-026-1188 and 04-004-6690 were used as references for Li₂S and TiS₂, respectively). (**f**) Raman spectra of bare Li₂S@TiS₂ structures. (**g**) *Ab initio* simulations showing the most stable binding configuration of Li₂S with a single layer of TiS₂, with a calculated binding energy of 2.99 eV. RT, room temperature.

acetate, followed by the addition of a controlled amount of TiCl₄ precursor to react directly with some of the Li₂S on the surface to form a TiS₂ coating $(TiCl_4 + 2Li_2S \rightarrow TiS_2 + 4LiCl; Fig. 1a)^{56}$. The in situ and direct reaction of TiCl₄ with Li₂S ensures a uniform coating of TiS₂ on the surface of the Li₂S particles. The assynthesized Li₂S@TiS₂ nanostructures were then washed by centrifugation and heated at 400 °C in an argon atmosphere to allow crystallization of the TiS₂ shell (Fig. 1a). Figure 1b shows a scanning electron microscopy (SEM) image of the Li₂S@TiS₂ nanostructures. The transmission electron microscopy (TEM) image in Fig. 1c shows the Li_2S particles (mostly <1 μ m in size) encapsulated within TiS₂ shells ($\sim 20 \text{ nm}$ thick; Supplementary Fig. 1a). From the high-resolution TEM image, we see that the TiS₂ shell is layered and crystalline in nature with interlayer spacing of 0.57 nm (Fig. 1d), which is consistent with that of TiS_2 (ref. 57). The crystalline nature and identity of the TiS₂ shell was also ascertained using X-ray diffraction (XRD; Fig. 1e). The uniform surface coating of TiS₂ on the Li₂S particles was further confirmed using Raman spectroscopy. We see that the Raman spectrum of bare Li₂S shows the characteristic T_{2g} peak of Li₂S at 372 cm⁻¹ (Fig. 1f)^{42,47}. On the other hand, for the Li₂S@TiS₂ structures, the A_{1g} peak of TiS₂ at 335 cm⁻¹ can be clearly seen⁵⁸ while the peak of Li₂S becomes less prominent (Fig. 1f). Since Raman spectroscopy is a surface-sensitive technique, this observation indicates that the Li2S particles have been uniformly encapsulated with TiS₂ shell. Using energy-dispersive X-ray spectroscopy (EDX), the ratio of Li₂S:TiS₂ in the composite was determined to be 78:22 by weight, which is consistent with the amount of TiCl₄ precursor added to react with Li₂S based on the reaction stoichiometry (see Supplementary Fig. 2 for details).

D.C. conductivity measurements of the Li₂S@TiS₂ structures were performed at 25 °C after the samples were dry-pressed into a pellet and sandwiched between two blocking electrodes (Supplementary Fig. 3). The electronic conductivity of the Li₂S@TiS₂ structures was measured to be 5.1×10^{-3} S cm⁻¹, which is ~10 orders of magnitude higher than that of bare

 Li_2S (10⁻¹³ S cm⁻¹)^{50,52}. In terms of confining Li_2S and Li_2S_n species, the unique 2D layered structure of TiS2 would enable it to act as a good physical barrier to entrap these species within the shell during cycling. To probe the further possibility of chemical interaction between Li₂S and TiS₂, ab initio simulations were carried out in the framework of density functional theory (see Methods section for details)^{59–62}. The results of the simulations in Fig. 1g indicate strong Li-S interaction (between the Li atoms in Li₂S and S atoms in TiS₂), as well as strong S-S interaction (between the S atoms in Li₂S and S atoms in TiS₂). The binding energy between Li₂S and a single layer of TiS₂ was calculated to be 2.99 eV. This value is 10 times higher than that between Li₂S and a single layer of carbon-based graphene (0.29 eV; ref. 17), which is a very common encapsulation material used in the literature²⁹. The much stronger interaction between Li₂S and TiS₂ can be explained by their similar ionic bonding and polar nature, unlike graphene which is covalently bonded and nonpolar in nature. Previous results have shown that entities that bind strongly to Li_2S exhibit strong binding with Li_2S_n species as well owing to their similar chemical bonding nature^{27,53}. Overall, the dual effect of physical entrapment and chemical binding would enable TiS₂ to be effective in confining Li_2S and Li_2S_n species within the shell during cycling.

To verify the above-mentioned point, the Li₂S@TiS₂ structures and bare Li₂S particles were dispersed directly onto conductive carbon fibre substrates to prepare working electrodes, and pouch cells were assembled using lithium foil as the counter electrodes. Some cells were charged to a high cutoff voltage of 3.8 V versus Li⁺/Li to delithiate the Li₂S (ref. 52) and then disassembled in the charged state. Others were charged in the same way and then discharged to 1.8 V versus Li⁺/Li for lithiation to re-form Li₂S, before being disassembled in the discharged state (see Supplementary Fig. 4 for the voltage profiles). After disassembly of the cells, the working electrodes were examined using SEM. The SEM image in Fig. 2a shows the bare Li₂S particles on carbon fibre substrate before cycling. At the end of charge, only the



Figure 2 | Morphology of bare Li₂S and Li₂S@TiS₂ structures during a charge-discharge cycle. (a-c) SEM images of bare Li₂S particles (a) before cycling, (b) at the end of charge and (c) at the end of discharge. (d-i) SEM images of Li₂S@TiS₂ structures (d) before cycling, (e) at the end of charge and (f) at the end of discharge, as well as (g-i) their corresponding TEM images. Scale bars, $5 \mu m$ (a-f) and 500 nm (g-i).

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underlying carbon fibre substrate could be observed, but not the particles that were originally on the surface (Fig. 2b). This is attributed to the delithiation of Li_2S upon charging to form Li_2S_n species (n = 4 - 8) that dissolve readily into the electrolyte owing to the complete lack of encapsulation (it is known that solid S₈ is not re-formed at the end of initial charge⁵²). At the end of discharge, the original Li₂S particle morphology was not recovered as well; irregularly shaped and -sized Li₂S particles were formed on the electrode surface instead (Fig. 2c). This is due to uncontrolled dissolution of intermediate Li_2S_n species leading to random precipitation of Li₂S all over the electrode upon discharge. On the other hand, in the case of the Li₂S@TiS₂ structures, little change in particle morphology was observed before cycling versus at the end of charge as seen under SEM (Fig. 2d,e). TEM imaging also shows that core-shell structure was preserved and the protective TiS₂ shell remained intact (Fig. 2g,h and Supplementary Fig. 1b,c). At the end of discharge (lithiation to re-form Li₂S), the Li₂S@TiS₂ particles were seen to maintain their original morphology as well, as evidenced by both SEM and TEM (Fig. 2f,i and Supplementary Fig. 1d). This indicates that TiS₂ is effective in confining the charge and discharge species $(Li_2S_n \text{ and } Li_2S, \text{ respectively})$ within the shell during the chargedischarge cycle, hence resulting in the observed preservation of morphology.

Electrochemical performance. To evaluate their electrochemical performance, working electrodes were prepared by mixing the

Li₂S@TiS₂ nanostructures with conductive carbon black and polyvinylidene fluoride (PVDF) binder (65:30:5 by weight) in *N*-methyl-2-pyrrolidinone to form a slurry, which was then coated onto aluminium foil and dried in a glove box. Bare Li₂S cathodes were also prepared in the same way for comparison. 2032-Type coin cells were then assembled using lithium foil as the counter electrode. The electrolyte used was lithium bis(trifluoromethanesulphonyl)imide (1 M) in 1:1 (v/v) 1,2-dimethoxyethane and 1,3-dioxolane, with LiNO₃ additive (1 wt%) to help passivate the lithium anode surface²¹. The typical mass loading was ~1 mg_{Li,S} cm⁻² unless otherwise stated.

The impedance spectrum of the as-assembled Li₂S@TiS₂ cells at open-circuit voltage showed a smaller semicircle in the highfrequency region compared with bare Li₂S cells, which indicates lower charge-transfer resistance in the former case (Fig. 3a and Supplementary Fig. 5)¹³. This is consistent with the much higher conductivity of the Li₂S particles upon TiS₂ coating. The asassembled cells were first charged to a high cutoff voltage of 3.8 V versus Li⁺/Li to delithiate the Li₂S (ref. 52). In the case of bare Li₂S cathodes, a high potential barrier at ~ 3.5 V was observed during initial charging (Fig. 3b) owing to the high charge-transfer resistance involved in delithiating Li₂S, which is insulating in nature (Li₂S \rightarrow Li_{2-x}S + xLi⁺ + xe⁻)⁵². On the other hand, the height of the potential barrier was found to be reduced to 3.0 V in the case of the Li₂S@TiS₂ cathodes (Fig. 3b), indicating improved conductivity and lowered charge-transfer resistance upon TiS₂ coating, which is consistent with results of the impedance measurements. After initial charging, galvanostatic cycling of the



Figure 3 | **Electrochemical performance of Li₂S@TiS₂ cathodes in comparison with bare Li₂S cathodes.** (a) Impedance spectra at open-circuit voltage, (b) first cycle charge voltage profiles and (c) specific capacities at 0.2 C ($1C = 1,166 \text{ mA g}^{-1}_{Li_2S}$) for Li₂S@TiS₂ and bare Li₂S cathodes. (d) Typical discharge-charge voltage profile showing various DoD and SoC (points 1-10) and the corresponding percentage of sulphur measured in the electrolyte relative to the total sulphur mass on the electrode at these various points for Li₂S@TiS₂ and bare Li₂S cathodes. (e,f) Low- and high-magnification (inset) SEM images of the surface of (e) bare Li₂S and (f) Li₂S@TiS₂ cathodes after 100 cycles in the discharged state. Scale bars, 100 µm in (e,f) and 1µm (e,f; inset).

Li₂S@TiS₂ cells was then carried out from 1.8 to 2.6 V versus Li⁺/ Li at 0.2C, where $1C = 1,166 \text{ mA g}^{-1}_{\text{Li},\text{S}}$. The discharge cutoff voltage was set at 1.8 V to avoid the irreversible reduction of $LiNO_3$ additive in the electrolyte²¹. The capacity contribution of TiS₂ was found to be negligible in this voltage range (Supplementary Fig. 6). As shown in Fig. 3c, the Li₂S@TiS₂ cathodes exhibited high initial specific capacity of $806 \text{ mAh g}^{-1}_{\text{Li,S}}$ (~1,156 mAh g⁻¹_S) and stable cycling performance at 0.2C. Relative to the initial cycle, the capacity retentions achieved at the end of 50, 100 and 150 cycles were 90%, 89% and 86%, respectively. In comparison, the bare Li₂S cathodes showed lower initial capacity and greater capacity decay under identical testing conditions (Fig. 3c). Relative to the initial specific capacity of 708 mAh $g^{-1}_{Li,S}$, the capacity retention of the bare Li₂S cathodes was only 66% after 100 cycles (compared with 89% for Li₂S@TiS₂ structures). This indicates a greater degree of dissolution of Li_2S_n species into the electrolyte in the case of bare Li₂S cathodes.

The above conclusion is supported by disassembly of the cells at various intermediate stages of cycling and testing the electrolyte for sulphur content using inductively coupled plasma-optical emission spectroscopy (ICP-OES; see Methods section for details)^{42,47}. Points 1–10 in Fig. 3d correspond to various depths of discharge (DoD) and states of charge (SoC) during cycling, where 100% DoD (point 6) and 100% SoC (point 10) refer to the maximum discharge and charge capacities attained, respectively. The ICP-OES results for the bare Li₂S cathodes showed a huge variation in sulphur content detected in

the electrolyte at various stages of cycling (Fig. 3d) owing to lack of control over the Li_2S_n dissolution process. On the other hand, in the case of Li2S@TiS2 cathodes, we see significantly less variation and lower percentage loss of sulphur into the electrolyte during cycling (Fig. 3d). For example, at points 3, 6 and 9 during the cycling process (25% DoD, 100% DoD and 75% SoC), we measured 17%, 9% and 18% of the total sulphur mass on the electrode dissolved into the electrolyte, respectively, for the Li₂S@TiS₂ cathodes (Fig. 3d). In comparison, the percentage loss of total sulphur mass into the electrolyte was found to be much higher in the case of bare Li₂S cathodes: 91%, 35% and 93% at points 3, 6 and 9, respectively, (Fig. 3d). The cells were also disassembled in the discharged state at the end of 100 cycles to examine the morphology of the cathode surface after cycling. In the case of bare Li₂S cathodes, an insoluble dense film of Li₂S was formed on the surface owing to uncontrolled dissolution of intermediate Li_2S_n species into the electrolyte (Fig. 3e; see inset for a high-magnification image). The presence of this insulating Li₂S film passivates the electrode surface, thereby leading to low active material utilization and rapid capacity decay upon cycling^{8,9}. On the other hand, there was no such passivating Li₂S film formed on the surface of the Li₂S@TiS₂ cathodes after 100 cycles (Fig. 3f and Supplementary Fig. 7), thus ensuring continued good access of electrolyte and Li+ to the active materials throughout the cycling process.

To further evaluate their electrochemical cycling performance, the $Li_2S@TiS_2$ cathodes were subject to prolonged cycling. From Fig. 4a, we see that the $Li_2S@TiS_2$ cathodes showed stable



Figure 4 | Further electrochemical performance of Li₂S@TiS₂ cathodes. (a) Specific capacity and Coulombic efficiency of Li₂S@TiS₂ cathodes upon prolonged 400 charge-discharge cycles at 0.5 C ($1C = 1,166 \text{ mA g}^{-1}_{\text{Li}_{2}\text{S}}$). (b) Specific capacity and (c) charge-discharge voltage profiles of Li₂S@TiS₂ cathodes cycled from 0.2 to 4 C. (d) First cycle discharge voltage profile and (e) areal capacity of Li₂S@TiS₂ cathodes with high mass-loading cycled from 0.1 to 0.6 mA cm⁻².

cycling performance at 0.5C over 400 charge-discharge cycles. Relative to the initial specific capacity of $666 \text{ mAh g}^{-1}_{\text{Li},\text{S}}$ $(\sim 956 \,\mathrm{mAh}\,\mathrm{g}^{-1}\mathrm{s})$ at 0.5C, the cells retained 77% of their capacity at the end of 400 cycles, which corresponds to a small average capacity decay of 0.058% per cycle. The average Coulombic efficiency was calculated to be 98% (Fig. 4a). Next, the Li₂S@TiS₂ cathodes were cycled at different C-rates to evaluate their rate capability and electrode kinetics (Fig. 4b,c). When the C-rate was increased successively from 0.2C to 0.5C, 1C, 2C and 3C, the cells delivered high stabilized specific capacities of 700, 650, 608, 595 and 560 mAh $g^{-1}_{Li,S}$, respectively (Fig. 4b,c). The capacities achieved at 0.5C, 1C, 2C and 3C correspond to 93%, 87%, 85% and 80%, respectively, of the capacity that was reached at 0.2C. Even at a high C-rate of 4C (4,664 mA $g^{-1}_{Li_2S}$), a reversible specific capacity of 503 mAh $g^{-1}_{Li_2S}$ (~722 mAh g^{-1}_{S}) could be attained (Fig. 4b,c). To the best of our knowledge, this is the first time such a high specific capacity has been achieved at 4C for Li₂S cathodes on metal foil, which indicates good conductivity and charge-transfer kinetics in our Li2S@TiS2 cathodes. When the C-rate was switched abruptly from 4C back to 0.2C again, the original capacity was mostly recovered (Fig. 4b), indicating robustness and stability of the cathode material.

We note that publications on Li₂S cathodes in the literature typically only report specific capacity values that are normalized by the mass of Li_2S (refs 41–47). The mass loading of Li_2S on metal foil used in the literature is usually $< 1 \text{ mg}_{\text{Li,S}} \text{ cm}^{-2}$, which limits the typical areal capacity values to $< 1 \text{ mAh cm}^{-2}$ (refs 41-47). However, high mass loadings and high areal capacities are essential for practical applications in commercial batteries. Therefore, we tested thick Li₂S@TiS₂ cathodes on aluminium foil with much higher mass loading of $5.3 \text{ mg}_{\text{Li},\text{S}} \text{ cm}^{-2}$. Upon cycling at 0.1 mA cm⁻², an initial specific capacity of 566 mAh g⁻¹_{Li₂S} was achieved that corresponds to an unprecedented areal capacity of 3.0 mAh cm^{-2} (Fig. 4d). This is the highest areal capacity value reported for Li2S cathodes on metal foil so far. Upon cycling at higher current densities of 0.3 and 0.6 mA cm^{-2} , areal capacities of 2.2 and 1.6 mAh cm⁻² were achieved, respectively, (Fig. 4e). Cycling of a high mass-loading Li₂S cathode places high demands on the conductivity of the active materials, as well as the ability to confine Li_2S and Li_2S_n species within the shell. The performance demonstrated in this work shows the importance of selecting an effective encapsulation material such as TiS₂ in order to achieve stable cycling and high areal capacity in Li₂S cathodes.

Generalization to other transition metal disulphides. Finally, to show the generality of using 2D transition metal disulphides as encapsulation materials for Li2S cathodes, we also synthesized Li₂S@ZrS₂ and Li₂S@VS₂ core-shell structures (Fig. 5a,b) using the same reaction mechanism: $MCl_4 + 2Li_2S \rightarrow MS_2 + 4LiCl$ $(M = Ti, Zr and V)^{56}$. For further characterization of these materials using TEM, XRD and EDX, please refer to Supplementary Fig. 8. The conductivities of the Li₂S@ZrS₂ and $Li_2S@VS_2$ structures were measured to be 4.0×10^{-9} and $3.8 \times 10^{-9} S cm^{-1}$, respectively, which are ~4 orders of magnitude higher than that of bare Li_2S ($10^{-13} S cm^{-1}$; refs 50,52). The results of ab initio simulations also show strong binding of Li₂S to ZrS₂ and VS₂, with calculated binding energies of 2.70 and 2.94 eV, respectively, (Fig. 5c,d), which are \sim 9–10 times higher than that between Li₂S and carbon-based graphene (0.29 eV; ref. 17). Working electrodes on aluminium foil were prepared for the Li₂S@ZrS₂ and Li₂S@VS₂ structures, and the cells were subject to galvanostatic cycling as well. Using $\sim 1~mg_{Li_2S}\,cm^{-2}$, the $Li_2S@ZrS_2$ and $Li_2S@VS_2$ cathodes exhibited high initial specific capacities of 777 and



Figure 5 | Generalization to other transition metal disulphides. (a,b) SEM images of (a) $Li_2S@ZrS_2$ and (b) $Li_2S@VS_2$ structures. Scale bars, 5 μ m. (c,d) *Ab initio* simulations showing the most stable binding configuration of Li₂S with a single layer of (c) ZrS₂ and (d) VS₂ with calculated binding energies of 2.70 and 2.94 eV, respectively. (e) Specific capacity of Li₂S@ZrS₂ and Li₂S@VS₂ cathodes cycled at 0.2 C (1C = 1,166 mA g⁻¹_{Li₂S}). (f) Areal capacity of Li₂S@ZrS₂ and Li₂S@ZrS₂ and Li₂S@VS₂ cathodes with high mass loading cycled from 0.1 to 0.6 mA cm⁻².

747 mAh g⁻¹_{Li,S}, respectively, at 0.2C, with capacity retentions of 85% and 86%, respectively, after 100 cycles (Fig. 5e), both of which are much higher than in the case of bare Li₂S cathodes (66% after 100 cycles). The morphologies of the electrode surfaces were also examined after 100 cycles in the discharged state, both of which show the absence of a passivating Li₂S film (Supplementary Fig. 9), similar to the case of Li₂S@TiS₂ cathodes after cycling. Both the Li₂S@ZrS₂ and Li₂S@VS₂ cathodes were also subject to cycling under high mass-loading conditions. Using 4.8 mg_{Li,S} cm⁻² for the Li₂S@ZrS₂ cathodes and current densities of 0.1, 0.3 and 0.6 mA cm⁻², we achieve areal capacities of 2.7, 2.0 and 1.7 mAh cm⁻², respectively, (Fig. 5f). The areal capacities attained are similarly high in the case of Li₂S@VS₂ cathodes containing 5.0 mg_{Li₂S} cm⁻²: 2.7, 1.9 and 1.6 mAh cm⁻², respectively, at the abovementioned current densities (Fig. 5f).

Discussion

In this work, we have presented the electrochemical performance of Li₂S@TiS₂ structures with Li₂S core size of $<1 \,\mu m$ and TiS₂ shell thickness of $\sim 20 \text{ nm}$ (Li₂S:TiS₂ = 78: 22 by weight). For practical applications in which high percentage of active material (Li₂S) is desired, the ratio of Li₂S:TiS₂ should be further optimized. To this end, we investigated the cycling performance of Li₂S@TiS₂ composites with three different TiS₂ shell thicknesses: ~ 11 , 20 and 55 nm, which were synthesized by varying the amount of TiCl₄ precursor added (Supplementary Fig. 10a-c). Upon galvanostatic cycling at 0.2C, the specific capacity of the Li₂S@TiS₂ cathode with a 11-nm thin shell was found to fade faster than that of a 20-nm shell (Supplementary Fig. 10d), because the former shell is not thick enough to act as a physical barrier to the dissolution of Li_2S_n species. On the other hand, the cycling performance of the cathode with a 55-nm thick shell was comparable to that of a 20-nm shell (Supplementary Fig. 10d), which explains our choice of 20 nm as the TiS₂ shell thickness in this work.

Instead of decreasing the TiS₂ shell thickness, another way to increase the percentage of Li₂S is to increase the size of the Li₂S core. To this end, we coated TiS₂ onto larger, non-ball-milled Li₂S particles that are >1 µm in size (Supplementary Fig. 11a). The percentage of Li₂S in the resulting composite was determined to be higher using EDX (Li₂S:TiS₂ = 87: 13 by weight; Supplementary Fig. 11b). Upon galvanostatic cycling at 0.2C, 0.5C and 1C, similarly good cycling performance can be achieved for the Li₂S@TiS₂ cathodes with larger versus smaller Li₂S core (Supplementary Fig. 11c). However, at a higher C-rate of 2C, the cathode with smaller Li₂S core exhibited higher specific capacity and better cycling stability (Supplementary Fig. 11c) because of the shorter Li⁺ diffusion lengths in smaller Li₂S particles. There is a compromise to be reached in terms of the size of the Li₂S particles and their rate capability.

In conclusion, we have demonstrated the use of 2D layered transition metal disulphides for effective encapsulation of Li_2S cathodes owing to their combination of high conductivity and strong binding with $\text{Li}_2\text{S}/\text{Li}_2\text{S}_n$ species. Further work is currently ongoing to pair these stable-cycling $\text{Li}_2\text{S}@M\text{S}_2$ cathodes with lithium metal-free anodes (such as silicon) to achieve a full-cell configuration. This work overcomes the major constraint associated with conventional carbon-based materials and opens up the new prospect of using transition metal disulphides for effective encapsulation of other high-capacity electrode materials.

Methods

Materials synthesis. Owing to the sensitivity of Li2S to moisture, all the material synthesis procedures were carried out in an argon-filled glove box with moisture and oxygen levels below 0.5 p.p.m. Commercial Li₂S particles (99.9%, Alfa Aesar) were first ball-milled for 1 h using a SPEX 5100 Mixer/Mill. The ball-milled Li₂S particles (10 mmol) were then dispersed in anhydrous ethyl acetate, followed by addition of MCl₄ precursor (M = Ti, Zr and V; 1 mmol) using a glass syringe to convert 20% of the Li₂S on the surface into MS₂ (MCl₄ + 2Li₂S \rightarrow MS₂ + 4LiCl; ref. 56). After overnight reaction at room temperature, the as-synthesized Li₂S@MS₂ core-shell structures were washed by centrifugation three times using anhydrous tetrahydrofuran to remove the LiCl side product. These were then heated at 400 $^{\rm o}{\rm C}$ under argon gas atmosphere to remove the ethyl acetate solvent and allow crystallization of MS2. The ratio of Li2S: MS2 in the Li2S@MS2 structures was determined using EDX to be 78:22, 72:28 and 75:25 by weight for M = Ti, Zr and V, respectively, all of which are consistent with the amount of MCl₄ precursor added to react with Li₂S based on the reaction stoichiometry (Supplementary Figs 2 and 8c,f).

Characterization. To prevent moisture contamination of Li₂S, special precautions were taken during characterization. SEM, EDX and TEM were performed using a FEI Quanta 250 FEG, FEI XL30 Sirion and Tecnai G2 F20 X-TWIN, respectively. The samples were first tightly sealed in foil/polybags before being transferred into the microscope chamber via an argon-filled glove bag. XRD patterns were obtained

on a PANalytical X'Pert diffractometer (Cu K α radiation) after the samples were tightly sealed using Kapton tape. Raman spectra were obtained using a WITEC Raman spectrometer (531 nm excitation laser) after the samples were tightly sealed in a glass holder. D.C. conductivity measurements were performed at 25 °C in an argon-filled glove box using a Bio-Logic VMP3 potentiostat after the samples were dry-pressed into a pellet and sandwiched between two pieces of carbon-coated aluminium foil as the blocking electrodes.

Ab initio simulations. Ab initio simulations were performed using the Vienna Ab Initio Simulation Package in the framework of density functional theory^{59,60}. The projector augmented-wave pseudopotential⁶¹ and the generalized gradient approximation exchange-correlation function described by Perdew–Burke–Ernzerhof⁶² were adopted. To ensure convergence, 500 eV was chosen as the cutoff energy of the plane-wave basis. The vacuum between MS₂ (M = Ti, Zr and V) and its image exceeds 30 Å, while the distance between Li₂S and its image is no <15 Å along the periodic direction. These systems were large enough to avoid any artificial interaction caused by periodicity. The binding energy, $E_{\rm b}$, was defined as the energy difference between the Li₂S-MS₂ adsorbed system ($E_{\rm tot}$) and the summation of pure Li₂S ($E_{\rm Li_2S}$) and pure MS₂ ($E_{\rm MS2}$): $E_{\rm b} = (E_{\rm Li_2S} + E_{\rm MS2}) - E_{\rm tot}$. The 3D visualization models were constructed using VESTA 3 software⁶³.

Electrochemical measurements. Owing to the sensitivity of Li2S to moisture, all the electrode preparation and cell assembly procedures were carried out in an argon-filled glove box with moisture and oxygen levels below 0.5 p.p.m. The Li₂S@MS₂ structures (M = Ti, Zr and V) were mixed with conductive carbon black (Super P) and PVDF binder in a weight ratio of 65:30:5, followed by dispersion in N-methyl-2-pyrrolidinone to form a slurry. After overnight stirring, the slurry was then coated onto aluminium foil (carbon-coated) using doctor blade and dried at 60 °C to form the working electrodes. Based on the Li2S content in the Li2S@MS2 structures (Supplementary Figs 2 and 8c,f), we can determine the weight percentage of Li₂S in the electrodes to be \sim 51%, 47% and 49% for M = Ti, Zr and V respectively. The typical mass loading was $\sim 1\,mg_{Li_2S}\,cm^{-2}$ unless otherwise stated. The high mass-loading electrodes were prepared on aluminium foil in the same way. For comparison, bare Li2S cathodes were also prepared by mixing ball-milled Li₂S with Super P and PVDF binder in the same weight ratio of 65:30:5 and coating the slurry onto aluminium foil. 2032-Type coin cells were then assembled using lithium foil as the counter electrode. The electrolyte used was a solution of lithium bis(trifluoromethanesulphonyl)imide (1 M) in 1:1 (v/v) 1,2-dimethoxyethane and 1,3-dioxolane containing LiNO3 additive (1 wt%). Using eight-channel MTI battery testers, the cathodes were first activated at C/20 ($1C = 1,166 \text{ mA g}^{-1}_{\text{Li,S}}$) by charging to a high cutoff voltage of 3.8 V versus Li⁺/Li⁵². Galvanostatic cycling was then carried out at the specified C-rate from 1.8 to 2.6 V versus Li+/Li. Impedance measurements were carried out using a Bio-Logic VMP3 potentiostat in the frequency range from 200 kHz to 100 mHz. For analysis of sulphur content in the electrolyte, all the cell assembly procedures are the same as described above except that a sulphur-free lithium salt of LiClO₄ was used as the electrolyte salt instead of lithium bis(trifluoromethanesulphonyl)imide^{42,47}. The cells were disassembled at various points 1-10 during a discharge-charge cycle and the contents (cathode, anode and electrolyte-soaked separator) were washed with 1,3-dioxolane. This polysulphide-containing solution was then oxidized with concentrated HNO3 and diluted with deionized water for analysis of sulphur content using ICP-OES (Thermo Scientific ICAP 6,300 Duo View spectrometer).

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Author contributions

Z.W.S. and Y.C. conceived the idea. Z.W.S. carried out materials synthesis and electrochemical tests. Z.W.S., J.H.Y., W.L., P.-C.H., H.W., Y.S. and H.Y. performed materials characterization. Q.Z. carried out *ab initio* simulations. Z.W.S. and Y.C. co-wrote the paper. All the authors discussed the results and commented on the manuscript.

Additional information

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