Interface engineering by atomically thin layer tungsten disulfide catalyst for high performance Li–S battery

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A B S T R A C T
Owing to high aspect ratio of edge sites and superior catalytic activity, atomically thin transition metal dichalcogenides (TMDCs) show great promise to tailor the electrolyte/electrode interface properties for high performance lithium-sulfur battery (Li–S battery). However, the TMDCs that engineer the electrode/electrolyte interface are usually produced through chemical hydrothermal methods, which show low crystallinity and thick multilayer structure. Herein, a highly crystalline and atomically thin tungsten disulfides on carbon cloth (WS2@CC) was developed via chemical vapor deposition (CVD) and served as an effective electrode/electrolyte interface for Li–S battery. Our results demonstrate that the atomically thin WS2 with high crystal quality and abundant edges sites can effectively accelerates the redox kinetics of sulfur/lithium polysulfides and regulates the precipitation/decomposition of insoluble Li2S. More importantly, it was revealed that the hierarchical flower-stacked WS2 with excessive exposed catalytic edges shows extremely strong polysulfide adsorption, which causes the sulfur species aggregation and passivation on the WS2@CC surface, thus resulting in deformed rate performance and poor cycling stability as compared to the few-layer WS2@CC. Our work provides a new insight into the structural engineering of TMDCs by CVD for Li–S battery, and suggests the importance of rational chemisorption and catalysis of the interface to realize the high-performance Li–S battery.

1. Introduction

Advances in rechargeable batteries technology for sustainable and clean energy applications such as electric vehicles, portable electronic devices and smart grid storage remain challenging due to the limited theoretical energy density and high cost of the current lithium ion batteries (LIBs) technology [1–3]. Lithium-sulfur (Li–S) batteries have emerged as a promising alternative to resolve the issue of renewable energy intermittency due to their low cost, high energy density (2600 Wh kg−1), and environmental friendliness [1,4–6]. However, the implementation of Li–S battery for practical applications has been impeded by the following intrinsic issues: (a) the poor electronic conductivity of sulfur and its discharge products (Li2S/Li2S2) that results in sluggish redox kinetics and low sulfur utilization [7–9], (b) the diffusion of intermediate lithium polysulfide species during cycling causes shuttle effect and parasitic reaction to lithium anode, resulting in a rapid capacity decay and short cycle life [2,9,10], and (c) the large volumetric changes of the electrode, which leads to the cathode electrode pulverization that significantly affects its cycling stability [11]. Considerable efforts have been made to solve the above-mentioned issues, such as cathode host material design, electrolyte modifications, and etc [12–14]. Although great progress has been made, however, in some cases, these strategies cannot realize high sulfur loading, stable cycling, fast redox transformation simultaneously. Recently, engineering the interface between electrolyte and separator by inserting a functional interlayer such as carbon cloth, carbon nanotube coated separator [15,16], has been developed for the absorption of soluble polysulfide and reuse of the absorbed active material. However, the diffusion of polysulfides is prone to the precipitation of polysulfides on electrode/separator interfaces, resulting in the passivation of active surface, aggregation of solid polysulfide on the interlayer [17,18]. Notably, the precipitation of insoluble polysulfides is highly relied on the surface
chemistry where sulfur redox reactions occur. Designing an effective collaborative sulfur/polysulfide physicochemical transformation interface between electrolyte and electrode with high electrical conductivity, strong sulfur/sulfides chemisorption, superior electrocatalysis and intense catalytic reactive sites simultaneously is essential for improving the sulfur utilization, and realizing stable and high-rate Li–S batteries. In searching for an efficient collaborative sulfur/polysulfide physicochemical transformation interface to suppress the polysulfide shuttle effect and regulate the solid sulfur species deposition, two-dimensional (2D) transition metal dichalcogenides (TMDCs) are attractive owing to their high catalytic reactive surface, superior chemical stability, and low cost [19–23]. The catalytic activity of this type of materials highly depends on the number of exposed edge sites that exhibits unique chemical and electronic structure compared to their basal planes [5, 24]. It has been proven that atomically thin layered structures with high aspect ratio of edge sites and high effective catalytic surface is an effective catalytic interfacial candidate for sulfur redox reaction [5]. So far, intensive efforts have been done to improve the aspect ratio of active catalytic sites in TMDCs through nanostructure engineering [5, 25–28]. However, these TMDCs are usually obtained through chemical hydrothermal method, which show unsatisfactory catalytic effect due to their low crystallinity and stacked multilayer structure [29, 30]. Besides, the intrinsic defects in the crystal structure such as sulfur vacancy induce poor structural stability to restrain the lamella pulverization and active site invalidation, thus resulting in poor electrochemical performance. Chemical vapor deposition (CVD) is a promising, highly controllable method to synthesize high crystallinity and atomically thin layer 2D materials. Up to date, several types of TMDCs have been prepared via CVD to construct the catalytic active sites and accelerate the sulfur redox conversion, however, the large-scale production of ultrathin TMDCs as well as the potential application of TMDCs as catalytic interface are rarely reported.

In this contribution, a conductive and catalytic interface constructed by atomically thin layer WS2 catalysts on conductive support matrix is proposed to effectively inhibit the polysulfides shuttle effect, facilitate the polysulfides redox transformation and regulate the Li2S deposition. A low-pressure CVD method was employed to synthesize the atomically thin WS2 on carbon cloth (WS2@CC) on a large scale to imitate the electrocatalysis-driven process for achieving the commercial demand of the battery application. By tuning the precursor quantity, growth period, and growth times, different morphologies of the WS2 nanostructures such as few-layer planar flakes or layer-by-layer grown hierarchical flower-stacked structure were obtained. In addition, this strategy also demonstrates the substrate-independent growth mechanism, suggesting a versatile growth route for WS2 nanostructures with diverse substrate. Compared with the multilayer flower-stacked WS2, the atomically thin layer WS2@CC provides a more effective interface with strong chemisorption, high reactive catalytic sites and high electrical conductivity for promoting the redox conversion kinetics of sulfur intermediates and eliminating the polysulfide shuttle effects. Therefore, the cell with atomically thin layer WS2@CC interlayer delivers a high initial specific capacity of 1198 mAh g⁻¹ at 0.2 C, excellent rate capability (830 mAh g⁻¹ at 2 C) and long cycle life at 0.5 C (0.07% capacity decay per cycle). Our works inspire the exploration of large-scale production of atomically thin layer TMDCs by CVD method, which opens a new avenue for developing efficient energy storage applications.

2. Results and discussions

Chemical vapor deposition (CVD) is a widely used technique for controllable synthesis of atomically thin layer transition metal dichalcogenides (TMDCs). In our CVD synthesis, atomically thin WS2 grows onto carbon cloth (WS2@CC), which serves as a multifunctional interface among electrolyte/electrode for high-performance lithium-sulfur (Li–S) battery. In order to synthesize atomically thin WS2@CC, a modified low-pressure CVD approach was applied. Prior to the growth process, the carbon cloth substrate was first treated with nitric acid to enhance its hydrophilicity and hence to facilitate the growth of atomically thin WS2 nanosheets. As illustrated in Fig. 1a, a treated carbon cloth was located above the tungsten trioxide (WO3) powder in a parallel geometry with a 5 mm gap. This configuration allows the uniform growth of atomically thin WS2 nanosheets onto the carbon cloth. 15 sccm H2, a reducing agent for WO3, was used to promote the reduction of WO3 during the WS2 synthesis. The growth of atomically thin WS2 flakes usually takes place in a wide temperature range of 850–1000 °C. Here, we employed a high growth temperature of 1000 °C and low pressure of 10 torr throughout the experiment to ensure high evaporation rate of tungsten sources. The synthesis process is illustrated in Fig. 1b.

To understand the synthesis mechanism of WS2 nanostructures, different growth conditions, such as substrate, growth period, precursor quantity and growth times have been studied. Firstly, we synthesized the WS2 nanostructures onto carbon cloth and sapphire concurrently as shown in the scanning electron microscopy (SEM) images (Fig. 2a–c). As shown in Fig. 2a, abundant epifacial grown few-layer WS2 nanostructure of random shape were grown uniformly on the carbon cloth at a growth temperature of 1000 °C with a growth period of 1 h. The high magnification SEM image in Fig. 2b shows that some underlying buffer layers uniformly grow on the carbon cloth surface, and the secondary planar WS2 nucleates and grows on the buffer layers. The presence of few-layer WS2 crystals on carbon cloth is confirmed by Raman and photoluminescence (PL) characterization respectively, as shown in Figs. S1a and S1b. The relative peak intensity ratio of the E2g to A1g modes reflects the atomically thin WS2 layer. Interestingly, this strategy also demonstrates the similar growth mechanism of few-layer WS2 nanostructures on the typical growth substrates such as sapphire. As shown in Fig. 2c and d, the SEM and atomic force microscopy (AFM) images show the formation of few-layer stacked WS2 and monolayer WS2 on sapphire. The line scan of the edge illustrates that the thickness of the basal plane is 0.8 nm, indicates the initial formation of monolayer WS2 basal plane on the substrate. The high-resolution transmission electron microscopy (TEM) image of WS2 nanosheets (Fig. S2) reveals clear lattice fringe with a d-spacing of 0.27 nm, attributed to the (100) plane of hexagonal WS2, indicates that the as-grown WS2 nanosheets are well crystallized.

Different growth conditions have been further studied by varying the growth period, precursor quantity and growth time. It is worth to note that the growth period, precursor quantity and growth time significantly affect the overall thickness, nucleation site and morphology of the as-grown WS2 crystals. As shown in Figs. S3 and S4, increasing the precursor quantity and growth period respectively, they will enhance the epitaxial nucleation, and promote the formation of dense WS2 nanosheets. Through conducting WS2 growth under a continuous supply of tungsten source by multiple growth time, we could observe that high density flower-stacked WS2 nanostructures by a layer-by-layer growth are formed. To shed light on the detailed synthesis process of WS2 on carbon cloth, the evolution of WS2 nanostructures was monitored by multiple growth times and synthesized concurrently on the sapphire and carbon cloth. As aforementioned, during the first growth (Fig. 2a–d), planar few-layer WS2 flakes randomly form on the carbon cloth. When tungsten sources continue to supply by multiple growth, initial planar WS2 growth eventually alters to
upward growth, results in layer-by-layer growth flower-stacked WS$_2$ crystals (Fig. 2e and f). The transition growth mode directly demonstrates by the coexistence of 2D WS$_2$ planar flakes and three-dimensional (3D) hierarchical flower-stacked in SEM images. The AFM height images in Fig. 2d and h correspond to the first growth and multiple growth of WS$_2$, also further show the transition growth mode of WS$_2$ from isolated planar monolayer flakes to stacked planar flakes and finally to layer-by-layer hierarchical-oriented flower-stacked nanosheets. As shown in Fig. S5a, the Raman spectrum shows the two typical characteristic peaks of WS$_2$ at 355 cm$^{-1}$ ($E_{2g}$ mode) and at 420 cm$^{-1}$ ($A_{1g}$ mode) for flower-stacked WS$_2$@CC. Besides, the presence of a direct band gap
PL peak indicates the few-layer nature of WS2 and further confirms the layer-by-layer growth mechanism. Fig. S5b shows the obtained samples exhibit the typical X-ray diffraction (XRD) pattern of WS2 crystal phase. Sharp WS2 crystal XRD peaks are detected, indicating large crystalline domain, high crystal quality and high purity for the CVD obtained samples. The elementary mappings of carbon, sulfur and tungsten further confirm the structure of WS2@CC composite (See Fig. S6). Overall, the results demonstrate that the morphology of the as-grown WS2 nanostructures is highly affected by the continuity precursor source supply through controlling the precursor quantity, growth period and the growth times. By optimizing the synthesis process, direct control over the density and morphology can be ultimately achieved, suggesting the high controllability and versatility of this CVD method for practical applications.

To reveal the function mechanism of atomically thin WS2 nanosheets as sulfur/polysulfide physicochemical transformation interfaces in Li–S batteries, cyclic voltammetry (CV) in symmetric cells was further measured with identical pristine few-layer WS2@CC (flower-stacked WS2@CC or CC) interlayer working and reference electrodes in a 1/3 M Li2S6 electrolyte within −1 to 1 V voltage window (See Fig. 3a). The few-layer and flower-stacked WS2@CC electrodes exhibit two distinct reduction peaks at −0.19, −0.50 and −0.07, 0.41 V, respectively and two prominent oxidation peaks at 0.19, 0.50 and 0.07, 0.41 V, respectively whereas CC electrodes without WS2 nanosheets shows broad redox features at 0.18, 0.6, −0.18 and 0.6 V. The two reduction peaks ascribe to the reduction of Li2S to Li2S3/Li2S2 on the working electrode, while the two oxidation peaks correspond to reconstitution of Li2S2 by the oxidation of Li2S/Li2S2 on the working electrode [31]. Therefore, the pair of cathodic and anodic peaks are redox reaction of the symmetric cell. In addition, it is worth to note that redox pair with sharp and narrow peak width exhibits an excellent electrochemical reversibility and facile polysulfide conversion [32,33]. The observed narrower and sharper redox peaks of the few-layer and flower-stacked WS2@CC electrodes than CC electrodes further reveal the enhanced electrochemical reversibility and reaction kinetics enabled by atomically thin layer WS2, suggesting WS2@CC as an effective catalyst for polysulfide conversion.

To further verify the polysulfide adsorption ability of atomically thin layer WS2, a polysulfide adsorption test was performed with 3 mL DOL/DME electrolyte including 2/3 μmol Li2S6 (Fig. 3b). After overnight stirring, the Li2S6 solution with few-layer WS2@CC shows more pale color than that of pristine CC, confirming the strong polysulfide adsorption by atomically thin layer WS2. The results are consistent with previous reported studies on the sulfophilic ability by layered transition metal dichalcogenides [5]. X-ray photoelectron spectroscopy (XPS) was then employed to probe the nature of the intrinsic chemical interaction between adsorbed species and WS2 nanosheets. Fig. 3c shows the fitting spectra of the high resolution XPS of S 2p peaks corresponding to pristine WS2@CC interlayer, few-layer WS2@CC interlayer after Li2S6 absorption test and few-layer WS2@CC interlayer after one cycling. The S 2p core-level spectrum of pristine WS2@CC interlayer shows the typical peaks at 162.8 and 164.0 eV, which are ascribed to the S2− state in WS2. However, the 2p spectra of the few-layer WS2@CC interlayer after Li2S6 absorption display additional four predominant peaks, corresponding to the terminal (S0) sulfur and bridging sulfur atoms of Li2S6, thiosulfate, and polythiosulfate complexes, respectively. The thiosulfate complex peaks at 167.2 and 164.8 eV should arise from the salt-solvent redox reaction between Li2S6 and WS2, while the polythiosulfate complex formed at 169.1 and 170.2 eV, which is originated from further reaction between long chain polysulfide and thiosulfate [5,31]. The redox reaction of Li2S6 to thiosulfate and polythiosulfate is accompanied by an increase in the W oxidation, as shown in Fig. 57. We attribute this upshift of W oxidation to a strong interaction of exposed W site with surrounding sulfur ligand. Interestingly, after the 1st cycling, the polysulfides are nearly absent and a strong signal at 169.4 eV can be observed, which is from the Bis(trifluorometane) sulfonamide lithium salt (LiTFSI) in the electrolyte [18]. The results suggest that almost all the polysulfide species have dissolved and deposited back into cathode. Therefore, in the presence of electric field, polysulfide conversion most likely occurs at the catalytic active edge sites on the atomically-thin WS2 catalyst surface.

To further investigate the function mechanism of WS2 nanoflakes of different layers and morphologies on the electrochemical performance, four different interlayers: pristine separator, bare CC, few-layer WS2@CC and flower-stacked WS2@CC were designed for Li–S battery (Fig. S8). In the electrochemical study, the cathode material was prepared by infusing the commercial sulfur into ketjenblack powder with a high sulfur content of 70% (Fig. S9). To study the role of atomically thin WS2 in catalytic decomposition of Li2S, galvanostatic discharge/charge measurements (Fig. 4a–c and S10) were conducted at a constant current rate of 0.1 C (1 C = 1675 mA g−1). The CC interlayer without WS2 catalyst

Fig. 3. (a) Cyclic voltammetry (CV) of symmetric cells with identical electrodes of carbon cloth (CC) and WS2@CC at scan rate of 0.5 mV s−1. (b) Adsorption tests of CC and WS2@CC with 3 μl of 1/3 M Li2S6 catholyte in 2 ml of 1:1 DOL/DME mixture after midnight stirring. (c) High resolution XPS spectra of S 2p for pristine WS2@CC, few-layer WS2@CC after Li2S6 absorption and few-layer WS2@CC after discharging.
exhibits high potential barrier at about 2.32 V in the initial charging process, suggesting a sluggish activation process with high charge transfer resistance (Fig. 4a). After introducing the few-layer WS₂, the cell demonstrates a voltage jump about 2.30 V during the activation process because of the semiconducting nature of WS₂ [34]. While the charge plateaus after the voltage jump indicate the phase conversion reaction from Li₂S to intermediate Li-polysulfides and finally to sulfur (see Fig. 4b) [34]. Compared with the other interlayers, the few-layer WS₂@CC interlayer exhibits the highest discharge plateaus at 2.34 and 2.08 V, and two lowest charge plateaus between 2.3 and 2.4 V, respectively (Fig. 4a–c and S11). In addition, few-layer WS₂@CC interlayer shows flatter and longer plateaus with a lower polarization. A similar charging phenomenon is observed for the flower-stacked WS₂@CC interlayer with an initial voltage jump at 2.32 V but with a broader activation plateaus, indicating a sluggish activation process with high internal resistance induced by high density nanosheet WS₂ catalyst. Overall, the lower potential barrier and charge-discharge polarization of few-layer WS₂@CC interlayer indicates the effective catalytic effect of few-layer WS₂ towards polysulfide redox kinetics, Li₂S nucleation and deposition, which considerably enhances the sulfur utilization and energy conversion efficiency in the cell [34]. The obtained results are consistent with the CV measurements (see Fig. 4d), where the few-layer WS₂@CC interlayer shows the narrowest redox peaks separation (oxidation peaks at 2.41 and 2.41 V, reduction peaks at 2.34 and 2.02 V) among all the cells. The narrow redox peaks separation of the few-layer WS₂@CC interlayer indicates the low lithiation/delithiation polarization and accelerated polysulfide redox kinetics by atomically thin layer WS₂. Furthermore, the redox peak shifts of few-layer WS₂@CC interlayer cell over the four CV initial cycles are negligible, further suggesting good electrochemical stability (see Fig. S11).

The proposed atomically thin layer active polysulfide catalysts interface also enables the stable cycling performance of Li–S batteries. Fig. 4e presents the cycling performance of the cells with several interlayers. The few-layer WS₂@CC interlayer delivers a much higher initial discharge/charge capacity of 1198/1169 mAh g⁻¹ at 0.2 C and nearly 100% coulombic efficiency over 100 cycles, accompanied by a good stability with a capacity retention of 86.71% for 100 discharge/charge cycles. While for the flower-stacked WS₂@CC interlayer, a lower initial discharge/charge capacity of 998/960 mAh g⁻¹ and capacity retention of 78.03% are observed. The worse cycling performance of flower-stacked WS₂@CC interlayer may be due to the extremely strong polysulfides absorption and physicochemical transformation by high density atomically thin layer WS₂ that lead to the active surface passivation by aggregated insoluble sulfur species, and thus to the low sulfur utilization. In contrast, the cells with only PP separator or CC interlayer exhibit much lower initial discharge/charge capacities of 691/698 and 1157/1027, respectively and show capacity retention of 61.5% and 69.81% respectively after 100 cycles. The results imply that the few-layer WS₂@CC interface enables high sulfur utilization and cyclability due to the effective electrocatalytic activity and physicochemical adsorption of the atomically thin WS₂.

To further elucidate the role of atomically thin layer WS₂@CC on accelerating sulfur redox kinetics, the rate capability of the four cells were then evaluated at different rates from 0.1 to 2 C (see Fig. 4f). The few-layer WS₂@CC interlayer shows high average
capacities of 1366, 1219, 1117, 981 mAh g\(^{-1}\) at 0.1, 0.2, 0.5, and 1 C respectively, much better than the other three cell configurations. Even at a higher rate of 2.0 C, a high reversible capacity of 793 mAh g\(^{-1}\) can be achieved. And the capacity is able to recover to a high value of 1226 mAh g\(^{-1}\) when the rate returns to 0.1 C, further showing the excellent redox stability of the few-layer WS\(_2\)@CC interlayer. Such outstanding rate capability is superior to most of other transition metal sulfide-based materials reported previously for Li–S battery, as shown in Fig. S12. It is worth to note that the flower-stacked WS\(_2\)@CC interlayer delivers a high discharge capacity of 1280 mAh g\(^{-1}\) at 0.1 C, but a lower discharge capacity of 1065, 969, 852, and 698 mAh g\(^{-1}\) at 0.2, 0.5, 1 and 2 C respectively, suggesting the slower reaction kinetics and poorer stability of the flower-stacked WS\(_2\)@CC interlayer cell at higher current rate. In contrast, the typical cells with and without CC interlayer show lower average discharge capacities and poorer stability under the same conditions. The superb rate performance of the few-layer WS\(_2\)@CC is attributed to the enhanced sulfur redox kinetics by high aspect ratio of catalytic active edge sites of few-layer WS\(_2\)@CC interface among electrolyte/electrode. Moreover, the discharge/charge profiles at various rates of the few-layer WS\(_2\)@CC show two typical discharge plateaus and long charge plateaus (Fig. S13), further implying that the few-layer WS\(_2\)@CC interlayer cell can deliver high performance as well as at high current rate, and the redox conversion between sulfur and Li\(_2\)S at various rate are highly reversible. Long term cycling performance after rate performance measurement was further investigated at a rate of 0.5 C (Fig. 4g). Remarkably, the few-layer WS\(_2\) interlayer still exhibits a high capacity of 870 mAh g\(^{-1}\) after 300 cycles, showing a high capacity retention of 77.7% (0.07% capacity decay per cycle), in contrast to the flower-stacked WS\(_2\) interlayer cell with a lower capacity of 513 mAh g\(^{-1}\) and capacity retention of 60.42% (0.13% capacity decay per cycle) after 300 cycles. In short, the results imply that although the cell with WS\(_2\) catalyst on CC interlayer can enhance the polysulfide redox kinetics and increase the sulfur utilization, but interlayer with overmuch catalyst may induce a large amount of Li\(_2\)S precipitation on the interlayer, which in turn causes the passivation of interlayer and loss of electronic contact with S cathode, leading to low sulfur utilization [18].

To further investigate the electrochemical kinetics of the few-layer and flower-stacked WS\(_2\)@CC interlayer cell, the electrochemical impedance spectroscopy (EIS) measurement for few-layer and flower-stacked WS\(_2\)@CC interlayer before and after CV cycles were performed (Figure S14, 4h and S15). Overall, the cell with few-layer WS\(_2\) interlayer exhibits a much smaller charge-transfer resistance than the bare cell before and after cycling, suggesting that the internal resistance of the Li–S battery is reduced by introducing few-layer WS\(_2\) catalyst. The Nyquist plots of the pristine flower-stacked WS\(_2\)@CC interlayer shows higher charge transfer resistance (45 Ω) than that of the few-layer WS\(_2\)@CC interlayer (17 Ω), which can be explained by the increase of internal resistance of the cell by high-density atomically thin layer WS\(_2\) catalysts (Fig. S14). After four cycles, the few-layer WS\(_2\)@CC interlayer cell still exhibits a lower charge transfer resistance (14 Ω) as that of flower-stacked WS\(_2\) interlayer cell, while an additional resistance attributed by the solid-state of the accumulated lithium sulfide can be observed with the flower-stacked WS\(_2\)@CC interlayer cell (Fig. 4h and S15) [35]. The cycling performance of sulfur cathode with a higher sulfur loading were further compared by using few-layer WS\(_2\)@CC functional interlayer as shown in Fig. S16. The cell with high sulfur loading of 2.2 mg cm\(^{-2}\) delivers initial capacities of 1362 mAh g\(^{-1}\) at 0.1 C and an approximate capacity of 856 mAh g\(^{-1}\) was retained after 100 cycles at 0.5 C, corresponding to a capacity retention of 89.22%. It implies that the functional WS\(_2\)@CC interlayer can enable a high sulfur loading cathode with stable cycling performance and is highly potential for high energy density Li–S battery.

The catalytic ability of WS\(_2\) is determined by the polysulfide accessibility to the active catalytic sites, while the density and morphology of the catalyst, is of paramount significance to affect the catalytic ability and thus the electrochemical stability [5,24]. To further elucidate the effects of catalyst morphology and density of the interface on the electrochemical performance, ex-situ SEM imaging have been conducted on the few-layer WS\(_2\)@CC interlayer and flower-stacked WS\(_2\)@CC interlayer before and after discharge-charge cycles. Fig. 5a–d shows the ex-situ SEM images of few-layer and flower-stacked WS\(_2\)@CC interlayer before and after washing with ethanol. Ethanol was employed to remove liquid polysulfides on the interlayer surface. No obvious solid precipitates are observed in the ethanol with few layer WS\(_2\)@CC (see Fig. S17 and 60 min). Besides, it is clear that few-layer WS\(_2\)@CC interlayer surface before washing is almost smooth with few aggregated solid sulfur species (Fig. 5a). After removing the surface polysulfide species, the few-layer WS\(_2\)@CC shows the same few-layer WS\(_2\) flakes morphology as the pristine one (Fig. 5b). In contrast, the cycled flower-stacked WS\(_2\)@CC interlayer shows serious solid sulfur species aggregation on the CC (Fig. 5c). After washed with ethanol, the flower-stacked WS\(_2\) shows corrugated morphology similar to the pristine one, clearly observed (Fig. 5d). These results indicate the extremely strong sulfur/sulfides absorption and chemical transformation by hierarchical flower-stacked WS\(_2\), causing nucleation and aggregation of solid sulfur/polysulfides on the interface. With continuous physicochemical transformation reaction on the interlayer surface, the severe aggregation of solid polysulfide intermediates and corrugated WS\(_2\) layer could depress the mass transportation and induce loss of electronic contact with sulfur cathode and formation of a “dead sulfur” layer on the interface, resulting in low sulfur utilization [18]. This will further reduce the charge transfer efficiency and result in poor cycling stability and lower capacities at a higher current density. In contrast, the almost smooth surface of few-layer WS\(_2\)@CC interlayer and XPS analysis after the 1st cycle indicates that almost most of the sulfur species have dissolved and reacted back into the catholyte. The results further confirm the effective sulfur/Li-polysulfide physicochemical transformation interface by few-layer WS\(_2\) towards polysulfide conversion.

According to our experimental results, the enhanced electrochemical performance of the few-layer WS\(_2\)@CC interlayer cell can be readily explained as followed (See Fig. 5e). Firstly, the inherent sulfophilic property of WS\(_2\) leads to superb Li-polysulfides absorption on its surface and hence regulating the polysulfides diffusion. Secondly, the intrinsic electrocatalytic properties of WS\(_2\) reduce the sulfur redox reaction barrier, promote the reversible conversion of active sulfur and hence improve the specific retention capacity of the cell. Thirdly, the high aspect ratio of catalytic active edge sites of the CVD-grown atomically thin layer WS\(_2\) allows large accessible catalytic active surface and hence promote the effective sulfur/Li-polysulfide redox conversion during electrochemical cycling and regulate the precipitation of insoluble sulfur species. However, the overmuch catalytic active edge sites of hierarchical flower-stacked WS\(_2\) exhibit extremely strong sulfur/polysulfide absorption and high sulfur conversion rate, causing the severe precipitation of sulfur species on interlayer, and raising the sulfur redox conversion barrier (See Fig. 5f). The continuous precipitation of the solid sulfur species will result in corrugated and stacked WS\(_2\) nanosheets, loss of electronic contact with the sulfur cathode and lead to deformed rate performance and poor cycling stability as compared to the cell with few-layer WS\(_2\)@CC. Therefore, designing the 2D CVD-based active materials with controllable density and morphology is important to design an optimized physicochemical interface with high conductivity, superb electrocatalytic and strong chemisorption.
3. Conclusion

In summary, we have developed a novel strategy for controllable synthesis of large-area and atomically thin WS2 nanosheets on carbon cloth via a low-pressure CVD method, which can be used as a multifunctional interlayer for Li–S battery. The formation mechanism of atomically thin WS2 nanosheet on carbon cloth is investigated. Benefiting from the layer-by-layer growth mechanism by our growth process, the obtained few-layer WS2@CC with abundant atomically thin fresh edges shows strong anchoring effect for polysulfides, high conductivity, and excellent catalytic properties. As a result, the few-layer WS2@CC interlayer cell exhibits excellent rate capability, and good cycling stability. Our results further reveal that hierarchical flower-stacked WS2@CC with abundant exposed catalytic edges shows extremely strong polysulfide adsorption and high conversion rate to low order solid species, which leads to severe precipitation of sulfur species on interlayer and results in low electrochemical stability and poor rate capability. Our work demonstrates CVD as a good alternative for large-scale atomically thin layer TMDCs on other substrate and open up an effective way of utilizing TMDCs nanosheets on conductive matrix for energy storage applications.

Author contribution

Mei Er Pam: Conceptualization, Methodology, Experiment; Shaozhuang Huang: Data analyzing, Writing- Original draft preparation; Shuang Fan: Visualization, Investigation. Dechao Geng: Writing- Reviewing and Analysing; Dezhi Kong: Experiments; Meng Ding: Experiments, Investigation. Lu Guo: Experiments, Investigation; Lay Kee Ang: Computation, Validation.: Hui Ying Yang: Supervision, Writing- Reviewing and Editing.

Declaration of competing interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

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