

Article

In Situ Hybridization Strategy Constructs Heterogeneous Interfaces to Form Electronically Modulated MoS₂/FeS₂ as the Anode for High-Performance Lithium-Ion Storage

Dazhi Li ¹, Changlong Sun ¹, Zeqing Miao ², Kesheng Gao ³, Zeyang Li ¹, Wei Sun ¹, Shengjing Guan ⁴, Xiaofei Qu ^{1,*} and Zhenjiang Li ^{1,*}

¹ College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China; wslidazhi@163.com (D.L.); changlongsun@qust.edu.cn (C.S.); m2043714499@126.com (Z.L.); weisun098@163.com (W.S.)

² College of Electromechanical Engineering, Qingdao University of Science and Technology, Qingdao 266061, China; happymiaozeqing@163.com

³ Songshan Lake Materials Laboratory, Dongguan 523808, China; gaokesheng2023@163.com

⁴ School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255049, China; guanshengjing2022@126.com

* Correspondence: quxiaofei@qust.edu.cn (X.Q.); zhenjiangli@qust.edu.cn (Z.L.)

Abstract: The interfacial effect is important for anodes of transition metal dichalcogenides (TMDs) to achieve superior lithium-ion storage performance. In this paper, a MoS₂/FeS₂ heterojunction is synthesized by a simple hydrothermal reaction to construct the interface effect, and the heterostructure introduces an inherent electric field that accelerates the de-embedding process of lithium ions, improves the electron transfer capability, and effectively mitigates volume expansion. XPS analysis confirms evident chemical interaction between MoS₂ and FeS₂ via an interfacial covalent bond (Mo–S–Fe). This MoS₂/FeS₂ anode shows a distinct interfacial effect for efficient interatomic electron migration. The electrochemical performance demonstrated that the discharge capacity can reach up to 1217.8 mA h g^{−1} at 0.1 A g^{−1} after 200 cycles, with a capacity retention rate of 72.9%. After 2000 cycles, the capacity retention is about 61.6% at 1.0 A g^{−1}, and the discharge capacity can still reach 638.9 mA h g^{−1}. Electrochemical kinetic analysis indicated an enhanced pseudocapacitance contribution and that the MoS₂/FeS₂ had sufficient adsorption of lithium ions. This paper therefore argues that this interfacial engineering is an effective solution for designing sulfide-based anodes with good electrochemical properties.

Keywords: MoS₂/FeS₂; heterojunction; interfacial effect; electronically modulate



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1. Introduction

Lithium-ion batteries (LIBs) garner extensive attention as energy storage devices, owing to their stable voltage platform and outstanding energy density [1,2]. However, the unsatisfactory discharge capacity, charging time, and cycle life of the graphite anode seriously limit the widespread application of LIBs [3]. Therefore, substitutable anodes with higher structure stability and practical capacity have been widely sought after in the last few years [4,5]. TMDs generally have the advantages of higher theoretical capacity and lower reaction potential, which makes them a kind of anode material with excellent prospects for development. Among them, MoS₂ has received extensive attention from researchers as an anode material for lithium-ion batteries with prospects for industrial applications due to its high theoretical capacity (670 mA h g^{−1}) and simple preparation process. According to a previous report, the high capacity of MoS₂ is achieved via lithium-ion insertion (MoS₂ + xLi⁺ + xe[−] ↔ Li_xMoS₂) and conversion reaction (Li_xMoS₂ + (4 − x) Li⁺ + (4 − x) e[−] ↔ Mo + 2Li₂S) [6]. The formation of Li₂S, however, results in the dissolution of Li₂S into the liquid electrolyte and disrupts the electrical

contact between the TMDs and the current collector. Consequently, this phenomenon significantly compromises cycling stability and induces excessive capacity decay during cycling. The interstitial of the MoS₂ lattice can be adjusted via structural design and phase transition engineering to control the amount of lithium-ion insertion, thus realizing the purpose of controlling the capacity. Meanwhile, the good structural stability guarantees its stable lithium-ion storage performance [7]. Therefore, MoS₂-based anodes attract significant attention for high-efficiency lithium-ion storage, with potential application prospects [8]. However, the MoS₂-based anode still suffers from low electronic conductivity, unsatisfied lithium-ion transport kinetics, and large volume expansion. As a result, the MoS₂-based anode exhibits limited capability under the long-term charge/discharge process and rate capability. Moreover, the solid electrolyte interphase (SEI) film can give rise to “dead lithium” and unstable Coulombic efficiency (CE) [9].

To address the above issues, morphological modification, structural optimization, and vacancy design are adopted [10]. Jiao et al. reported an outer-wall-free hollow nanotube composed of intersecting small-sized MoS₂ nanosheets. The metal nanotubes are hierarchical, hollow, and have a porous arrangement, which aid electrolyte transport and diffusion, avoid the re-stacking of 2D nanosheets, and shorten the ionic diffusion path, thus maintaining the stability of electrochemical cycling and improving the rate performance [11]. Chen et al. prepared nanoflowers crossed by MoS₂-MnS heterojunction nanosheets, confirming the phenomenon of sequential phase transition of MoS₂ and MnS in Li/Na storage, and electrochemical reaction kinetics and ex situ tests confirmed the roles of phase transition and interfacial engineering in the reaction [8]. Bai et al. prepared 1T-MoS₂/C by hydrothermal reaction and confirmed that 1T phase-transformed MoS₂ has a high conductivity characteristic due to the nature of the metallic phase, which facilitates rapid transport of lithium ions and electrons and thus improves the electrochemical performance [12]. However, the design reported above mainly focuses on the exterior morphology control, electrochemical conductivity, and reaction kinetics of the reported MoS₂ anode, which are inferior to those of the graphite anode, and the volume change is not fully released during the electrochemical reaction. It is unclear whether good adsorption ability toward lithium ions, good conductivity for charge transfer, and conversion kinetics are achieved simultaneously in those reported MoS₂ anodes. Moreover, the inadequate interfacial interaction in MoS₂-based anodes further influences the electrochemical conductivity and reaction kinetics [13]. Therefore, the reported lithium-ion storage performance of MoS₂ anodes is inferior, and constructing a multi-advantage MoS₂ anode is highly required.

An interfacial engineering strategy is considered as an effective route to accelerate the charge transfer kinetics, adsorption, and intercalation ability of lithium-ion batteries via a strong interfacial bonding effect at the interface to achieve high-performance lithium-ion storage [14,15]. Moreover, the interfacial design can create sufficient active sites at the interface, which is significant for excellent lithium-ion storage capacity. However, an interfacial engineering strategy has rarely been reported to construct MoS₂ anodes, and the internal mechanism of interfacial interaction remains unclear. FeS₂ has the advantages of high chemical stability and high theoretical capacity (890 mA h g⁻¹), which makes it a satisfactory candidate for constructing MoS₂-based composites [16]. Its incorporation enhances the stability of the material and improves the ionic conductivity and kinetic behavior of the MoS₂ anode. Sufficient interfacial contact between MoS₂ and FeS₂ would provide abundant interfacial sites to adsorb lithium ions. After the interfacial design, the interfacial region can adsorb a great deal of lithium ions and guarantee high electron transfer efficiency [17]. As a result, the lithium-ion storage capacity and reaction kinetics of MoS₂/FeS₂ are prominently enhanced. However, constructing interfacial regions and enhancing the lithium-ion storage capacity of MoS₂/FeS₂ have seldom been researched so far.

Herein, phase transition engineering and interfacial engineering strategies are adopted to construct the MoS₂/FeS₂ anode. The interfacial covalent bond (Mo–S–Fe) is confirmed by TEM and XPS analyses. Enhanced pseudocapacitance contribution and improved charge transfer efficiency are further revealed by electrochemical kinetic analysis. Consequently,

this well-designed $\text{MoS}_2/\text{FeS}_2$ anode demonstrates excellent cycling capacity, rate capability, and cycling life in half cells. This interfacial design strategy can enhance lithium-ion storage performance via the combined impact of surface sulfide and interfacial interaction, as well as provide a deeper understanding of re-designing traditional metal sulfide anodes [18].

2. Results

$\text{MoS}_2/\text{FeS}_2$ nanoflower spheres are synthesized by a simple and low-cost hydrothermal reaction. More details about the synthetic process can be found in the Materials and Methods section. During the hydrothermal reaction, the transition from 2H- MoS_2 to 1T- MoS_2 in some MoS_2 is induced by a change in coordination modes between certain molybdenum and sulfur atoms. In Figure 1a, the XRD results reveal that the diffraction peaks of pure MoS_2 correspond to MoS_2 (PDF#37-1492), and the diffraction peaks of pure FeS_2 correspond to FeS_2 (PDF#65-3321). For $\text{MoS}_2/\text{FeS}_2$, the characteristic peaks at 14.38° , 39.54° , and 49.79° correspond to the (002), (103), and (105) planes of MoS_2 , and the characteristic peaks at 33.03° , 37.07° , 47.41° , and 56.26° correspond to the (200), (210), (220), and (311) planes of FeS_2 . In addition to this, the diffraction peak appearing at about 9° is widely regarded as a characteristic peak of 1T-phase MoS_2 , obtained by the transformation of part of the 2H-phase MoS_2 during heterojunction formation [19–21]. The XRD results reveal that the hydrothermal reaction successfully constructed $\text{MoS}_2/\text{FeS}_2$ nanoparticles. SEM is performed to demonstrate the microstructure morphology before and after hydrothermal reaction (Figure S1). The SEM results (Figure 1b–d) confirm that the $\text{MoS}_2/\text{FeS}_2$ nanoflower spheres are composed of intercrossed small-sized nanosheets, with an average dimension of around 200 nm. The morphology of pure MoS_2 is irregular particles, and pure FeS_2 is a plate strip nanosheet (Figure S2). The nanoflower spheres exhibit significantly enlarged specific surface area, facilitating the presence of more active sites and promoting the adsorption and rapid migration of lithium ions. Moreover, interlocking nanosheets contribute to maintaining the structural stability of the material. The rough surface of $\text{MoS}_2/\text{FeS}_2$ nanoflower spheres is confirmed, and the rough surface and stable chemical characteristics can improve the reversible conversion kinetics and lithium-ion adsorption capacity of $\text{MoS}_2/\text{FeS}_2$ anodes.

TEM is conducted to demonstrate the presence of an interfacial structure between MoS_2 and FeS_2 . In Figure 1e, the $\text{MoS}_2/\text{FeS}_2$ nanoflower spheres are clearly visible with irregular ball-like morphology in the low-magnification TEM image, and the rough surface is crucial for interfacial interaction and lithium-ion storage. The size of the grains measures approximately 200 nm, which aligns with the findings from Figure 1d in the SEM analysis. In Figure 1f, the presence of distinct boundaries between the MoS_2 and FeS_2 lattice fringes indicates simultaneous execution of the vulcanization process during hydrothermal reaction [22]. As marked by the orange rectangular box, distinct heterointerface structure regions exist between MoS_2 and FeS_2 , and this sufficient heterointerface structure shows efficient interatomic electron migration via a covalent chemical bond interaction to improve interfacial charge transfer kinetics and lithium-ion storage performance. The lattice spacing of about 0.27 nm in the figure is the (200) plane of FeS_2 , and the lattice spacing of 0.62 nm is the (002) plane of MoS_2 . The intact and distinct lattices both of MoS_2 and FeS_2 indicate that the crystallinity of $\text{MoS}_2/\text{FeS}_2$ obtained through hydrothermal reaction is excellent (Figure 1g,h). The corresponding Selected Area Electron Diffraction (SAED) further proves the existence of MoS_2 and FeS_2 (Figure S3). Thus, strong electrostatic attraction is formed via MoS_2 , and FeS_2 is generated simultaneously after a hydrothermal reaction. The reconstructed interfacial layer can offer sufficient active reaction sites for lithium-ion adsorption, and it is beneficial for high electronic conductivity and fast electrochemical reaction kinetics [23]. The elemental mapping analysis (Figure 1i–l) shows the rectangular distribution of Mo (green), Fe (red), and S (blue) in $\text{MoS}_2/\text{FeS}_2$. The intimate contact interface between MoS_2 and FeS_2 significantly optimizes the lithium-ion transport path and enhances lithium-ion storage performance [24].

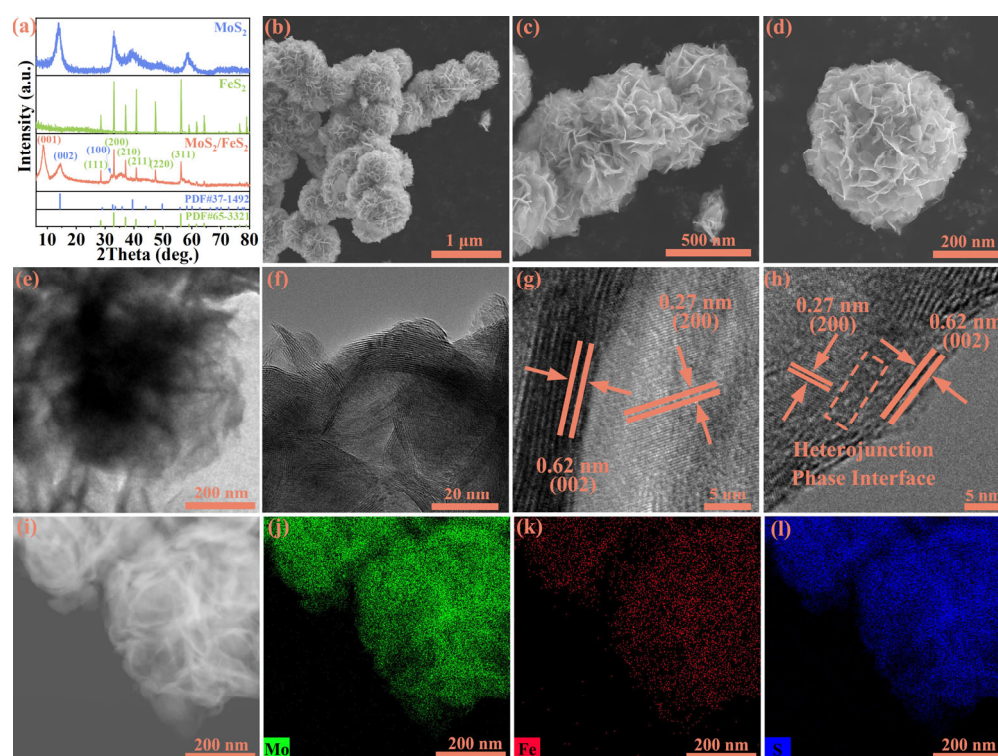


Figure 1. (a) XRD patterns of MoS₂/FeS₂, pure MoS₂, and FeS₂. (b–d) SEM of MoS₂/FeS₂ nanoflower spheres. (e–h) TEM and HRTEM of MoS₂/FeS₂ nanoflower spheres, respectively. (i–l) TEM (inset) and elemental mapping analysis of Mo, Fe, and S in MoS₂/FeS₂ nanoflower spheres, respectively.

The interfacial interaction and chemical composition of MoS₂/FeS₂, pure MoS₂, and FeS₂ are further analyzed by XPS. Indeed, Mo 3d, Fe 2p, and S 2p are detected in the survey spectrum of MoS₂/FeS₂ (Figure 2a). Only Mo 3d and S 2p are detected in the survey spectrum of MoS₂. Similarly, Mo 3d is not detected in the survey spectrum of FeS₂. For FeS₂, the peak at 225.6 eV in the survey spectrum is S 2s instead of Mo 3d [25]. In Figure 2b, the high-resolution Mo 3d spectra of MoS₂/FeS₂ show that the peaks at 228.4 and 231.6 eV belong to Mo 3d_{5/2} and Mo 3d_{3/2} of 1T-MoS₂, respectively, while the peaks in the 2H phase are located at 229.4 and 232.6 eV, respectively [26]. Compared with pure MoS₂, the peak of MoS₂/FeS₂ is shifted toward low binding energy, and distinct electrostatic attraction is formed with the formation of an efficient electron transport path [18]. The good electronic conductivity of MoS₂/FeS₂ is favorable for high reaction kinetics. Therefore, this result shows the evident chemical interaction and strong imbalanced charge distribution between MoS₂ and FeS₂, and the distinct interfacial contact provides sufficient interfacial sites for lithium-ion storage [27]. The chemical state of Fe in MoS₂/FeS₂ is further analyzed. In Figure 2c, the high-resolution Fe 2p spectrum can be deconvoluted to the Fe–S bond (Fe 2p_{3/2} and Fe 2p_{1/2}) at 707.4 and 720.2 eV, respectively. In addition, the high-resolution Fe 2p spectrum also exhibits an obvious peak of Fe combined with O with the formation of a Fe–O bond at 709.2 and 722.2 eV, which is widely regarded as unavoidable oxidation of the lesser samples [28]. Compared to MoS₂/FeS₂ with pure FeS₂, a higher binding energy shift for the Fe–S bond is clearly observed.

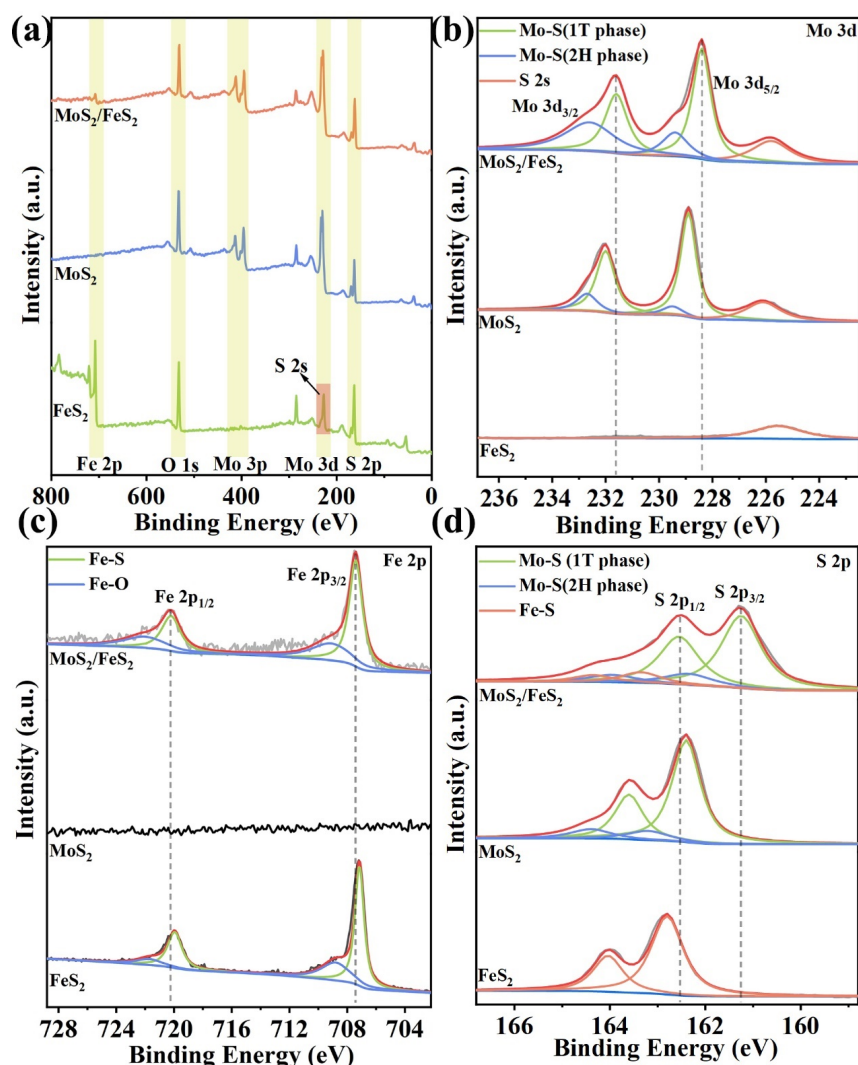


Figure 2. XPS of (a) survey spectra, (b) Mo 3d, (c) Fe 2p, and (d) S 2s of MoS₂/FeS₂, pure MoS₂, and FeS₂, respectively.

Similarly, the S 2p high-resolution spectrum of MoS₂/FeS₂ (Figure 2d) exhibits two distinct sets of peaks associated with the Mo–S bond. Specifically, the peaks observed at 161.3 eV and 162.6 eV correspond to the 1T phase, while those detected at 162.4 eV and 164.0 eV are indicative of the presence of the 2H phase. In addition, the remaining set of peaks belonging to Fe–S can be deconvoluted to 163.4 eV and 164.4 eV, respectively. Compared with pure MoS₂ and pure FeS₂, all the peaks corresponding to Mo–S bonds move to the direction of low binding energy, while all the peaks corresponding to Fe–S bonds move to the direction of high binding energy, and this phenomenon fully confirms the process of electron transfer from FeS₂ to MoS₂. Widespread Mo–S bonds and Fe–S in MoS₂/FeS₂ provide good electron conductivity and Faradaic pseudocapacitance. Furthermore, the heterogeneous interface leads to a lopsided charge distribution near the interface, and the corresponding interfacial interaction can boost the electron transfer reactions and offer sufficient active reaction sites for lithium-ion storage. The changes in the Mo–S and Fe–S binding energies demonstrate the interaction between MoS₂ and FeS₂, which further enhances the adsorption of lithium ions at the interface. Therefore, the XPS analysis confirms that MoS₂ and FeS₂ were formed synchronously during the hydrothermal reaction. The imbalanced charge distribution occurring in the interfacial region can create an inner electric field [29], and the partial phase transition produces 1T-MoS₂ with metallic conductor properties favoring the electronic conductivity of the

MoS₂/FeS₂. Moreover, the heterogeneous interface demonstrates strong covalent chemical bond interaction between the MoS₂ layer and FeS₂ layer, which is important for interfacial lithium-ion storage. The XPS analysis unambiguously shows that heterogeneous interfaces are formed through the simultaneous generation of the hydrothermal reaction MoS₂ and FeS₂ and that heterogeneous interfaces enhance interfacial charge migration for lithium-ion storage.

The lithium-ion storage performance of the MoS₂/FeS₂ anode is evaluated by standard half-cell tests. As shown in Figure 3a, the MoS₂/FeS₂ anode can be clearly observed within the circle of the first cycle curve. There are two reduction peaks at 0.50 V and 1.26 V, which correspond to the formation of the SEI layer and the conversion of MoS₂/FeS₂ to Mo, Fe, and Li₂S, respectively. In the next cycle, the reduction peak moves to around 1.42 V, and a new peak appears at 2.05 V due to the irreversible phase transition formed by S and Li₂S. There is an oxidation peak at 1.81 V, which corresponds to the reaction of Mo, Fe, and Li₂S to form Li_xMoS₂ and Li_xFeS₂. There is another oxidation peak at 2.28 V, corresponding to the decomposition of Li_xMoS₂ and Li_xFeS₂ to MoS₂ and FeS₂. As the cycle progresses, the oxidation peak located at 2.28 V undergoes a small shift towards higher voltages. This phenomenon is thought to result from the potential deviation from the equilibrium potential caused by irreversible resistance [30]. The reduction peak at 0.50 V fades away in the next cycle due to the SEI layer forming an anodic surface coating, and the other peaks do not change much, indicating good electrochemical reversibility. The overlapped CV curves imply its outstanding structure and cycling stability. This result is related to efficient covalent bond interaction at the interface of MoS₂/FeS₂. Figure 3b shows the cycling performance and Coulombic efficiency of MoS₂/FeS₂, pure MoS₂, and FeS₂ at 0.1 A g^{−1}. For MoS₂/FeS₂, the first discharge-specific capacity is about 1670.6 mA h g^{−1}, and the initial Coulombic efficiency (ICE) is ~79.63%. In comparison, the ICE of MoS₂ is only 73.99%, with a first discharge-specific capacity of 1151.3 mA h g^{−1}, and an ICE of FeS₂ (81.65%); although slightly higher than that of MoS₂/FeS₂, it has a first discharge-specific capacity of only 1080.9 mA h g^{−1}. Unlike conventional conversion reaction anodes with major structure invalidation and capacity loss, the interfacial engineering strategy can accelerate charge transfer kinetics, adsorption, and intercalation ability. For the MoS₂/FeS₂ anode, the discharge capacity can stabilize at 1217.8 mA h g^{−1}, and the Coulombic efficiency can be maintained at about 100% after 200 cycles. In contrast, the discharge capacity of the MoS₂ negative electrode decreased continuously at a current density of 0.1 A g^{−1} and was only 463.1 mA h g^{−1} after 200 cycles. Although the discharge capacity of the FeS₂ negative electrode recovered during the cycling process, it still decreased to 672.3 mA h g^{−1} after 200 cycles, which was much lower than that of the MoS₂/FeS₂ negative electrode. In Figure 3c, the GCD curves show superior electrochemical stability and minimum polarization of the MoS₂/FeS₂ anode compared to the pure MoS₂ and FeS₂ anodes (Figure S4). This is ascribed to the enhanced interfacial interaction and efficient interatomic electron migration caused by distinct heterointerface structures and covalent chemical bond design [31]. In Figure 3d, the trend regarding discharge capacity change is precisely analyzed by capacity retention. Selecting the first discharge capacity as a check, the discharge capacity retentions of the MoS₂/FeS₂ anode are calculated. Meanwhile, the discharge capacity retentions of the pure MoS₂ and FeS₂ anodes are also calculated (Figure S5). After 200 cycles, the capacity retention rate of the MoS₂/FeS₂ anode is 72.9%, which is much higher than the capacity retention rate of 40.22% for the MoS₂ anode and 62.2% for the FeS₂ anode. By comparison, the MoS₂/FeS₂ anode exhibits higher and stabler capacity retention, which indicates a more stable lithium-ion storage reaction.

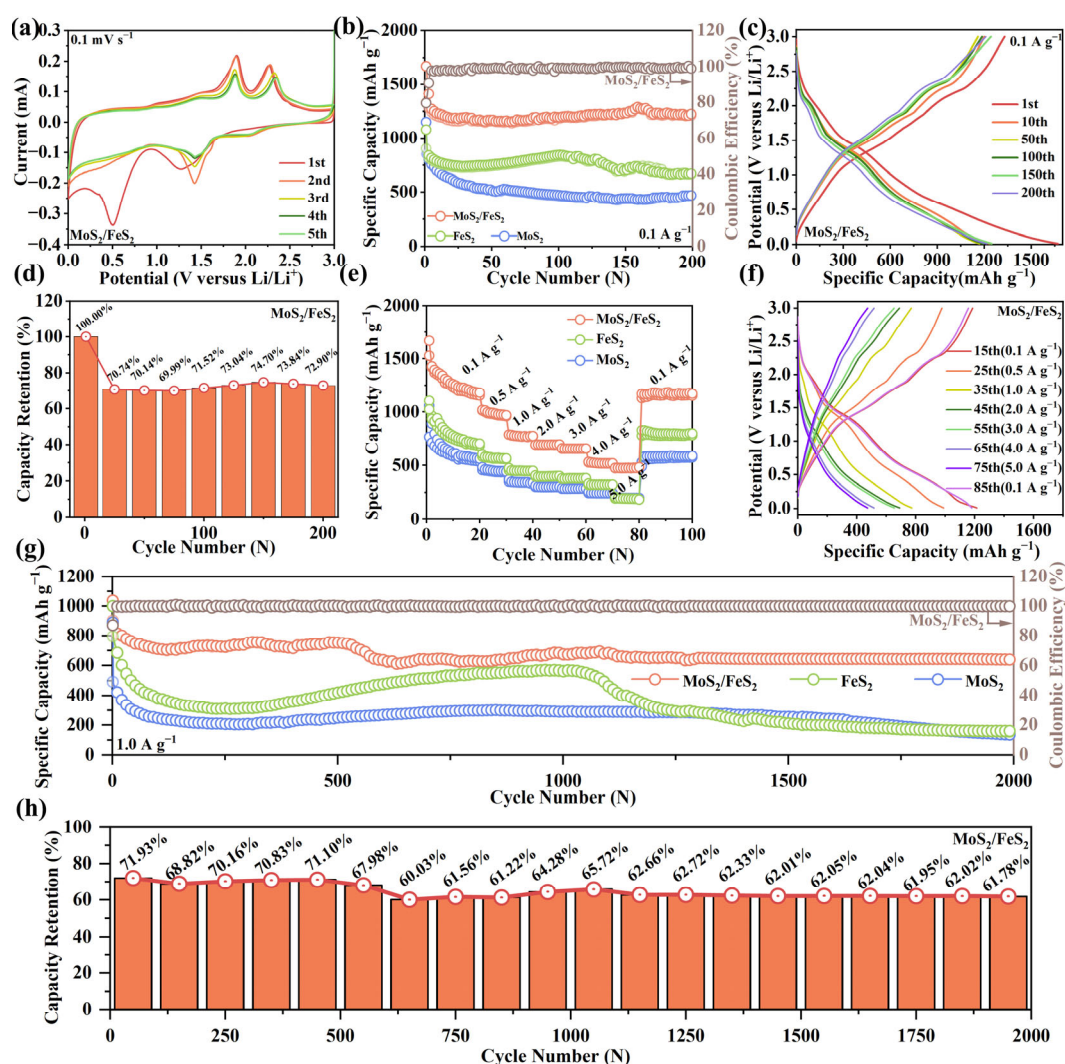


Figure 3. (a) Cyclic voltammetry (CV) curves at 0.1 mV s⁻¹. (b) Cycling performance of MoS₂/FeS₂, pure MoS₂, and FeS₂ at 0.1 A g⁻¹, and Coulombic efficiency of MoS₂/FeS₂ at 0.1 A g⁻¹. (c) Galvanostatic charge–discharge (GCD) curves and (d) capacity retention of MoS₂/FeS₂ at 0.1 A g⁻¹. (e) Rate capability and (f) corresponding GCD curves from 0.1 to 5.0 A g⁻¹. (g) Long cycling performance and (h) capacity retention of MoS₂/FeS₂ at 1.0 A g⁻¹.

In Figure 3e, the rate capability values of the pure MoS₂, FeS₂, and MoS₂/FeS₂ anodes are further analyzed from 0.1 to 5.0 A g⁻¹. For the MoS₂/FeS₂ anode, reversible capacity of 1180.2, 967.3, 773.6, 694.3, 656.5, and 517.1 mA h g⁻¹ can be achieved at 0.1, 0.5, 1.0, 2.0, 3.0, and 4.0 A g⁻¹, respectively. Notably, even at 5.0 A g⁻¹, the discharge capacity can be maintained at 480.9 mA h g⁻¹. At 0.1 A g⁻¹, the discharge capacity can return to 1169.5 mA h g⁻¹ after 80 cycles, showing good structural tolerance and electrochemical reversibility. Rate capability analysis shows good lithium-ion adsorption and diffusion kinetics of the MoS₂/FeS₂ anode. In addition, the rate capability values of the pure MoS₂ and FeS₂ anodes are much inferior to that of the MoS₂/FeS₂ anode. This result can be ascribed to the decomposition of the irreversible electrolytes at low potential and volume expansion during the repeated lithium-ion storage reaction. The excellent reversibility of the half cell is further confirmed by the corresponding GCD curves at different current densities in Figure 3f. The enhanced electronic conductivity and lithium-ion transfer kinetics contribute to its remarkable rate capability.

In Figure 3g, the long cycling capacity is further evaluated at 1.0 A g⁻¹. The pure MoS₂ anode shows the highest discharge capacity as the first cycle progresses, and then

the discharge capacity starts to decline. For pure FeS₂, the discharge capacity reduces to 136.6 mA h g^{−1} after 2000 cycles. For FeS₂, the discharge capacity of 1000.5 mA h g^{−1} for the first cycle is essentially the same as that of MoS₂/FeS₂, but the capacity decays rapidly as the cycle progresses. Although the discharge capacity rebounded at 500–1000 cycles, it slowly decayed in the subsequent cycles and dropped to 158.6 mA h g^{−1} after 2000 cycles. Compared with pure MoS₂ and FeS₂ anodes, the MoS₂/FeS₂ anode displays outstanding cycle durability at 1.0 A g^{−1}. For the MoS₂/FeS₂ anode, the first discharge capacity is about 1037.2 mA h g^{−1}, and the first charge capacity is 903.7 mA h g^{−1}, with a high ICE of 87.13%, which is much higher than that of 55.31% for the MoS₂ anode and 79.47% for the FeS₂ anode. The discharge capacity is maintained at 638.9 mA h g^{−1}, and the Coulombic efficiency stabilizes at about 100% after 2000 cycles. In Figure 3h, capacity retention analysis is performed to refine the discharge capacity fluctuation of the MoS₂/FeS₂ anode, and the capacity retention analysis of the pure MoS₂ and FeS₂ anodes is also calculated (Figure S6). At a current density of 1.0 A g^{−1}, the capacity retention of MoS₂/FeS₂ is at a high level, and, after nearly 2000 cycles, the capacity retention of MoS₂/FeS₂ is still 61.78%. The capacity retention of MoS₂ and FeS₂ stays at a low level, 16.33% and 15.89%, respectively, after nearly 2000 cycles. Compared with the pure MoS₂ and FeS₂ anodes, the cycling durability of MoS₂/FeS₂ is the highest. The good capacity retention of the MoS₂/FeS₂ anode is ascribed to the distinct heterointerface structural design between MoS₂ and FeS₂, and the sufficient heterointerface structure can enhance interatomic electron migration with abundant active sites via covalent chemical bond interaction to improve interfacial charge transfer kinetics. Obviously, the MoS₂/FeS₂ anode shows its high-efficiency interfacial interaction and lithium-ion storage performance for potential application.

With the scan rate increasing, the oxidation and reduction peaks shift slightly (Figure 4a). The lithium-ion storage capacity is usually composed of diffusion capacity and surface capacity [32]. Meanwhile, qualitative analysis of diffusion capacity and surface capacity can be performed via the following equation:

$$i = av^b \quad (1)$$

where a is an adjustable parameter, and the current (i) is calculated via the law relationship of sweep rate (v) [33]. The b -value is the slope of $\log(i)$ versus $\log(v)$, which is used to distinguish diffusion capacity ($b = 0.5$) and surface capacity ($b = 1.0$) [34]. In Figure 4b, they are calculated to be 0.7942 and 0.8017, showing the coexistence of diffusion capacity and surface capacity in the MoS₂/FeS₂ anode. Quantitative analysis of diffusion capacity and surface capacity can be obtained via the following equation [35]:

$$i(V) = k_1v + k_2v^{1/2} \quad (2)$$

At specific potential (V), the current (i) can be separated as surface capacity (k_1v) and diffusion capacity ($k_2v^{1/2}$) [36]. In Figure 4c, the pseudocapacitance of the MoS₂/FeS₂ anode is as high as 76% at 1.0 mV s^{−1}. It is clear that pseudocapacitive behavior dominates the electrochemical processes in the MoS₂/FeS₂ heterojunction anode. The distinguished diffusion capacity and surface capacity are shown in Figure 4d. It can be observed that the surface capacity gradually improves, showing the higher surface capacity at high current density. At 0.1 mV s^{−1}, the surface capacity is still higher than 50%, resulting in enhanced electrochemical kinetics and excellent rate capability. This pseudocapacitance analysis shows sufficient lithium-ion adsorption in MoS₂/FeS₂. Moreover, electrochemical impedance spectra (EIS) analysis is conducted to show the advanced lithium-ion reaction kinetics in the MoS₂/FeS₂ anode. In Figure S7, MoS₂/FeS₂ and pure MoS₂ and FeS₂ anodes have similar EIS curves, which are constituted of a semicircle at medium–high frequency (R_{ct}) and an inclined line at low frequency (R_w). By comparison, the MoS₂/FeS₂ anode exhibits lower charge transfer resistance ($R_{ct} = 80.6 \, \Omega$) and lithium-ion transfer resistance than those of the pure MoS₂ anode ($R_{ct} = 253.4 \, \Omega$) and the FeS₂ anode ($R_{ct} = 335.9 \, \Omega$). This suggests that the heterogeneous interface constructed by the in situ hybridization

strategy provides low internal resistance and strong lithium-ion migration capability to the MoS₂/FeS₂ anode. The improved electrochemical kinetics can be ascribed to the sufficient active sites and the intimate covalent chemical bond interaction.

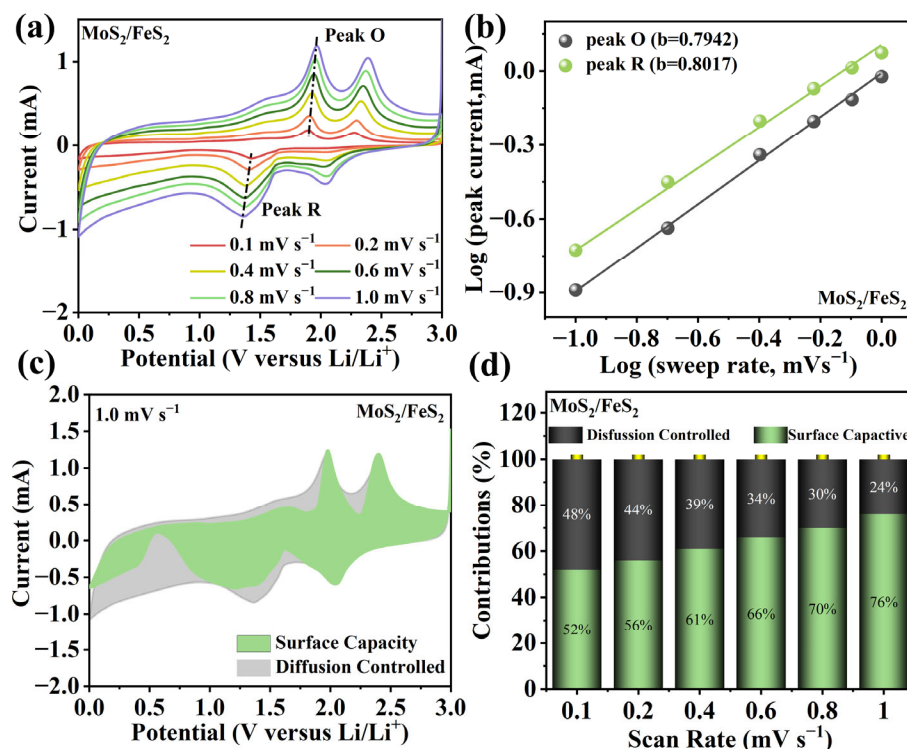


Figure 4. (a) CVs analysis, (b) *b*-values, (c) area ratio image of pseudocapacitance at 1.0 mV s⁻¹, and (d) pseudocapacitance contribution at different scan rates from 0.1 to 1.0 mV s⁻¹ of the MoS₂/FeS₂ anodes.

3. Materials and Methods

3.1. Synthesis of Precursor

Weigh 0.05 mol Na₂MoO₄, add the appropriate amount of deionized water, and stir until completely dissolved. Then, add self-configured 1 M HCl drop by drop until the solution pH = 3, then add 0.05 mol FeCl₃, stirring well to obtain a golden yellow suspension. It was washed with deionized water and anhydrous ethanol several times, filtered under reduced pressure, and put into a constant temperature vacuum drying oven at 80 °C, and dried for 48 h. After complete drying, the precursor was obtained by grinding.

3.2. Synthesis of MoS₂/FeS₂ Nanoflower Spheres

Measure 60 mL of deionized water, add 0.15 g of precursor, stirring until completely dispersed. Then, add 0.6 g CH₄N₂S and 0.03 g CH₃(CH₂)₁₁OSO₃Na, ultrasonic treatment for 1 h until fully mixed, and then add self-configured 1 M NaOH solution drop by drop until the solution pH = 13, and finally transfer to 100 mL PTFE-lined stainless steel kettle, 200 °C hydrothermal reaction for 24 h. After the end of the hydrothermal reaction, cool to room temperature. After washing with deionized water and anhydrous ethanol several times and filtration under reduced pressure, it was put into a constant temperature vacuum drying oven at 60 °C for 48 h. After complete drying, it was milled to obtain the MoS₂/FeS₂ nanoflower spheres. To avoid oxidation as much as possible, the final product MoS₂/FeS₂ nanoflower spheres are stored in a vacuum glove box.

4. Conclusions

In conclusion, a MoS₂/FeS₂ interface was successfully constructed via a simple hydrothermal reaction. This well-designed MoS₂/FeS₂ efficiently combines interatomic

electron migration and lithium-ion adsorption with enhanced charge transfer kinetics. Electrochemical analysis also confirmed the enhanced charge transfer rate and reduced reaction resistance of the MoS₂/FeS₂ anode. Benefiting from this interfacial engineering strategy, the MoS₂/FeS₂ anode shows a superior cycling capacity of 1180.2 mA h g^{−1} at 0.1 A g^{−1} and a rate capacity of 480.9 mA h g^{−1} at 5.0 A g^{−1}. After 200 cycles at 0.1 A g^{−1}, the discharge capacity is 1217.8 mA h g^{−1}, revealing its good cycling stability. After 2000 cycles at 1.0 A g^{−1}, the specific capacity is 638.9 mA h g^{−1} with capacity fading rates of about 0.019% per cycle, respectively, and the corresponding Coulombic efficiency is close to 100%. Overall, the interfacial structural design strategy employed in this study yields a structurally stable MoS₂/FeS₂ anode with superior lithium-ion storage performance.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/molecules29061387/s1>, Figure S1: SEM of MoS₂/FeS₂ ex-situ growth mechanism; Figure S2: SEM of pure (a,b) MoS₂ and (c,d) FeS₂; Figure S3: Selected Area Electron Diffraction (SAED) of MoS₂/FeS₂; Figure S4: Galvanostatic charge-discharge (GCD) curves of pure MoS₂ and FeS₂ at 0.1 A g^{−1}; Figure S5: Capacity retention of pure MoS₂ and FeS₂ at 0.1 A g^{−1}; Figure S6: Capacity retention of pure MoS₂ and FeS₂ at 1.0 A g^{−1}; Figure S7: EIS of MoS₂/FeS₂, pure MoS₂ and FeS₂.

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