Electrochemically intercalated intermediate induced exfoliation of few-layer MoS₂ from molybdenite for long-life sodium storage

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ABSTRACT Two-dimensional (2D) molybdenum disulfide (MoS₂) holds significant promise as an energy storage material, whereas the exfoliation of MoS₂ into few-layer from natural molybdenites remains a challenge. An efficient electrochemical strategy was proposed for the preparation of few-layer MoS₂ through cationic intercalation. Few-layer MoS₂ without the impurity phases was obtained with high yield through Raman mapping analysis, and the intermediate (TBA⁺)_xMoS₂^{x-} was captured by *in-situ* Raman. Note that the charge transport kinetics of the exfoliated few-layer MoS₂ was further enhanced by the introduction of graphene, which could efficiently enhance the Na⁺ diffusion mobility, alleviate the volume change of MoS₂ and stabilize the reaction products. Commendably, the exfoliated MoS₂/graphene hybrid shows a reversible specific capacity of 642.8 mA h g⁻¹ at 0.1 A g⁻¹, superior rate performance (447.8 and 361.9 mA h g⁻¹ at 1 and 5 A g⁻¹, respectively) and remarkable long-cycle stability with 328.7 mA h g⁻¹ at 1 A g⁻¹ after 1000 cycles for sodium-ion batteries (SIBs). Therefore, this efficient electrochemical exfoliation method can be driven to prepare other few-layer 2D materials for SIBs.

Keywords: electrochemical exfoliation, MoS₂, *in-situ* Raman, high performance, sodium-ion batteries

INTRODUCTION

Two-dimensional (2D) transition metal dichalcogenides have aroused enormous attention due to their distinct electronic and optical attributes [1–3]. Notably MoS₂, a typical 2D layer structure material, has been broadly ap-

plied in electrocatalysts, sensors, optoelectronics and energy storage [4–11]. The 2 hexagonal (2H)-phase MoS₂, as a 2D semiconductor material, is derived from natural molybdenites. Theoretical studies suggest that it has a wide band gap from an indirect gap of 1.2 eV in the bulk to a direct gap of 1.9 eV for monolayer through controlling the layer thickness [12,13]. Layered MoS₂ contains a stable in-plane bonding through the S–Mo–S bonds with a large interlayer spacing of 0.62 nm, allowing the reversible insertion of Na ions and a weak out-of-plane interaction by van der Waals forces [14]. Therefore, it can be readily exfoliated into monolayer or few-layer nanosheets.

Large-area, few-layer and atomically thin MoS₂ nanosheets have been prepared by utilizing different approaches to fulfill various applications. MoS₂ nanosheets were mechanically exfoliated and used for basic research [15,16]. Nevertheless, the strategy has a low efficiency, and it is uncontrollable for the thickness and size of MoS₂ nanosheets. Afterward, MoS₂ nanosheets were obtained by using liquid-phase exfoliation in various organic solvents or aqueous surfactant solutions by ultralong sonication-assisted exfoliation [17,18], whereas the as-obtained MoS₂ nanosheets presented multilayers and extensive defects. Recently, lithium intercalation has been reported to exfoliate MoS₂ nanosheets [12]. However, a mass of electrons were injected into the MoS₂ crystal in the intercalation process, resulting in a phase transition from the semiconducting 2H phase to the metallic 1 trigonal (1T) phase [19,20]. Moreover, this method has a

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rigorous requirement for preparation conditions. Very recently, the electrochemical exfoliation approach has attracted tremendous attention because of its simple procedure, high controllability and good efficiency, and it has been successfully employed in the exfoliation of some 2D materials including graphene, phosphorene, Bi_2Se_3 and Bi_2Te_3 , and WS_2 [21–25]. Therefore, it is crucial that high-quality MoS_2 nanosheets with few layer are prepared by a simple and efficient strategy.

MoS_2 has been proposed as a potential anode material for sodium-ion batteries (SIBs) owing to its large inter-layer spacing, high theoretical specific capacity and superior rate capability. However, constitutionally poor conductivity, large volumetric expansion in the sodiation/desodiation process result in the pulverization and bad cycle performance [10,14,26]. To address these issues, various methods have been employed including exfoliation of the MoS_2 bulk into few-layer nanosheets, coating with polypyrrole and polyaniline, and combining with some carbon materials [27,28]. Particularly, 2D graphene with a superior electrical property, may be a good support for MoS_2 to improve the conductivity and alleviate the volume variation. Additionally, graphene-modified MoS_2 can enhance the adsorption energy of Na^+ and keep the fast Na^+ diffusion mobility [26]. Nevertheless, the carbon-coated MoS_2 shows a low initial-sodiation-efficiency because of the low sodium storage activity of carbon materials and the ineffectively exposed MoS_2 nanosheets. Hence, choosing an excellent conductive matrix is critical to improve the electronic conductivity of MoS_2 for battery applications.

Herein, we report an efficient electrochemical method for the preparation of few-layer MoS_2 by introducing tetrabutylammonium cation (TBA^+) intercalation into natural molybdenite layers. This method shows high yield, simplicity and scalability, more importantly, the absence of impurity phases. To improve charge transport kinetics, graphene was employed as conductive matrices to anchor exfoliated few-layer MoS_2 (E- MoS_2/Gr). Benefitting from the virtue of short Na^+ diffusion distance and enhanced Na^+ diffusion mobility, the as-obtained E- MoS_2/Gr material exhibits superior electrochemical properties for SIBs.

EXPERIMENTAL SECTION

Exfoliation of the few-layer 2H-phase MoS_2

Few layer 2H phase MoS_2 was prepared by electrochemically triggering cationic intercalation into the natural molybdenite layers, followed by sonication-assisted

exfoliation. In the two-electrode system, natural molybdenite flake and Pt foil were used as the working electrode (cathode) and the counter electrode (anode), respectively. A 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (TBAP) solution in dimethyl formamide (DMF) was served as the electrolyte. Two electrodes were immersed into the electrolyte, and kept a distance of 2 cm. The electrochemical exfoliation was triggered by utilizing a direct current (DC) power supply (LW10J2, Shanghai LiYou Electric Co., Ltd.) with an applied voltage of -10 V after a wetting process at -1.5 V for 2 min, and after the intercalation process was continued for 2 h, natural molybdenite flake was gradually formed into an expanded and shaggy structure. After that, 20 mL absolute ethylalcohol was added and the expanded molybdenite was thoroughly exfoliated by continuously sonicating for 2 h at a working power of 500 W. The top two thirds of the dispersions were collected by vacuum filtration after standing for 1 h, and washed several times with DMF and ethylalcohol, respectively, followed by drying at 60°C for 12 h in a vacuum oven.

Preparation of the E- MoS_2/Gr hybrids

The E- MoS_2/Gr hybrid was prepared according to a chemical activation method. Briefly, 100 mg of the exfoliated MoS_2 and varying mass of graphene by controlling the mass ratio of MoS_2 to graphene with 4:1, 3:2, 1:1 and 1:2 were thoroughly dispersed into 100 mL of DMF, and then, the above mixture was heated to 140°C , and maintained for 6 h. Finally, the mixture was collected, and washed completely with deionized water and absolute ethylalcohol, successively, and dried in oven with 60°C for 12 h.

Material characterizations

The morphologies of the few-layer MoS_2 and E- MoS_2/Gr were observed with transmission electron microscope (TEM) (JEM-2100F) and scanning electron microscope (SEM) (Hitachi S-4800). The layer numbers of the exfoliated few-layer MoS_2 were figured out by atomic force microscopy (AFM) (Bruker Dimension Icon). In addition, the nanostructure was investigated through X-ray diffraction (XRD) (RIGAKU Ultima IV) and Raman spectra (WITec Alpha 300R). The formation of intermediate in the exfoliation process from molybdenite to few-layer MoS_2 was analyzed by *in-situ* Raman spectra (WITec Alpha 300R). The peak intensities of the few-layer MoS_2 and E- MoS_2/Gr hybrid were detected by Raman mapping. The elements of the few-layer MoS_2 and E- MoS_2/Gr hybrid were analyzed through energy dispersive

X-ray spectroscopy (EDS) elemental mapping and X-ray photoelectron spectroscopy (XPS) (K-Alpha 1063) which was calibrated by C 1s with a binding energy of 284.8 eV. The content of the active material was measured by thermogravimetry analysis (TGA) (NETZSCN, STA 2500 Regulus).

Electrochemical characterization

The electrochemical properties of the as-prepared materials were investigated through fabricating half-cells in an argon-filled glove box by utilization of the E-MoS₂/Gr hybrid as the working electrode, sodium metal as the counter electrode, and Celgard 2400 as the separator. The working electrode was obtained through mixing the E-MoS₂/Gr sample, super P and carboxymethyl cellulose binder with a mass ratio of 70:15:15 in deionized water, which was coated on copper foil after stirring for 12 h, and then dried in a vacuum oven at 80°C for 12 h. Sodium perchlorate (1 mol L⁻¹) in propylene carbonate with 5% fluoroethylene carbonate was used as the electrolyte. The mass loading of active material (E-MoS₂) was about 0.7 mg, and the area of the working electrode was around 1.2 cm². Cyclic voltammetry (CV) was measured on a Autolab PGSTAT101 with a potential range of 3–0.01 V (*vs.* Na/Na⁺) at different sweep rates of 0.1, 0.3, 0.5, 0.7, 0.9 mV s⁻¹. Galvanostatic charge-discharge tests were performed on an Arbin battery cycler (BT2000) within the potential range of 3–0.01 V (*vs.* Na/Na⁺) at various current densities.

RESULTS AND DISCUSSION

To avoid the excess electron injection inducing the phase transition, the larger TBA⁺ can fit into the natural molybdenite layers. Fig. S1a shows the electrochemical exfoliation device using natural molybdenite (Fig. S2a, b) as the working electrode, and the exfoliation procedure is displayed in Scheme S1. The solution variation from colorless to bold yellow was clearly observed during the TBA⁺ intercalation and expanded process (Figs S1b and S2c), suggesting that redox reaction occurred in the electrolyte [28]. The E-MoS₂ was dispersed in DMF to obtain a stable homogeneous canary yellow dispersion (Fig. S1c). Moreover, the Tyndall effect can be clearly observed (Fig. S1c), indicating the formation of relatively thin, semiconducting nanosheets [29].

The morphology of the as-obtained few-layer MoS₂ was investigated by SEM and TEM. As shown in Fig. 1a, b, plenty of thin nanosheets were distinctly observed, suggesting that molybdenite bulk was resoundingly exfoliated into the few-layer MoS₂ nanosheets in

comparison with a stacked multilayer structure of the natural molybdenite (Fig. S3a, b). Moreover, AFM was further performed to measure the thickness of E-MoS₂ (Fig. 1c), and the thickness is distributed from 1.23 to 4.96 nm (Fig. 1d), corresponding to 2–8 layers, proving that the electrochemical method is a feasible and efficient approach for the exfoliation of MoS₂. Note that monolayer, bilayers and few-layer E-MoS₂ emerged in the TEM image (Fig. 1e), and a rippled and wrinkled structure of MoS₂ was obviously observed. The high-resolution TEM (HR-TEM) image (Fig. 1f) shows that the interplanar spacings of 0.62 and 0.27 nm (Fig. 1g, h) are corresponding to the (002) and (100) lattice planes of 2H-phase MoS₂ [30], respectively. Additionally, XRD patterns display a distinct shift of the (002) plane at 14.38° to a lower angle *versus* the natural molybdenite at 14.60° (Fig. 2a), and the XRD patterns in Fig. 2b show that the intensities of diffraction peaks at 32.75° ((100) plane), 39.56° ((103) plane), 44.18° ((006) plane) and 60.40° ((108) plane) are obviously varied in comparison with natural molybdenite, suggesting the remarkably enlarged interlayer distance along the *c*-axis of the 2H-phase MoS₂ after the electrochemical exfoliation [31,32]. Raman spectra (Fig. 2c) reveal that the in-plane E_{2g}¹ vibration stiffens (blue shifts) to 382.3 cm⁻¹ and the out-plane A_{1g} vibration softens (red shifts) to 405.5 cm⁻¹ compared with the natural molybdenite [33,34], which can be attributed to the decreased layer thickness of the 2H-phase MoS₂ after the electrochemical exfoliation [34].

Raman mapping analysis was performed to confirm the thickness of E-MoS₂ using the peak position mapping analysis and the integral intensity ratio maps of E_{2g}¹/A_{1g} modes. [35,36] Previous report indicated that the peak position of E_{2g}¹ mode ranged from 380 to 386 cm⁻¹, and A_{1g} mode varied from 410 to 403 cm⁻¹, corresponding to the bulk to monolayer of MoS₂ [34]. The spatial distribution maps demonstrate that E-MoS₂ consists of the majority of the few-layer MoS₂ from E_{2g}¹ mode (red regions, Fig. 1i) and A_{1g} mode (purple regions, Fig. 1j), and the minority multilayers. The integral intensity ratio map of E_{2g}¹/A_{1g} modes is calculated from the line-mapping of E-MoS₂ (Fig. S4a). Previous studies confirmed that the integral intensity ratios with 0.7, 0.6, 0.3 and 0.1 corresponded to bulk, trilayers, bilayers and monolayer of MoS₂ [34,37]. From Fig. 1k, the integral intensity ratios range from 0.45 to 0.5, indicating that molybdenite bulk was successfully exfoliated into the majority of the few-layered MoS₂ without the impurity phases.

In consideration of this efficient exfoliation method, the electrochemical intercalation exfoliation mechanism was

Figure 1 (a, b) SEM images, (c) AFM image, (d) the corresponding thickness, (e) TEM image, and (f) HR-TEM image of E-MoS₂. (g, h) The calibration for measuring the lattice fringes of E-MoS₂. (i, j) Raman mappings correspond to peak positions of E_{2g}¹ and A_{1g} modes, respectively. (k) Raman mapping of integral intensity ratio of E_{2g}¹/A_{1g} modes.

further explored by *in-situ* Raman. The formation of intermediate (TBA⁺)_xMoS₂^{x-} can be captured through comparing its Raman spectra with that of DMF and TBAP (Fig. S5) when molybdenite is allowed to intercalate for 2 min (Fig. 3a) or longer time (Fig. 3b). The cause of the formation of intermediate (TBA⁺)_xMoS₂^{x-} is that the intercalation of every TBA⁺ need corresponding electrodes from the external circuit to inject into MoS₂ crystal for balancing the charge (Equation (1)), which is analogous to Li⁺, Na⁺ and tetraheptylammonium cation intercalation [28,38]. XRD patterns of the intermediate MoS₂ (Inter-MoS₂) (Fig. S6) indicate that the expansion is not competent to induce severe structure deformation. Simultaneously, the electrolyte solution around anode was detected by *in-situ* Raman, as shown in Fig. 3c. The intensities of peaks at 560.0, 657.0, 863.8, 1100.9 and 2428.0 cm⁻¹ show a significant change and they even

disappear, indicating that the component of the electrolyte is gradually varied, which can be validated to be the electrooxidation of DMF solution by a yellow solution [28]. After the intercalation process was completed (Fig. 3d), the few-layer MoS₂ was obtained by quenching using ethyl alcohol (EtOH) (Equation (2)) after sonication.

Additionally, the electrochemical intercalation process was recorded by CV with a three-electrode system at 10 mV s⁻¹. In the blank electrolyte (DMF), no obvious cathodic peak was observed (Fig. S7). A weak anodic peak at about -9.4 is displayed because of the oxidation of DMF. The CV response containing 0.1 mol L⁻¹ TBAP displays a peak around -0.54 V (Fig. 3e, f), which is as-

Figure 2 (a) XRD patterns of the natural molybdenite, E-MoS₂ and E-MoS₂/Gr hybrid, inset: the corresponding XRD patterns of the (002) plane peak. (b) The intensity variation of the various plane peaks ranging from 25° to 65° in Fig. 3a. (c) Raman spectra of the natural molybdenite, E-MoS₂ and E-MoS₂/Gr hybrid. (d) XPS spectrum of the E-MoS₂/Gr hybrid. (e, f) High-resolution S 2p (panel e) and Mo 3d (panel f) XPS spectra.

cribed to the adsorption of TBA⁺ on the molybdenite electrode. [39] Two distinct peaks at approximately −1.95 and −8.74 V (Fig. 3e) emerge due to TBA⁺ insertion into MoS₂ crystal and the formation of intercalation compounds based on previous studies [18,28,40,41]. An anodic peak at −9.41 V (Fig. 3e) is related to the deintercalation of TBA⁺ and the oxidation of DMF [39]. This deintercalation process depends on the magnitude of the applied cathodic potential. Therefore, a peak around −1.68 V (Fig. 3f) appeared due to an inaccessible kinetics of the deintercalation of TBA⁺ at low potential. According to the CV recorded, the electrochemical exfoliation process can be divided into three steps as shown in Fig. 3g. Firstly, TBA⁺ cations are adsorbed on the molybdenite electrode in a proper wetting process at −1.5 V. Afterwards, TBA⁺ is gradually inserted into molybdenite layers, resulting in a large expansion. Finally, exfoliated few-layer MoS₂ is obtained with the assistance of sonication. CV recorded can clearly illustrate the intercalation exfoliation process, which provides a guide for exfoliation of other 2D materials.

As can be seen from the SEM images of the E-MoS₂/Gr hybrid (Fig. 4a, b and Fig. S3d–f), graphene with wrinkled structure is intersected in the adjacent MoS₂ nanosheets for providing a fast-electronic transferring channel. EDS

(Fig. S3c) proves the existence of Mo, S, C and O elements in the E-MoS₂/Gr hybrid. The structure of the E-MoS₂/Gr hybrid was further imaged by TEM. It is evident that MoS₂ nanosheets are anchored on the wrinkled graphene (Fig. 4c), and the interplanar spacings of 0.62 and 0.27 nm (Fig. 4d) are assigned to the (002) and (100) lattice planes of the 2H-phase MoS₂ [30], respectively. EDS mapping (Fig. 4e) demonstrates that Mo, S and C elements are well distributed in the E-MoS₂/Gr hybrid. The Raman mapping was measured from the line-mapping of the E-MoS₂/Gr hybrid (Fig. S4b), corresponding to the peak positions of E_{2g}¹ and A_{1g} modes (Fig. 4f, g), which are similar to that of E-MoS₂. Besides, the peak positions of D and G bands for graphene are detected as shown in Fig. 4h, i, respectively. The results evidently reveal a good uniformity of the E-MoS₂/Gr hybrid [36,37].

The emerged diffraction peaks for the XRD patterns of the E-MoS₂/Gr hybrid (Fig. 2a and Fig. S8) are in accord with the 2H-phase MoS₂ after exfoliation, and a (002) plane of hexagonal crystalline graphite was observed at 27.5° [12]. Raman spectra show the E_{2g}¹ and A_{1g} vibrations of E-MoS₂ at 382.3 and 405.5 cm^{−1} (Fig. 2c and Fig. S9), respectively. Moreover, two typical peaks at 1351 and 1598 cm^{−1} are assigned to the D and G bands of

Figure 3 (a) Raman spectra of TBA⁺ intercalation for 2 min. *In-situ* Raman spectra of (b) TBA⁺ intercalation process, (c) the electrolyte solution around anode, and (d) the Inter-MoS₂. (e) CV curve in 0.1 mol L⁻¹ TBAP in DMF. (f) Amplified CV profile. (g) The electrochemical exfoliation mechanism of the natural molybdenite.

graphene. The chemical element compositions of the E-MoS₂/Gr hybrid were conducted by XPS. The full XPS patterns indicate that Mo, S, C and O elements exist in the E-MoS₂/Gr hybrid (Fig. 2d). In the high-resolution S 2p XPS spectra (Fig. 2e), two peaks at 161.7 and 162.8 eV are related to S 2p_{3/2} and S 2p_{1/2} [10]. Two strong peaks locate at 228.9 and 232.1 eV in high-resolution Mo 3d XPS spectra (Fig. 2f) are attributed to Mo 3d_{5/2} and Mo 3d_{3/2} [2]. Besides, a hump at 226.1 eV corresponds to Mo-S bond. The high-resolution C 1s XPS spectra in Fig. S10 show the sp³ C and sp² C at 284.0 and 284.6 eV, and the C=O and C-O bonds are observed at 285.9 and 285.3 eV [42,43], respectively, indicating that graphene suffers from oxygen-containing functional groups.

Initially, the conversion mechanism of MoS₂ was further studied by *ex-situ* XRD. As displayed in Fig. 5a, the (002) plane of the 2H-phase MoS₂ at 14.38° gradually shifts to a lower angle when it is discharged to 1.6, 1.2, 0.8, 0.6 V, respectively, which is ascribed to the exfoliation effect of Na⁺ consecutive insertion into the 2H-phase MoS₂ layers. Simultaneously, a new peak emerges at 9.82°, suggesting the formation of the 1T-phase MoS₂, which agrees well with the previous report [10]. When charged to 2.0, 2.2, 2.4 and 2.8 V, respectively, the (002) plane at 9.78° and the (004) plane at 15.46° of the 1T-phase MoS₂ were clearly observed, demonstrating the accomplishment of transformation from the 2H-phase MoS₂ to the 1T-phase MoS₂. According to the reaction process, five

Figure 4 (a, b) SEM images, (c) TEM image, (d) HR-TEM image and (e) EDS mapping of the E-MoS₂/Gr hybrid. (f, g) Raman mappings correspond to the peak position of E_{2g} and A_{1g} modes of E-MoS₂. (h, i) The peak positions of the D and G bands of graphene in E-MoS₂/Gr.

states named as S1, S2, S3, S4 and S5 of Na⁺ storage mechanisms of E-MoS₂ are delineated in Fig. 5b, and further expounded in Table 1.

To achieve the excellent electrochemical properties of the E-MoS₂/Gr hybrid, the mass ratios of E-MoS₂ to graphene were optimized through evaluating the cycle performance at 0.5 A g⁻¹. The E-MoS₂ content in the E-MoS₂/Gr hybrid was calculated by TGA in Fig. S11. As shown in Fig. 6a, the as-prepared E-MoS₂/Gr hybrid with 75.9% E-MoS₂ exhibits the superior cycle performance and high specific capacity. CV profiles for the initial four consecutive cycles of E-MoS₂/Gr were measured in a potential window of 0.01–3.0 V at 0.1 mV s⁻¹. During the first discharge process (Fig. 6b), a peak observed at 2.3 V is attributed to the reduction of incorporated oxygen atoms and oxygen-containing groups [14]. Then, a broad peak at 1.03 V is related to Na⁺ insertion into MoS₂ layers for the formation of 2H-Na_xMoS₂ [44]. The conversion reaction of 2H-Na_xMoS₂ transformation into Na₂S and Mo is presented at 0.77 V [8,45]. A peak emerging at 0.64 V and disappearing in subsequent cycles is assigned to the formation of solid electrolyte interphase (SEI) [10]. Several observed oxidation peaks in the charge process

Figure 5 (a) *Ex-situ* XRD patterns of E-MoS₂ at different discharge-charge voltages. (b) Five states of Na⁺ storage mechanism of E-MoS₂.

are indexed to the gradual oxidation of metallic Mo to Mo⁴⁺ and stepwise desodiation process [8]. CV profiles

display a well overlap in the subsequent cycles, demonstrating a good reversibility of the E-MoS₂/Gr material. The E-MoS₂ electrode shows a similar CV profiles to the E-MoS₂/Gr electrode (Fig. S12a). The discharge/charge profiles of the E-MoS₂/Gr hybrid at 0.1 A g⁻¹ are displayed in Fig. 6c. A sloped plateau at 0.62 V is associated with the formation of SEI [46]. Subsequently, a distinct platform at 0.21 V is ascribed to the thorough conversion

reaction. Some hysteresis observed in the initial charge process are ascribed to the stepwise Na⁺ extraction process [46,47], which are similar to E-MoS₂ (Fig. S12b). The discharge/charge plateaus of E-MoS₂/Gr agree well with the CV profiles, and keep the same profile from the 2nd to 100th cycle, indicating a good reversibility of the E-MoS₂/Gr hybrid.

The cycle performances of the as-prepared materials are

Table 1 The electrochemical process of E-MoS₂/Gr for Na⁺ storage

Process	States	Chemical equation	Mechanism
Discharging	S1	$2\text{H-MoS}_2 + x\text{Na}^+ + x\text{e}^- \rightarrow 1\text{T-Na}_x\text{MoS}_2$	Intercalation
	S2	$1\text{T-MoS}_2 + \text{Na}^+ + x\text{e}^- \rightarrow 1\text{T-Na}_x\text{MoS}_2$	Intercalation
	S3	$1\text{T-Na}_x\text{MoS}_2 + (4-x)\text{Na}^+ + (4-x)\text{e}^- \rightarrow 2\text{Na}_2\text{S} + \text{Mo}$	Conversion
Charging	S4	$1\text{T-Na}_x\text{MoS}_2 + (4-x)\text{Na}^+ + (4-x)\text{e}^- \rightarrow 2\text{Na}_2\text{S} + \text{Mo}$	Conversion
	S5	$2\text{Na}_2\text{S} + \text{Mo} \rightarrow 1\text{T-Na}_x\text{MoS}_2 + (4-x)\text{Na}^+ + (4-x)\text{e}^-$	Inverse conversion
		$1\text{T-Na}_x\text{MoS}_2 \rightarrow 1\text{T-MoS}_2 + x\text{Na}^+ + x\text{e}^-$	Extraction

Figure 6 (a) The cycle performance of the E-MoS₂/Gr hybrid electrodes. (b) CV curves at 0.1 mV s⁻¹ and (c) discharge-charge curves for different cycles at 0.1 A g⁻¹ of the E-MoS₂/Gr hybrid. (d, e) The cycle performance at 0.1 and 1 A g⁻¹. (f) Rate performance at current densities from 0.1 to 5 A g⁻¹.

shown in Fig. 6d, e. The E-MoS₂/Gr hybrid delivers an initial specific capacity of 642.8 mA h g⁻¹ at 0.1 A g⁻¹ with a Coulombic efficiency of 85.8%. After 200 cycles, a high specific capacity of 618.3 mA h g⁻¹ is retained with retention of 83.9%. However, E-MoS₂ exhibits an initial specific capacity of 488.3 mA h g⁻¹ at 0.1 A g⁻¹, and a low specific capacity of 343.5 mA h g⁻¹ is maintained after 200 cycles due to the loss of S phase during the discharge process, resulting in an irreversible conversion reaction [47]. Additionally, the E-MoS₂/Gr hybrid shows an initial specific capacity of 446.5 mA h g⁻¹ at 1 A g⁻¹ after activation for three cycles at 0.1 A g⁻¹ (Fig. 6e). Additionally, it still delivers a high reversible specific capacity of 328.7 mA h g⁻¹ with retention of 73.6% after 1000 cycles. Nevertheless, a specific capacity of 95.2 mA h g⁻¹ for E-MoS₂ is only retained after 700 cycles. The results demonstrate a high reversibility and cycle stability of the E-MoS₂/Gr electrode. Moreover, the E-MoS₂/Gr hybrid shows an excellent rate performance with specific capacities of 642.3, 564.5, 495.8, 447.8, 402.3 and 361.9 mA h g⁻¹ at 0.1, 0.2, 0.5, 1, 2 and 5 A g⁻¹ (Fig. 6f). It still displays high specific capacities of 511.2 and 611.9 mA h g⁻¹ when the current densities are back to 0.5 and 0.1 A g⁻¹, respectively. Importantly, a specific capacity of 569.3 mA h g⁻¹ can be maintained after cycling up to 200 cycles at 0.1 A g⁻¹. The result is far superior to that of the E-MoS₂ electrode. Additionally, comparison of the electrochemical performance of the E-MoS₂/Gr hybrid with previous reports on the MoS₂-based materials for SIBs is shown in Table 2.

Electrochemical kinetics was studied to reveal the su-

perior electrochemical properties of the E-MoS₂/Gr hybrid by electrochemical impedance spectroscopy (EIS) and CV analysis. According to the Nyquist plots (Fig. S13a), the semicircle in the high frequency region is associated with the charge transfer resistance (R_{ct}), and a straight line in the low frequency region reflects the Na⁺ diffusion [48]. EIS fitted values are calculated as shown in Table S1. The E-MoS₂/Gr electrode shows a low R_{ct} value due to the improved electronic conductivity. The relationship of Z' (the resistance) against $\omega^{-1/2}$ (the angular frequency in the low frequency region) curve is displayed in Fig. S13b, the Na⁺ diffusion coefficient of 0.94×10^{-12} (calculated by Equation S1) for E-MoS₂/Gr is larger than that of E-MoS₂ (1.67×10^{-13}), demonstrating that graphene can efficiently enhance the charge transfer and Na⁺ diffusion mobility of the E-MoS₂ electrode, leading to a better stability for long-time cycles.

Fig. 7a, b show the CV profiles at various scanning rates. Note that the potential difference value of the redox peaks for the E-MoS₂/Gr electrode demonstrates a lower polarization effect due to the enhanced electrochemical kinetics [49]. Furthermore, the charge storage mechanism was qualitatively studied through the relationship of peak current (i) versus sweep rate (v) from the CV profiles according to the Equations (3 and 4), the constant b values of E-MoS₂ and the E-MoS₂/Gr electrodes are calculated to be 1.07 and 0.94 by linear fitting of the $\log(i)$ versus $\log(v)$ (Fig. 7c), indicating a typical pseudocapacitive behavior [48]. Moreover, the Na⁺ insertion/extraction kinetics was carried out by Trasatti analysis to quantitate the pseudocapacitive contributions (k_1v) and

Table 2 Comparison of the electrochemical property of E-MoS₂/Gr with previously reported MoS₂-based anode for SIBs

Materials	Cycling performance			Ref.
	Capacity (mA h g ⁻¹)	Current density (mA g ⁻¹)	Cycle number	
BD-MoS ₂	350/272	2000/5000	1000	[7]
MoS ₂ /C@C	312	2000	1000	[8]
MoS ₂ @NHCS ^a	200.4/150.2	1000/5000	300	[9]
MoS ₂ /C MTs ^a	493.6	1000	500	[10]
C@MoS ₂ @PPy ^a	294	5000	3000	[11]
MoS ₂ /carbon fibers	181	1000	100	[14]
MoS ₂ /carbon nanofibers	282	1000	600	[27]
MoS ₂ -PDC ^a	306.8	1000	340	[46]
MoS ₂ -SA/NRGO ^a	295	1000	2000	[47]
E-MoS ₂ /Gr	328.7	1000	1000	This work

a) Abbreviations. NHCS: N-doped mesoporous carbon spheres; MTs: microtubes; PPy: polypyrrole; PDC: popcorn derived carbon; NRGO: nitrogenous reduced graphene oxide.

Figure 7 CV curves of (a) E-MoS₂ and (b) the E-MoS₂/Gr hybrid at the scan rates of 0.1, 0.3, 0.5, 0.7 and 0.9 mV s⁻¹, respectively. (c) Relationship between the peak currents and scan rates in the logarithmic format; the capacitive contribution of (d) E-MoS₂ and (e) the E-MoS₂/Gr hybrid at 0.3 mV s⁻¹. (f) The capacitive contribution ratio of E-MoS₂ and the E-MoS₂/Gr hybrid at different sweep rates. (g–i) SEM images of the E-MoS₂ electrode after 700 cycles. (j–l) SEM images of the E-MoS₂/Gr electrode after 1000 cycles.

diffusion contributions ($k_2 v^{1/2}$) (Equation (5)), which plays a crucial role for the rate performance. The k_1 (slope) and k_2 (intercept) values were computed based on plotting $i(V)/v^{1/2}$ versus $v^{1/2}$ (Equation (6)). The ratios of the pseudocapacitive contributions are obtained through

the calculation of CV area. The percentages of the capacitive contribution of E-MoS₂/Gr are about 86.86%, 91.77%, 94.84% and 97.10% at 0.3, 0.5, 0.7 and 0.9 mV s⁻¹ (Fig. 7d, f), respectively, implying that the pseudocapacitive contributions show a dominant position with the

increased current densities due to the faster electron transfer, resulting in a better rate capability.

$$i = av^b, \quad (3)$$

$$\log(i) = b\log(v) + \log(a), \quad (4)$$

$$i(V) = k_1v + k_2v^{1/2}, \quad (5)$$

$$i(V)/v^{1/2} = k_1v^{1/2} + k_2. \quad (6)$$

Considering the superior electrochemical properties of the E-MoS₂/Gr hybrid, the morphologies of the as-prepared materials after long-time cycles at 1 A g⁻¹ were further characterized by SEM. A cracking position of the E-MoS₂ electrode exhibits pulverization and porous structure (Fig. 7g–i) due to the irreversibility of deconversion reaction and large volume expansion. However, the E-MoS₂/Gr electrode presents a comparative flat surface (Fig. 7j, k), and a well-maintained structure after 1000 cycles (Fig. 7l), indicating the absence of large volume change in the sodiation/desodiation process, which can be attributed to graphene layers offering an elastic space to mitigate the volume expansion of MoS₂, leading to a good reversibility and excellent electrochemical properties.

CONCLUSIONS

In summary, we propose a facile and scalable electrochemical cation intercalation strategy for exfoliation of the nature molybdenite into few-layer MoS₂. The electrochemical intercalation process was analyzed by CV, and *in-situ* Raman indicates the formation of intermediate (TBA⁺)_xMoS₂^{x-}. Moreover, the results of AFM and Raman mapping analysis demonstrate that the electrochemical intercalation exfoliation method is an efficient approach for preparation of few-layer MoS₂ from molybdenite without impurity phases. The electrochemical kinetics of the E-MoS₂ nanosheets is further improved through chemical activation anchoring graphene. The synergistic effect between graphene with superior electronic conductivity and the few-layer MoS₂ provides a fast electronic transferring and Na⁺ diffusion mobility, and mitigates the volume expansion of E-MoS₂, resulting in a high reversible specific capacity of 642.8 mA h g⁻¹ at 0.1 A g⁻¹, superior rate performance (447.8 and 361.9 mA h g⁻¹ at 1 and 5 A g⁻¹, respectively) and remarkable long-cycle stability with 1000 cycles for SIBs. Therefore, this electrochemical cation intercalation exfoliation method can be extended to prepare other few-layer 2D materials decorated graphene for various ap-

plications.

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Author contributions Shuai H conceived the idea, carried out the experiments, material characterizations and electrochemical measurements, and wrote the paper under the guidance from Ji X. Li J and Zhang X conducted the *in-situ* Raman characterization. Jiang F and Sun W offered the pristine molybdenite bulk. Xu L and Hu J conducted the XRD characterization. Duan H and Hu J gave pivotal advice. Hou H and Zou G assisted in the data analysis. All authors discussed the results and commented on the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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电化学插层中间体诱导从辉钼矿中剥离少片层 MoS_2 在长寿命钠储存中的应用

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摘要 二维结构的二硫化钼(MoS_2)是一种很有前景的储能材料, 然而从天然辉钼矿中剥离出少片层的二硫化钼层仍是一个难题. 本文提出了一种有效的电化学阳离子插层制备少片层 MoS_2 的策略. 通过原位拉曼捕获电化学插层过程中的中间产物 $(\text{TBA}^+)_x\text{MoS}_2^{x-}$, 拉曼映射分析结果表明获得了具有高产率和无相变的少片层 MoS_2 . 值得注意的是, 石墨烯的引入进一步增强了剥离的少片层 MoS_2 的电荷迁移动力学, 可以有效增强钠离子的扩散迁移率, 缓解 MoS_2 在充放电过程中的体积变化以及稳定反应产物. $\text{E-MoS}_2/\text{graphene}$ 作为钠离子电池负极材料, 其可逆比容量为 $642.8 \text{ mA h g}^{-1}$ ($@0.1 \text{ A g}^{-1}$), 并表现出优异的倍率性能(比容量分别为 447.8 和 $361.9 \text{ mA h g}^{-1}$ $@1$ 和 5 A g^{-1})以及卓越的长周期循环稳定性, 在 1 A g^{-1} 的电流密度下, 1000次循环后的可逆比容量为 $328.7 \text{ mA h g}^{-1}$. 这种高效的电化学剥离方法也可用于制备其他二维少片层钠离子电池电极材料.