



Facile synthesis of hybrid MoS₂/graphene nanosheets as high-performance anode for sodium-ion batteries

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Abstract

We report the facile synthesis of molybdenum disulfide (MoS₂) nanosheets on graphene nanosheets (MoS₂@GNSs) via simple thermal decomposition of ammonium tetrathiomolybdate in Ar-H₂ atmosphere. When used as anode materials for sodium-ion batteries (SIBs), the as-prepared MoS₂@GNSs electrode delivers reversible capacities of 389 and 383 mA h g⁻¹ at current densities of 200 mA g⁻¹ and 500 mA g⁻¹ after 200 cycles, respectively, which is much higher than that of the MoS₂ electrode (253 mA h g⁻¹ after 171 cycles at 200 mA g⁻¹). The superior sodium storage performance of MoS₂@GNSs including excellent cycle stability and rate performance can be attributed to the introduction of graphene materials, which not only buffer the volume changes of MoS₂ upon sodiation/desodiation but also improve the electrical conductivity.

Keywords MoS₂ · Graphene · Pyrolysis · Sodium-ion batteries

Sodium-ion batteries (SIBs) are attracting increasing interest and have been considered as a promising alternative for the currently widely used lithium-ion batteries (LIBs) [1–4], owing to the abundant and inexpensive sodium resources on earth. Even though SIBs show similar working mechanism with that of the LIBs, the current SIBs usually exhibit slower reaction kinetics, low specific capacity, and poor cycle life because of the large ionic radius of Na⁺ (ca. 1.02 Å) than that of Li⁺ (ca. 0.76 Å), and the heavier molar mass of Na⁺ (22.99 g mol⁻¹) than that of Li⁺ (6.94 g mol⁻¹) [5, 6]. Therefore, the ongoing researches on SIBs are mainly focusing on exploring novel electrode materials with higher sodium storage capacity and better cycling behavior, and

metal sulfides with a high theoretical specific capacity have been considered as promising anodes for rechargeable SIBs [7–9].

Among various candidate anode materials for SIBs, MoS₂ has attracted considerable attentions as a high-performance potential anode material for SIBs due to its layered structure and high theoretical capacity of 670 mA h g⁻¹ [10–13]. Notably, MoS₂ possesses a relatively wide interlayer structure, which is beneficial for fast Na⁺ insertion/extraction [14–17]. However, because of the low electronic conductivity and serious volume expansion of MoS₂ during sodiation, the battery usually displays low specific capacity and poor cycling stability, which makes it extremely challenging in practical applications [18]. To solve this problem, a common and effective method is to combine MoS₂ with a conductive carbonaceous material. For example, Bang et al. reported the synthesis of liquid-phase exfoliated MoS₂ nanosheets, delivering a discharge capacity of 165 mA h g⁻¹ after 50 cycles at a current density of 20 mA g⁻¹, when hybridized with rGO as anode for SIBs [19–21]. Yang et al. reported the synthesis of MoS₂/graphite composite for SIBs which displayed a high reversible capacity of 358.2 mA h g⁻¹ at 100 mA g⁻¹ [22]. Kong et al. reported MoS₂/graphene paper which can provide a capacity of 76.8 mA h g⁻¹ after 300 cycles at 100 mA g⁻¹ [23]. Chen et al. synthesized MoS₂/carbon nanofibers and the electrode showed discharge capacities of 380 mA h g⁻¹ after 50 cycles at 50 mA g⁻¹ [24, 25].

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However, due to the high cost and complexity of these sample preparation processes, these methods are still difficult for large scale applications. This has inspired us to design and develop a facile and low-cost synthesis process to improve the sodium-ion storage characteristics of MoS₂. Herein, MoS₂@GNSs with unique structure and excellent electrochemical performance is designed and manufactured by a facile and low-cost method, namely, via a simple thermal decomposition of ammonium tetrathiomolybdate with the presence of graphene nanosheets.

Experimental section

Material synthesis

For synthesis of MoS₂, 0.2 g of ammonium tetrathiomolybdate ((NH₄)₂MoS₄, J&K Scientific) was placed in a tube furnace and annealed at 800 °C for 2 h in mixed Ar-H₂ (10% H₂+ 90% Ar) at a heating rate of 10 °C min⁻¹. In the typical synthesis of MoS₂@GNSs, 5 mg of graphene nanosheets (GNSs) and 0.1 g of ammonium tetrathiomolybdate were mixed/dissolved in 4 mL of N, N-dimethylformamide (DMF, C₃H₇NO, Shanghai Macklin Biochemical) under ultrasound irradiation for 2 h, and then the solution was transferred and kept in an oven at 100 °C for 1 h, in order to completely evaporate the DMF. Thus, obtained black product was annealed at 800 °C for 2 h under the same condition.

Material characterization

The phase structure of the products were characterized by X-ray diffraction (XRD) analysis under Cu K α radiation ($k = 1.5418 \text{ \AA}$) at 30 kV and 10 mA in the range of 10–80°. Scanning electron microscopy (SEM) was carried out with Quanta 250F FEI SEM. Transmission electron microscopy (TEM) was performed with JEOL-2100 TEM operated at 200 kV. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C min⁻¹ in air using a Mettler Toledo Thermal Analysis TGA-DSC thermal analyzer system. The composition and chemical state of the products were recorded using a Physical Electronics PHI-5802 analysis system by X-ray photoelectron spectroscopy (XPS) with a monochromatic Al K α X-ray source. Raman measurements were performed on a Renishaw RE01 system with an excitation wavelength of 633 nm.

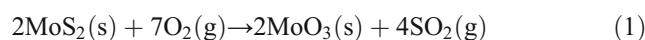
Electrochemical measurements

The electrochemical properties were tested using CR2025 coin-type cell assembled in an Ar-filled glovebox where the contents of H₂O and O₂ were less than 0.1 ppm. The active materials, carbon black, and polyacrylic acid (PAA) were mixed at a weight ratio of 80:10:10 and pasted on a copper foil current collector, followed by drying under vacuum at

60 °C for 12 h. The loading of the active material was in the range of 1.0–1.2 mg cm⁻². The sodium foil was used as the counter electrode and a Whatman glass fiber membrane was used as the separator. The electrolyte was prepared by dissolving 1 M NaClO₄ in ethylene carbonate/dimethyl carbonate (EC/DMC, volume ratio 1:1) with addition of 5% of fluoroethylene carbonate (FEC) by volume. Cyclic voltammograms (CV) were performed using an electrochemical station (Autolab 302 N) with a voltage range of 0.01–3.0 V at a scan rate of 0.2 mV s⁻¹. The discharge-charge test was performed using a battery test system (Neware BTS, China) in the range of 0.01–3.0 V. Electrochemical impedance spectroscopy (EIS) was also performed using an electrochemical station in the frequency range of 10 MHz to 0.01 Hz. The specific capacity is calculated based on the composite mass of MoS₂ and MoS₂@GNSs.

Results and discussion

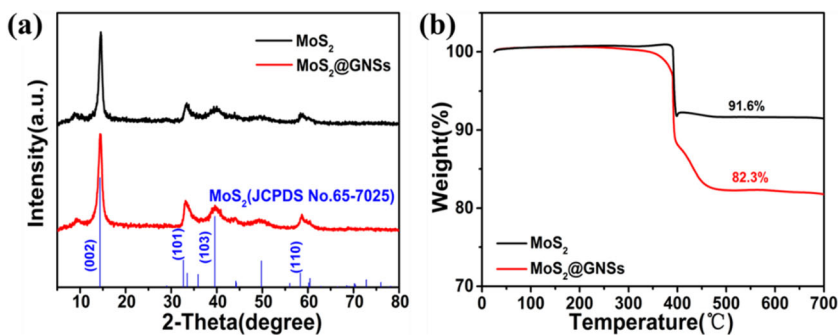
Figure 1a compares the X-ray diffraction (XRD) patterns of the MoS₂ and MoS₂@GNSs. Both products display almost identical diffraction profiles, and all the diffraction peaks can be indexed to the MoS₂ (JCPDS No. 65-7025), in which the prominent peaks located at 14.4°, 33.5°, 39.6°, and 58.3° can be assigned to the (002), (101), (103), and (110) planes of the MoS₂ phase. Notably, the presence of the outstanding (002) diffraction peak at 14.4° with d-spacing of ~0.61 nm indicates the layered crystalline structure. No peaks belonging to other materials can be observed, indicating the high purity of the product and the feasibility of producing layered MoS₂ by directly annealing (NH₄)₂MoS₄ under Ar-H₂ flow. To determine the graphene content in the MoS₂@GNSs composites, TGA test (Fig. 1b) was performed in the temperature ranging from 25 to 800 °C in air. The sharp weight loss at around 400 °C is attributed to the oxidation of MoS₂ to MoO₃, resulting the formation of MoO₃, while the weight loss at 400 to 500 °C is due to the oxidation of carbon to CO₂. On the basis of the following Eqs. (1–3) [26], the weight percentages of MoS₂ and graphene in the MoS₂@GNSs are calculated as 91.4% and 8.6%, which is consistent with the theoretical values.



$$\text{MoS}_2(\text{wt}\%) = 100 \times \frac{M_{\text{MoS}_2}}{M_{\text{MoO}_3}} \times \frac{\text{Final weight of MoO}_3}{\text{Initial weight of MoS}_2\text{-graphene}} \quad (3)$$

The morphology and the microstructure of MoS₂ were examined by SEM and TEM. Figure 2a and b show the typical

Fig. 1 **a** XRD patterns and **b** TGA curves of the MoS₂ and MoS₂@GNSs



SEM images of MoS₂, exhibiting an irregular morphology with aggregates of nanosheets. Figure 2c and d show the TEM/HRTEM images of an aggregate of MoS₂, which is composed of aligned nanosheets. Furthermore, HRTEM image clearly displays the well-defined lattice fringes with d-spacing of 0.61 nm, which can be indexed to the (002) reflection of the MoS₂ (Fig. 1d).

Figure 3a and b show the SEM images of MoS₂@GNSs which were obtained by annealing the (NH₄)₂MoS₄/GNSs under Ar-H₂ flow. Significantly, thinner nanosheets can be observed, as compared with the pure MoS₂ counterpart (Fig. 2a, b). As shown in the TEM image (Fig. 3c), the nanosheets are flexible to some extent. HRTEM image in Fig. 3d reveals that nanosheets are aggregated but with different orientation, and the lattice fringes with d-spacing of 0.62 nm correspond to the (002) plane of MoS₂. As revealed by HAADF-STEM image and the corresponding EDS maps, the thin MoS₂ nanosheets are standing on the graphene nanosheets. The Mo and S elemental maps are well overlapped,

while the graphene nanosheets serve as a support (Fig. 3e). In addition, N-doping may happen owing to the generation of the ammonium by the decomposition of (NH₄)₂MoS₄.

The chemical composition and the valence state of the obtained MoS₂@GNSs were examined by X-ray photoelectron spectroscopy (XPS). Figure 4 a shows the survey XPS spectrum of the MoS₂@GNSs, revealing the presence of Mo, S, and C elements [27]. In the Mo 3d XPS spectrum (Fig. 4b), two distinct characteristic peaks at 228.7 and 231.8 eV can be attributed to the Mo 3d_{5/2} and Mo 3d_{3/2}, respectively, with oxidation state of Mo⁴⁺. In addition, the minor peak at 235.4 eV can be assigned to the formation of Mo⁶⁺-O. The peak at 225.8 eV corresponds to S 2s. Figure 4c shows the core level S 2p spectrum of the MoS₂@GNSs, in which the deconvoluted two peaks at 161.5 and 162.7 eV correspondingly relate to the S 2p_{3/2} and S 2p_{1/2}, indicating that sulfur is present as S²⁻ ions. Figure 4d depicts the overlapped Ni1s and Mo 3p XPS spectrum, in which the prominent peaks with binding energy at 394.7 eV corresponds to Mo 3p_{3/2}, while

Fig. 2 **a, b** SEM images, **c** TEM, and **d** HRTEM images of MoS₂

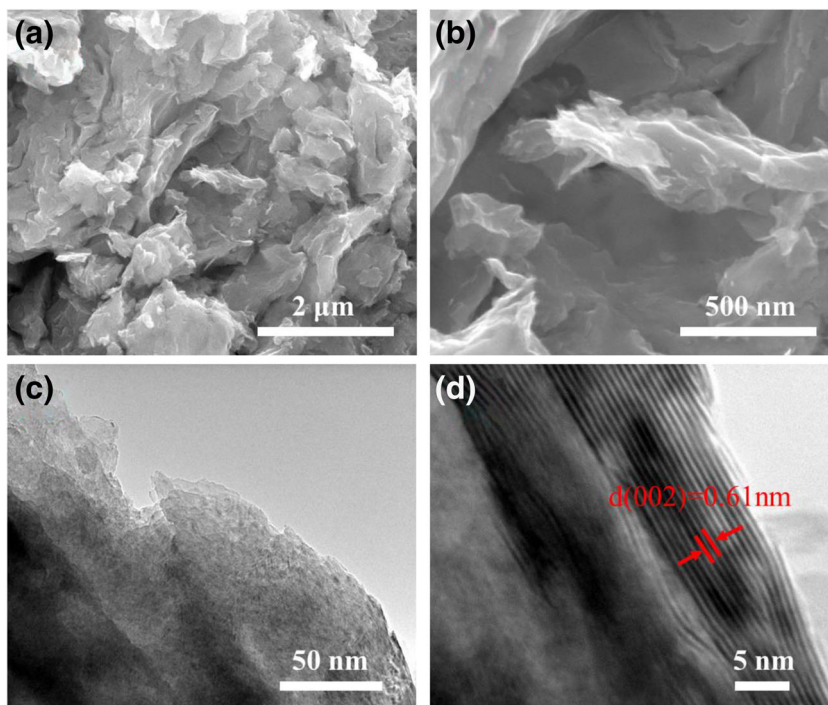
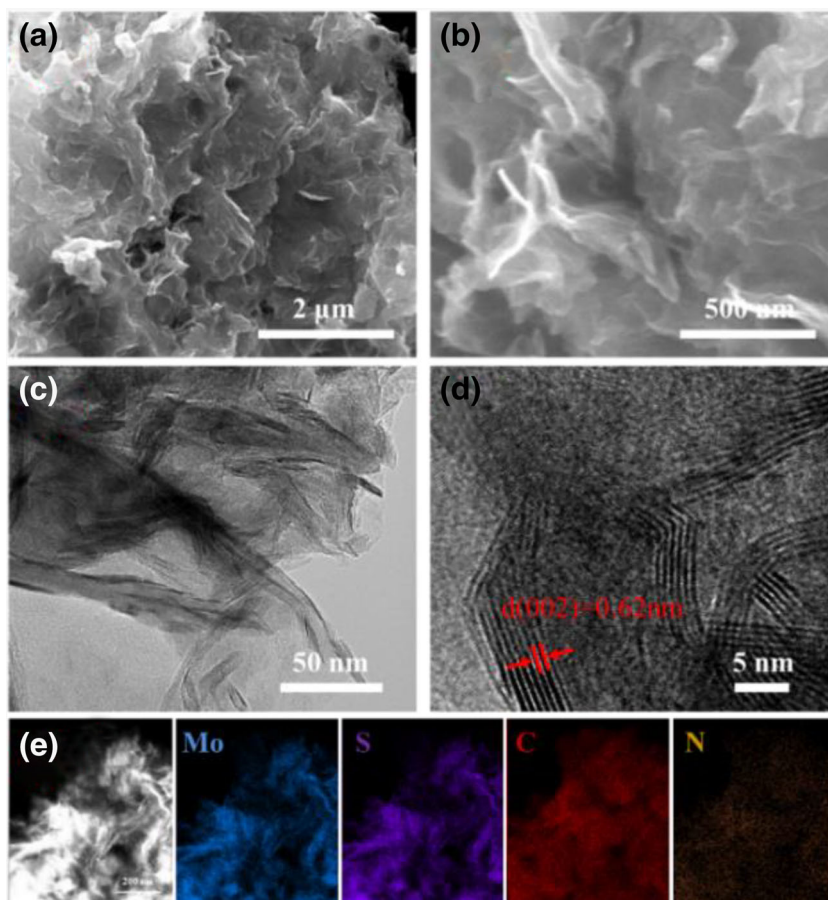


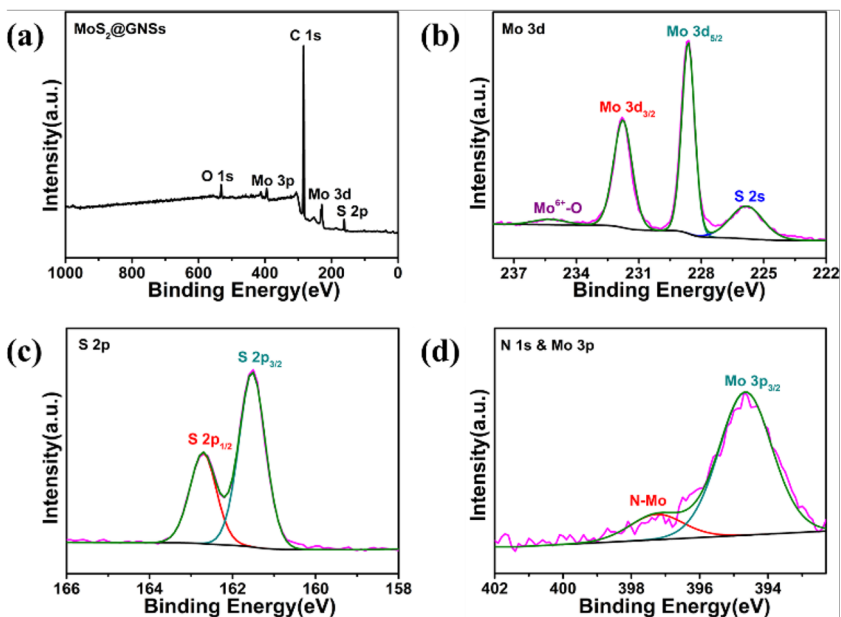
Fig. 3 **a, b** SEM images, **c** TEM, and **d** HRTEM images of MoS₂@GNSs. **e** STEM image and the corresponding elemental maps of Mo, S, C, and N in the MoS₂@GNSs



the peak with binding energy at 397.4 eV can be assigned to the nitride type of N atom, indicating the formation of N-Mo bond [28–30]. Raman spectrum of the MoS₂@GNSs shows two distinct peaks at about 378 and 406 cm⁻¹, corresponding

to the E1 2g and A_{1g} vibration modes of MoS₂, respectively. The A_{1g} mode comes from out-of-plane vibration, while the E1 2g mode originates from the Mo-S in-plane vibration [30–32]. Besides, two broad bands at about 1326 cm⁻¹

Fig. 4 XPS spectra of MoS₂@GNSs composite: **a** survey spectrum, **b** Mo 3d spectrum, **c** S 2p spectrum, **d** N 1s & Mo 3p spectrum



(disorder-induced D-band) and 1597 cm^{-1} (graphite G-band) are observed and originated from the graphene nanosheets (Figure S1) [33, 34].

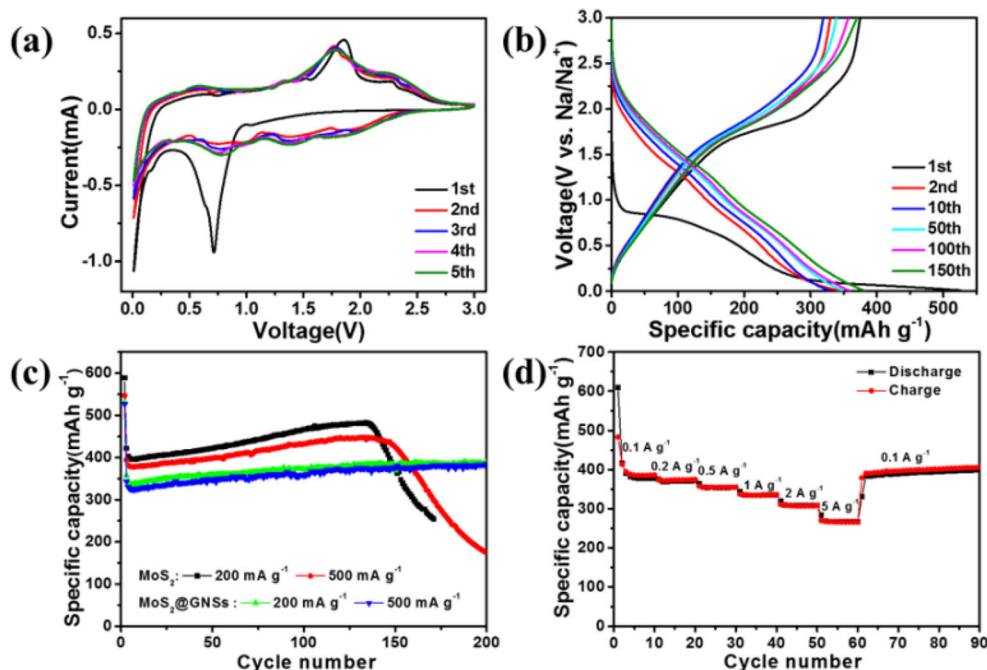
The electrochemical properties of the MoS_2 and MoS_2 @GNSs were examined as anode materials for SIBs using sodium foil as the reference and counter electrode. Figure 5a shows the initial five CV curves of the MoS_2 @GNSs electrode at a scan rate of 0.2 mV s^{-1} in the voltage range of 0.01 to 3 V. In the first cathodic scan, a distinct reduction peak located at around 0.71 V is observed, which can be attributed to the insertion of Na^+ into the MoS_2 interlayer ($\text{MoS}_2 + x\text{Na}^+ + xe^- \rightarrow \text{Na}_x\text{MoS}_2$) and formation of a solid electrolyte interphase (SEI) layer [35–37]. In the anodic scan, the broad peak at 1.85 V can be attributed to the oxidation of metallic Mo to MoS_2 . Since the second CV onwards, the prominent anode and cathode peaks are changed a little and locate at approximately 1.77 and 0.76 V, respectively. Except for the first cycle, the CV curves overlap well in the profile, which reflects the high reversibility and good cycle stability of MoS_2 @GNSs.

Figure 5b presents the discharge and charge voltage profiles of the MoS_2 @GNSs electrode at the 1st, 2nd, 10th, 50th, 100th, and 150th cycles at a current density of 0.5 A g^{-1} . The initial discharge and charge capacities of the MoS_2 @GNSs composite are 526.4 and 374.7 mA h g^{-1} , respectively, displaying a columbic efficiency of 71.2%. The irreversible capacity loss and thus resulting low columbic efficiency is attributed to the irreversible formation of the SEI layer on the surface of the electrode [38–40]. Surprisingly, the reversible capacity of 343 at the 2nd cycle increases to 380 mA h g^{-1} after 150 cycles, with a columbic efficiency as high as 97.3%.

This indicates that the MoS_2 @GNSs electrode provides a stable capacity at a current density of 0.5 A g^{-1} , implying high capacity and good reversibility.

Figure 5c compares the cycling performance of the MoS_2 and MoS_2 @GNSs electrodes at a current density of 0.2 and 0.5 A g^{-1} . Although the initial capacity of the MoS_2 @GNSs electrode is lower than that of MoS_2 , and both MoS_2 and MoS_2 @GNSs electrodes show increasing capacities with cycle number increasing to 130, the MoS_2 electrodes show abrupt fast capacity fading, which may be due to the electrode pulverization upon cycling. Notably, the MoS_2 @GNSs electrodes show stable cycle performance, delivering reversible capacities of 389 and 383 mA h g^{-1} after 200 cycles at current densities of 0.2 and 0.5 A g^{-1} , respectively. Furthermore, the rate performance of the MoS_2 @GNSs electrode is shown in Fig. 5d, and the MoS_2 @GNSs electrode exhibits discharge capacities of 377, 370, 354, 334, 308, and 267 mA h g^{-1} each after 10 cycles at successively increased current densities from 0.1, 0.2, 0.5, 1, 2 to even 5 A g^{-1} , respectively. When the current density is back to 0.1 A g^{-1} , the MoS_2 @GNSs electrode shows a high reversible capacity of 398 mA h g^{-1} , indicating the superior rate capability of the MoS_2 @GNSs electrode. The excellent sodium-ion storage properties of the MoS_2 @GNSs composite can be attributed to the efficient hybridization of the few-layer MoS_2 nanosheets with expanded d-spacing and the continuous graphene nanosheet networks. First, the reduced stacking of MoS_2 nanosheets can relax partial strain, and the larger d-spacing can lower the barrier for Na^+ insertion. Second, the dispersion of MoS_2 nanosheets by the graphene nanosheets facilitates the Na^+ accessibility into reaction sites and the infiltration of electrolyte during cycling.

Fig. 5 a Cyclic voltammetry (CV) curves of the MoS_2 @GNSs electrode at a scan rate of 0.2 mV s^{-1} . b Discharge/charge profiles of the MoS_2 @GNSs electrode at a current density of 0.5 A g^{-1} . c Cycling performance of the MoS_2 and MoS_2 @GNSs electrodes. d Rate capability of the MoS_2 @GNSs electrodes



Third, the flexible graphene nanosheets not only offer cushions to relieve volume expansion but also enhance the electrical conductivity of the composite.

Conclusions

In summary, a hybrid of MoS₂@GNSs with MoS₂ nanosheets grown on graphene nanosheets (GNSs) has been successfully prepared by a facile pyrolysis of ammonium tetrathiomolybdate-GNSs. Owing to the introduction of GNSs, thinner MoS₂ nanosheets were obtained and readily grown on the GNSs. When examined as anode materials for sodium-ion batteries, MoS₂@GNSs electrode delivered high reversible capacity of 383 mA h g⁻¹ after 200 cycles at 0.5 A g⁻¹, demonstrating high sodium storage capacity, superior cycle stability, and rate capability. More importantly, this work provided a new simplified route for synthesis of MoS₂ based anode materials for high-performance SIB materials, which can be expected for various applications in the field of electrochemical energy storage and conversion.

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