Article

Solid-State Synthesis of Layered MoS₂ Nanosheets with Graphene for Sodium-Ion Batteries

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Abstract: Sodium-ion batteries have potential as energy-storage devices owing to an abundant source with low cost. However, most electrode materials still suffer from poor conductivity, sluggish kinetics, and huge volume variation. It is still challenging to explore apt electrode materials for sodium-ion battery applications to avoid the pulverization of electrodes induced by reversible intercalation of large sodium ions. Herein, we report a single-step facile, scalable, low-cost, and high-yield approach to prepare a hybrid material; i.e., MoS₂ with graphene (MoS₂-G). Due to the space-confined effect, thin-layered MoS₂ nanosheets with a loose stacking feature are anchored with the graphene sheets. The semienclosed hybrid architecture of the electrode enhances the integrity and stability during the intercalation of Na⁺ ions. Particularly, during galvanostatic study the assembled Na-ion cell delivered a specific capacity of 420 mAhg⁻¹ at 50 mA g⁻¹, and 172 mAhg⁻¹ at current density 200 mA g⁻¹ after 200 cycles. The MoS₂-G hybrid excels in performance due to residual oxygen groups in graphene, which improves the electronic conductivity and decreases the Na⁺ diffusion barrier during electrochemical reaction, in comparison with a pristine one.

Keywords: SIB; solid-state method; MoS₂; graphene

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1. Introduction

Nowadays, lithium-ion batteries (LIBs) play a vital role in energy-storage applications. However, lithium reserves are limited, which is affecting the economics of LIBs. Therefore, focus has been directed to development of new-generation energy-storage systems for increasing demands of portable electronic products and the automobile sector. Recently, sodium-ion batteries (SIBs) are attracting more attention due to their low cost and suitable redox potential (−2.71 V vs. SHE), as well as abundant resources of sodium [1–3]. Therefore, sodium-ion energy-storage devices inclusive of Na-ion hybrid supercapacitors and Na-ion batteries have currently become a research hotspot [4–6]. However, Na⁺ (1.02 Å) has a larger ionic radii compared with Li⁺ (0.76 Å) because limited selective host materials are available [7]. Therefore, in SIBs, sluggish chemical kinetic behaviors with huge volume variation causes pulverization, leading to rapid capacity-fading [8].

Graphite is an good candidate for LIBs; however, it cannot be used for SIBs because sodium ions cannot intercalate in graphite. Hence, it is an important task for a designing electrode materials to host the Na⁺ ions with the larger radii [9,10]. For eradicating the obstacles in Na-ion batteries, the alloying- and conversion-based anode materials have been studied. In recent years, layered metal dichalcogenides such as NbSe₂, SnSe₂, MoSe₂, WS₂, MoS₂, VS₂, and SnS/SnS₂ have attracted great attention because of their two-dimensional (2D) structures with enlarged interlayer spacing, which provide alternatives for developing improved anodes for SIBs [11–17]. Among these 2D dichalcogenides, layered structured MoS₂ has attracted great attention due to its high theoretical capacity (670 mA h g⁻¹), which is double than that of graphite and comparatively cheaper [18,19]. The covalent bond between molybdenum and sulfur with weak van der Waals forces in MoS₂ is promising,

owing to its large interlaminar distance, which smoothens the intercalation of Na ions with environmental benignity [20]. The spacing between the adjacent layers of MoS₂ is 0.62 nm, which is larger than in graphite (0.35 nm) [21]. Due to these structural features, smooth intercalation and deintercalation of Na⁺ between the MoS₂ planes is possible. However, the practical application of MoS₂ is still hindered because of restacking of MoS₂ layers, which further decreases the availability of active sites for Na⁺ ions [22]. In addition, the poor electronic conductivity of MoS₂ limits the electrode reactions, and intercalation of Na ions induces a large mechanical strain, leading to pulverization and further exfoliation of MoS₂, and rapid capacity-fading occurs [6]. In order to overcome these issues, one potential method is the construction of an MoS₂ hybrid nanostructure. Some researchers reported hybrid nanostructures of MoS₂ with Nb₂O₅, FeCo, HfO₂, MoO₃, TiO₂, Fe₃O₄, etc., and explored these for a sodium-ion battery [1,7,23–26]. Some approaches, such as downscaling the bulk MoS₂ into few layers, expanding the interlayer space of MoS₂, adaptation with advanced carbonaceous materials, etc., have been developed to solve the as-discussed challenges. Among these, modifications with carbonaceous matrices was the most studied [13,21,25–27]. Within carbonaceous materials, graphene has excellent electrical, mechanical, and thermal properties. Thus, many researchers have focused on assembling 2D graphene (G) sheets to support the expanded MoS₂ to construct different architectures. This architecture was found to play a very important role in increasing the electronic conductivity of MoS₂, enlarging the adsorption energy of Na⁺ on the surface of MoS₂ layer and maintaining the high diffusion mobility of Na⁺ [13,28].

In this work, by taking advantage of MoS₂ and graphene integration of adsorption–intercalation–conversion Na⁺ ion-storage mechanisms, we synthesized a nanostructured MoS₂-G composite via a facile solid-state method. This 2D MoS₂ material was adroitly encapsulated into the graphene sheets and the fabricated nanostructure MoS₂-G composite, which was evaluated for SIBs. Herein, the layered MoS₂ with graphene can significantly trap electrons, thus changing the electron state on the multigrain boundary. This improves the charge transmission and increases the capacity. When MoS₂-G hybrids were explored as an anode material in SIBs, they demonstrated good rate capability with cycling stability.

2. Materials and Methods

2.1. Experimental

In a typical synthesis, the in situ solid state method was used to synthesize MoS₂ and MoS₂-graphene (MoS₂-G) nanocomposites. The analytical grade thiourea and diammonium molybdate ((NH₄)₂MoO₄) were taken in a ratio of 1:4 mol, and the graphene oxide was used as received. All precursors were thoroughly ground with a mortar and pestle, and the mixture was heated at 550 °C under an Ar atmosphere for 3 h. The graphene oxide content in the MoS₂-G nanocomposites were 1, 2.5, 5, and 10 wt %, which were denoted as MS-1, MS-2, MS-3, and MS-4, respectively. Further, the pure MoS₂ prepared without graphene oxide was denoted as MS-0.

2.2. Materials Characterization

The crystal structures and phases of the anode nanostructures were examined with the powder X-ray diffraction technique (XRD, Bruker Advanced D8 system, Karlsruhe, Germany) using a Cu K α radiation source in a 2 θ range from 20 to 80° at ambient temperature. The morphological and microstructural analysis of the as-synthesized nanostructures were conducted with field emission scanning electron microscopy (FESEM, Hitachi, S-4800, Kyoto, Japan) and field emission transmission electron microscopy (FETEM by JEOL; JEM-2200FS Kyoto, Japan). The surface chemical composition was studied with X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Co., Theta Probe, Waltham, MA, USA). Room-temperature micro-Raman scattering was performed using a HR 800-Raman.

2.3. Electrode Fabrication and Electrochemical Measurement

To perform electrochemical measurements for Na ions, 2032-type coin cells were fabricated. All the CR2032-type coin cells were assembled in a glove box (MTI, USA) filled with Ar gas. Metallic sodium foil and quartz filter paper were used as the counter electrode and separator, respectively. A ratio of 1M NaClO₄ in ethylene carbonate (EC):diethyl carbonate (DEC) (1:1 in volume) with 5% fluoroethylene carbonate was used as an electrolyte. The electrodes were prepared by mixing active material (80 wt %), conducting carbon (10 wt %) and polyvinylidene fluoride (PVDF, 10 wt %) dissolved in N-methyl-2-pyrrolidone (NMP), subsequently coated on the copper foil, and dried in a vacuum oven at 120 °C for 12 h. After drying, the coated tapes were cut into circular discs with a diameter of 16 mm, and were further used as working electrodes. Cyclic voltammetry behavior of the half cells was tested on the Autolab potentiostat/galvanostat (Metrohm Autolab) in a voltage range of 0.01 V to 3 V. The galvanostatic charge–discharge behavior was tested on an MTI battery analyzer (vs. Na/Na⁺) at room temperature. Electrochemical impedance spectroscopy (EIS) was carried out using an amplitude of 5 mV with a frequency range of 0.1 Hz to 1 MHz.

3. Results

Figure 1 shows the XRD patterns of pure MoS₂ (MS-0) and MoS₂-G (MS-1, MS-2, MS-3, and MS-4) that were recorded and compared to analyze phase purity. Peaks at 2θ values 13.44, 33.08, 39.47, 58.57, and 69.44 were assigned to the (002), (100), (103), (110), and (220) lattice planes of hexagonal 2H-MoS₂, respectively (JCPDS No. 37-1492). The XRD graph demonstrates that the (002@14.37) peak had noticeably shifted toward lower angles (002@13.44°). The shift implied an increase of the interlayer distance, which helps during intercalation of Na ions. According to Bragg's law, the (002) plane interlayer distance of the MoS₂ sample was calculated and observed to be ~0.63 nm, which was larger than that of standard data (0.61 nm). The (002) plane corresponding to the peak at 13.44° suggested a well-stacked layered structure. The (002) plane was broad and weak, which revealed the existence of a few-layer structure of the MoS₂ nanosheets [21,29–31]. The purity of the nanocomposite was confirmed via XRD.

Figure 1. XRD of pure MoS₂ (MS-0) and MoS₂-G (MS-1, MS-2, MS-3, and MS-4).

Field emission scanning electron microscopy (FESEM) was used to investigate the size and morphology of the synthesized samples. Figure 2 illustrates the amassed layered MoS₂ sheets with a loose stacking feature. During the synthesis, clusters of MoS₂ sheets were formed that were a few nanometers in thickness. The MoS₂ sheets could be thin MoS₂ layers curled up by the temperature annealing. With the presence of graphene oxide in the reaction mixture, the MoS₂-G composites exhibited a curved thin flaky appearance. This was an indication that the MoS₂ layers were well supported on the curved graphene surface. From the FESEM, it was quite clear that at a higher concentration of graphene, the MoS₂ sheets might be sandwiched in between graphene layers.

Figure 2. FESEM of (a) pure MoS₂ (MS-0), (b) MoS₂-G, (c,d) MS-1, (e,f) MS-2, (g,h) MS-3, and (i,j) MS-4 at different magnifications.

Further, a detailed structural study of the samples was conducted by field emission transmission electron microscopy (FETEM). Figure 3 shows the typical FETEM images of the MS-2 sample. These clearly demonstrate the formation of MoS₂ with a sheetlike structure and ultrathin layers. The typical few-layered MoS₂ nanosheets are clearly seen in Figure 2a,b. The individual nanosheets seemed to be transparent, which also indicated their thinness. These nanosized layered MoS₂ sheets with a loose stacking feature were anchored with the graphene sheets. The high-resolution FETEM image (Figure 3c) shows distinct lattice fringes of the MS-2 sample with *d*-spacing of 0.63 nm, which corresponded

to the (002) lattice plane of the layered MoS₂ (JCPDS: 37-1492). Figure 3d shows the semicrystalline nature of the MoS₂ along with the (100) and (106) planes.

Figure 3. (a,b) FETEM of MoS₂ (MS-2) at different magnifications; (c) FETEM of the individual MoS₂ layer; (d) corresponding selected area electron diffraction SAED patterns.

The Raman spectra of MoS₂ (MS-0) and MoS₂-G (MS-2) are shown in Figure 4. The Raman peaks appear at 379 and 402 cm^{−1}, corresponding to the E12g and A1g modes of the hexagonal MoS₂ crystal, respectively. The E12g mode involves the in-layer displacement of Mo and S atoms, whereas the A1g mode involves the out-of-layer symmetric displacements of S atoms along the c axis [32,33]. Several researchers have found that single-layer MoS₂ prepared by different methods would display an A1g Raman peak at 402–403 cm^{−1} [29,34,35]. Figure 4 is in excellent agreement with the characteristics of single-layer MoS₂, i.e., an A1g peak at 402 cm^{−1}, which confirms that the MoS₂ sheets in the composite were single layered. Additionally, in the MS-2 sample, the D (disordered) band and the G (graphite) band of carbon at around 1360 and 1592 cm^{−1}, respectively, belong to the graphene; while the Raman spectrum of pure MoS₂ showed the characteristic peak of MoS₂ without the D and G bands of carbon.

Chemical states and composition of the material was investigated using XPS. Figure 5a–c is a series of high-resolution XPS spectra of a typical sample of MS-2 for Mo, S, and C, respectively. The binding energy level of Mo 3d spectra at 229.4 and 232.6 eV depicts Mo 3d5/2 and 3d3/2, respectively. (Figure 5a) [36,37]. Figure 5b shows binding energies at 162.2 eV and 163.3 eV for S 2p3/2 and S 2p1/2, respectively [21]. These values confirmed the Mo in (IV⁺) oxidation state representing the presence of sulfur associated with Mo⁴⁺, which resonates with previous reports [38]. The peak of S2s centered at 226.5 eV was in the Mo 3D spectrum, and demonstrated +4 and −2 valences for Mo and S, respectively, which were maintained from S–Mo–S bonds. Figure 5c shows the C 1s spectra were deconvoluted into four separate Gaussian fitted peaks. The peak centered at 284.8 eV exhibited the conjugated sp² C=C bonding in graphitic structure, while the other two peaks located at 284.5 eV and 286 eV were assigned to multifarious oxygen-containing

functional groups such as C–O and C=O, respectively. The C1s spectrum shows bimodal distribution of peaks, which indicated significantly high oxygen contribution, which is beneficial for electrochemical reaction. The good performance of MoS₂-G hybrids was due to graphene with residual oxygen-containing groups, which consequently improved the electronic conductivity of graphene and decreased the Na⁺ diffusion barrier during the MoS₂-G interfaces, in comparison with the pristine one.

Figure 4. Raman spectra of pure MoS₂ (MS-0) and MoS₂-G (MS-2).

Figure 5. XPS spectra for MoS₂-G (MS-2): (a) Mo, (b) S, and (c) C.

The MoS₂-G layers were synthesized using diammonium molybdate, thiourea, and graphene oxide (GO). Usage of GO nanosheets as a substrate for the nucleation and subsequent growth of MoS₂ have been reported [39]. Initially, H₂S is formed via decomposition of thiourea, which is further decomposed into sulfur, which is attached on the surface of graphene through nucleation. Many researchers have reported the growth mechanism of graphene-based materials that used easy adsorption of cations on the GO surface, owing to the presence of negative charges on their surface [40,41]. During the calcination process, after dissociation of diammonium molybdate, molybdenum oxide and ammonia were

formed. Furthermore, the molybdenum oxide reacted with sulfur, resulting in the formation of MoS₂ nanosheets (2H phase) at 550 °C. During the reaction, reduction of graphene oxide (C_nH_n(OH)_n) took place and released –H and =OH, which helped in the combustion of carbon and other combustible compounds.

The electrochemical behaviors of the typical samples of MS-0 and MS-2 were first evaluated by cyclic voltammetry (CV) measurement. As displayed in Figure 6a,b, three reductive peaks of MoS₂ at 0.1 mV were well observed in the first cycle. The peaks located at 0.74 V corresponded to the insertion of Na⁺ into MoS₂, and the peaks located at around 1.3 V corresponded to the formation of Mo and Na₂S. The anodic peak located at 1.81 V was attributed to oxidation reaction from Mo to MoS₂. In the subsequent cycles, the anodic curves showed characteristics similar to those of the first cycle, whereas the cathodic curves showed a difference. This change arose due to the formation of SEI film during the first cycle. The CV curves at the third cycle were stable and similar to those of the second cycle, which demonstrated reversibility and a stable sodiation/desodiation process of the MoS₂, as per the following equations.

At counter electrode:

During discharge (intercalation at working electrode):

During charge (conversion reaction at working electrode):

where x represents the number of moles of corresponding intercalating Na ions or electrons in the active material.

Figure 6c shows the AC impedance spectra of the MS-0 and MS-2 electrodes, which were measured at the identical condition in the frequency range of 0.01 to 100 kHz at OCV. The charge-transfer resistance (R_{ct}) determined in the medium-frequency region from the semicircle was 750 and 70 Ω for MS-0 and MS-2, respectively. The MS-2 sample had a lower charge-transfer resistance due to the incorporation of graphene, which increased the electronic conductivity of MoS₂.

The exchange-current density (i_0) is inversely proportional to the charge transfer resistance. These charge-transfer resistance results revealed that the MS-2 sample had a higher exchange-current density than MS-0, which confirmed that graphene effectively increased the Na⁺ ion diffusion and electronic conductivity, which controlled the interfacial resistance between particles during the electrochemical reactions.

Additionally, to investigate the effect of graphene on MoS₂ in terms of Na⁺ ion diffusion calculated from the relationship between Z_{re} and $\omega^{-1/2}$ in the low-frequency region, we used the following equations:

$$Z_{re} = R_s + R_{ct} + \sigma_w \omega^{-1/2} \quad (5)$$

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma_w^2} \quad (6)$$

where ω is angular frequency in the low frequency region, σ_w represents the Warburg impedance coefficient, D is the Na⁺ diffusion coefficient, R is the gas constant, T is the absolute temperature, A is the area of electrode surface, n is the number of the electrons per molecule participating in the electronic transfer reaction, F is the Faraday constant, and C is the molar concentration of Na⁺. Figure 6d shows the correlation between Z_{re} and $\omega^{-1/2}$ for the MS-0 and MS-2 samples in the low-frequency region; the slope of the fitted line is the Warburg coefficient σ . The diffusion coefficients of sodium ions were calculated to be

1.61×10^{-13} and 1.84×10^{-12} for MS-0 and MS-2, respectively. The results clearly showed that due to graphene, the Warburg coefficient decreased, but the Na ion diffusion coefficient increased. As compared to pristine, the MoS₂-G enhanced the electronic conductivity, as well as sodium-ion diffusion, and lowered charge-transfer resistance, which was constructive for the electrochemical performance of the electrodes. The electronic conductivity of doped MS-2 was observed to be higher; therefore, electrochemical polarization decreased as compared to pristine.

Figure 6. The first three consecutive CV curves of (a) MS-0 and (b) MS-2 at a scan rate of 0.1 mVs⁻¹ (c) Electrochemical impedance spectrum at OCV (d) The relationship between Z_{re} and $\omega^{-1/2}$.

Figure 7a,b demonstrate the charge–discharge profiles of the MoS₂-G composite at a current rate of 50 mA g⁻¹, in which three plateaus at around 0.7 V, 0.6 V, and 0.1 V in the first discharge process, and one plateau at 1.8 V in the first charge process, are clearly observed. The second and third cycles showed similar characteristics, which was in good accordance with the CV results. The first discharge capacities of samples MS-0 and MS-2 were observed at 807.57 and 641.45 mAhg⁻¹, with reversible charging capacities of 305.21 and 420.43 mAhg⁻¹; the respective retention efficiencies were observed to be 37 and 65.52%. The lower retention for the MS-0 samples in the first cycle was attributed to the formation of more solid electrolyte interface (SEI) film compared to MS-2. The SEI layer formation took place due to the decomposition of electrolyte, as well as irreversible electrochemical reactions of MoS₂.

Figure 7. Electrochemical properties: the initial charge–discharge profiles at 50 mA g^{-1} current density for (a) MS-0; (b) MS-2.

To check the rate capability of the MoS_2 (MS-0 and MS-2), the detailed galvanostatic discharge/charge behaviors were examined at different current densities; i.e., 50, 100, 250, 500, and 1000 mA g^{-1} , and retained to 50 mA g^{-1} for the last five cycles, as shown in Figure 8a. Pure MoS_2 (MS-0) exhibited 305 mAh g^{-1} reversible capacity at 50 mA g^{-1} , and it was much less at 1000 mA g^{-1} . However, within different percentages of graphene, MS-2 exhibited better reversible capacity; i.e., 420 and 78 mAh g^{-1} at 50 and 1000 mA g^{-1} , respectively. With increased current density, the specific capacities continuously dropped for pure samples, while the MS-2 sample showed good rate performance. When the current reverted back to 50 mA g^{-1} , the MS-0 electrode delivered $121.99 \text{ mAh g}^{-1}$, while the graphene-modified MoS_2 (MS-2) exhibited $316.14 \text{ mAh g}^{-1}$. These results demonstrated that the cycling and rate performance of MoS_2 was greatly improved by optimum graphene doping. This revealed that the MS-2 nanosheets with 2.5% graphene could sustain various current rates while keeping their stable structure. An optimum amount of electronic conductor; i.e., graphene, gave stability to the active material, and also provided three-dimensional electronic channels that were favorable for the diffusion during the discharging/charging process. However, a higher percentage of graphene limited the active sites of MoS_2 for intercalation of Na ions due to the shielding effect of graphene layers, which might be responsible for the lower capacity. From the FESEM, it was quite clear that at higher concentrations of graphene, the MoS_2 sheets might be sandwiched in between graphene layers. Ultimately, it decreased ionic mobility prior to electronic conductivity. Hence, this experimental evidence clearly showed the necessity of optimum graphene.

The enhanced performance of MS-2 (MoS_2 -G) nanosheets was due to the expanded d -spacing of MoS_2 layers, which facilitated smooth intercalation of Na^+ ions. Simultaneously, nanosheets with a few-layer structure were prevented from volume expansion and pulverization of the electrode. Due to the space-confined effect, nanosized layered MoS_2 sheets with a loose stacking feature were anchored with the graphene sheets. Due to the mechanical and electrical properties of graphene, the electron transport accelerated, resulting in fast kinetics within the MoS_2 -G composites. The semienclosed hybrid architecture enhanced the stability and integrity of the electrode structure during intercalation of Na^+ ions.

Figure 8b shows the cycling performance of pure MoS_2 (MS-0) and MoS_2 -G (MS-2, considering better capacity), to check the stability of electrodes at 200 mA g^{-1} in the voltage range of 0.01 – 3 V . During this study, the coin cell was activated at current density 50 mA g^{-1} , and further, the electrode was cycled at 200 mA g^{-1} . The specific capacity of the pure MoS_2 anode at 100 mA g^{-1} was 98.79 mAh g^{-1} , and in the subsequent cycles, its capacity dropped continuously, whereas the MoS_2 -G (MS-2) electrode delivered a specific capacity of 172 mA h g^{-1} after 200 cycles, with a capacity retention of 70%. The coulombic

efficiencies of respective cycles were maintained at around 99% in the subsequent cycles, with marginal degradation.

Figure 8. Electrochemical properties: (a) the rate performance of all samples at different current densities; and (b) the cycling performance of MS-0 and MS-2 between 0.01 and 3 V at a current rate of 200 mA g⁻¹.

On the basis of the comparative results for the electrochemical performance of the as-prepared materials, the good capacity, good rate behavior, and cycling stability of MoS₂-G were attributed to the small size and ultrathin thickness of the MoS₂ nanosheets together with the conductive properties of graphene. The expanded interlayer space of MoS₂ facilitated the smoother intercalation of large-size Na ions, and also eased the volume expansion and pulverization of MoS₂ during Na ion insertion. Optimum graphene provided a continuous pathway for electron transport and facilitated the storage and diffusion of Na ions. The 2D nanosheets of MoS₂ with graphene could effectively buffer the stress induced by the large volume variation of electrode materials during the sodiation/desodiation process, and thereby benefited the structural stability and integrity of the electrode.

4. Conclusions

In summary, ultrathin MoS₂-graphene nanosheets were fabricated by a facile solid-state method and checked for feasibility in Na-ion batteries. Due to its structure, the electrode achieved a good reversible specific capacity of 420 mAh g⁻¹ at 50 mA g⁻¹, and exhibited 78 mAh g⁻¹ at 1000 mA g⁻¹. The improved performance of MoS₂-G over pristine MoS₂ was attributed to the expanded *d*-spacing, which facilitated smooth intercalation of Na⁺ ions. The nanosized layered MoS₂ sheets with a loose stacking feature, which were anchored on the graphene sheets, accelerated the ion and electron transport, thus resulting in fast kinetics for the electrochemical reactions. This hybrid structure prevented volume expansion and pulverization of the electrode during repeated intercalation of Na⁺ ions. The semienclosed hybrid architecture enhanced the stability and integrity of the electrode structure during intercalation of Na⁺ ions.

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