Constructing monodispersed MoSe₂ anchored on graphene: a superior nanomaterial for sodium storage

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ABSTRACT We reported a facile and robust one-pot wet chemistry strategy to achieve the growth of uniform three dimensional (3D) MoSe₂ ultrathin nanostructures on graphene nanosheets to form high quality MoSe₂/rGO hybrid nanostructures. Owing to the graphene as a support, it can significantly prevent the aggregation of MoSe₂ and the distribution of MoSe₂ on graphene was highly uniform. Importantly, due to the unique structures, the as-harvested MoSe₂/rGO hybrid exhibited excellent electrochemical performance as anode materials for sodium-ion battery (SIB). When evaluated in a half cell system, the MoSe₂/rGO hybrid nanostructures could deliver a capacity of 200.2 mA h g⁻¹ at 8 A g⁻¹ and maintain a capacity of 230.1 mA h g⁻¹ over 100 cycles at 5 A g⁻¹. When coupled with Na₃V₂(PO₄)₃ cathode in a full cell system, the material could deliver a discharge capacity of 363.1 mA h g⁻¹ at the current density of 0.5 A g⁻¹. Moreover, a discharge capacity of 56.4 mA h g⁻¹ could be achieved even at a high current density of 10 A g⁻¹, which clearly suggested the high power capability of MoSe₂/rGO hybrid nanostructures for sodium ion energy storage.

Keywords: MoSe₂/rGO hybrid nanostructure, sodium energy storage, high rate, long cycle

INTRODUCTION

Owing to the wide availability and low cost of sodium, sodium-ion batteries (SIBs) have attracted considerable attention in recent years as promising alternatives to lithium ion batteries [1–4]. Although the sodium intercalation chemistry is very similar to lithium, the larger ion radius and transport barrier restrict the choice of electrode materials for SIBs. Among the family of the commonly used SIB anode materials, hard carbon is most widely used due to its low cost; however it suffers from low specific capacity

(less than 300 mA h g⁻¹) [5,6]. In addition, insertion-type material, such as Na₂Ti₃O₇ [7,8] and amorphous TiO₂ [9,10], a type of materials with high stability have been investigated by previous reports. However, their energy density is still not satisfactory. Thus, it is a challenge to satisfy the demand of higher energy density for the energy storage devices.

Transition metal dichalcogenides (TMDs) MX₂ (M = Mo or W, X = S or Se) with the similar feature of layered structure to graphite have great potential as alternative anode materials for sodium ion energy storage [11–18]. In general, each layer of M atoms are sandwiched between two layers of hexagonally close-packed X atoms and the nearby X layers are connected by weak van der Waals interaction. Over the past few years, great attention has been paid to molybdenum sulfide (MoS₂) due to its high theoretical specific capacity and good cycling performance in sodium storage. However, as a close analogue to the layer structured MoS₂, the electrochemical sodium storage performance of MoSe₂ has been rarely investigated [16–19]. In addition, it is reported that MoSe₂ has smaller band gap and larger inter-planar space compared with MoS₂, suggesting its smaller structure resistance for intercalating and de-intercalating of Na ion from the layered MoSe₂ structure when used as anode material for SIBs [20]. The above advantages of MoSe₂ also suggest its rapid electrochemical process for SIBs, which is expected to attribute to better Coulombic efficiency and electronic conductivity.

Recently, Wang *et al.* [16] reported both experimental and theoretical assessment of layered MoSe₂ nanoplates as the anode material possessing a reversible sodium storage capacity of 369 mA h g⁻¹ at a rate of 0.1 C (about 0.042 A) af-

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ter 50 cycles. Ko *et al.* [17] synthesized hierarchical MoSe₂ yolk-shell microspheres via a facile selenization of MoO₃ microspheres, which possessed a reversible sodium storage capacity of 433 mA h g⁻¹ after 50 cycles at a current density of 0.2 A g⁻¹. Yang *et al.* [18] prepared porous hollow carbon spheres decorated with MoSe₂ nanosheets via a three-step process, which manifested a reversible sodium storage capacity of 580 mA h g⁻¹ after 100 cycles at a current density of 0.2 A g⁻¹. Zhang *et al.* [19] prepared a hierarchical MoSe₂/reduced graphene oxide (rGO) composite, and demonstrated its good rate performance and cycling stability of 430 mA h g⁻¹ after 200 cycles for sodium storage at a current density of 0.5 A g⁻¹.

Towards the achievement of high rate ability and good cycling stability for the MoSe₂ electrode (Supplementary information Table S1), we synthesized uniform layered MoSe₂ nanoflowers anchored on rGO nanosheets (MoSe₂/rGO hybrid) through a facile one-step chemistry synthesis approach, in which the MoSe₂ nanoflowers were formed by spontaneous assembly of layered MoSe₂ nanosheets. The support of rGO offered an efficient pathway to facilitate the migration of electron and sodium ions (Fig. 1). In addition, the as-prepared MoSe₂/rGO hybrid nanostructure anode was coupled with the Na₃V₂(PO₄)₃ (NVP) cathode as a full cell configuration and demonstrated outstanding rate performance as well as cycling stability.

EXPERIMENTAL SECTION

Synthesis of 3D structure assembled MoSe₂ nanosheets

In a typical procedure, a given amount of (NH₄)₂MoO₄ (0.5 mmol) and selenium powder (1.0 mmol) were added to 18 mL mixture of oleic acid (OA) and ethanol (volume ratio

= 1:1) and stirred for 30 min. Then the mixture was transferred to a 20-mL Teflon-lined autoclave, followed by heating at 160–200°C for 72 h in an oven. After cooling down to room temperature, the obtained precipitates were washed with ethanol for several times and then dried in a vacuum at 60°C overnight. In order to remove the unreacted selenium powder and organic residue, the products were treated in Ar/H₂ (95%:5%) at 500°C for 2 h. The processed MoSe₂ samples were used in all characterization and experiments of the SIBs.

Growth of MoSe₂ nanoflowers on graphene

GO was made by a modified Hummers method [21]. Twenty milligram of GO was dispersed in 4 mL of distilled water under constant sonication at room temperature for approximately 60 min until a clear and homogeneous solution was achieved. Then the synthesis process of MoSe₂/rGO hybrid was similar to the procedure for preparing MoSe₂ nanostructures, except additionally adding 4 mL of the prepared GO solution into the mixed solvent containing 9 mL OA and 5 mL ethanol in the 20-mL Teflon-lined autoclave.

Characterizations

A Quanta F250 scanning electron microscope with an accelerating voltage of 10 kV was used to obtain the SEM images of the samples. The transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) analysis were performed on a Hitachi HT-7700 transmission electron microscope (Japan) operated at an accelerating voltage of 100 kV and a Philips Tecnai F20 FEG-TEM (USA) operated at an accelerating voltage of 200 kV, respectively. The X-ray diffraction (XRD) patterns were recorded on a X-ray diffractometer (Rigaku D/MAX-RB) with monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in 2θ ranging from 10° to 80°. X-ray photoelectron spectroscopy (XPS) was conducted using a PHI Quantera SXM instrument equipped with an Al X-ray excitation source (1486.6 eV). Binding energies of the spectra were referenced to the C 1s binding energy set at 284.6 eV. Raman spectra of the powder samples were recorded on a LabRAM HR Raman spectroscopy with a laser excitation wavelength of 532 nm. Thermogravimetric analysis (TGA) analysis was conducted with a Perkin-Elmer TGA7 thermogravimetric analyzer at temperature ranging from 100 to 900°C with a heating rate of 10°C min⁻¹ under air flow.

Electrochemical test

NVP was prepared by a previously reported method [22].

Figure 1 The MoSe₂/rGO hybrid nanostructures formed by MoSe₂ nanoflowers anchored on rGO nanosheets facilitate the transport of Na ion in SIBs, consequently resulting enhanced performances.

In brief, NH_4VO_3 and NaH_2PO_4 and glucose were mixed and dispersed in ethanol, and then the mixture was ball milled for 24 h. After that, the ethanol was evaporated from the mixture at 80°C in an oven, and then the remaining precursor was calcined at 800°C for 4 h under protection of argon in a tube furnace. Finally, the NVP sample was obtained.

The electrochemical test of MoSe_2/rGO half cell was carried out using CR2032 coin-type cells, consisting of a MoSe_2/rGO cathode and sodium metal anode separated by a glass fiber. The MoSe_2/rGO cathode electrodes were prepared by milling a mixture of 80 wt.% active materials, 10 wt.% acetylene black and 10 wt.% poly(vinyl difluoride) (PVDF) in *N*-methylpyrrolidinone (NMP) to form a homogeneous slurry. The slurry of the mixture was pasted uniformly on a Cu foil current collector and the electrode was then dried under vacuum at 110°C for 12 h before cell assembly. The cell was assembled in a glove box filled with dried argon gas. The electrolyte was a mixture of ethylene carbonate and dimethyl carbonate 1:1 (w/w) containing 1 mol L^{-1} NaClO_4 and 5 wt.% fluoroethylene carbonate additive. For the full cell assembly, the NVP electrode was prepared under the same condition except that Al foil was employed as the current collector. Then the NVP electrode was used as cathode and MoSe_2/rGO was used as anode separated by a glass fiber, the electrolyte was a mixture of ethylene carbonate and dimethyl carbonate 1:1 (w/w) containing 1 mol L^{-1} NaClO_4 and 5 wt.% fluoroethylene carbonate additive. All SIBs were assembled by copper foil with a diameter of 1 cm that contained 1.0 mg of MoSe_2/rGO hybrid material.

The electrochemical performance of SIBs for MoSe_2 and MoSe_2/rGO hybrid nanostructures were characterized at room temperature on a CHI660D electrochemistry workstation and Land Battery Measurement System. For the half cell test, the electrochemical performance was conducted at various current densities in the voltage range of 0–3 V. Cyclic voltammetry (CV) studies were carried out between 0 and 3 V at scan rate of 0.5 mV s^{-1} . For the full cell test, the electrochemical performance was conducted at various current densities in the voltage range of 0–4 V. The CV studies were carried out between 0 and 4 V at scan rate of 0.5 mV s^{-1} .

RESULTS AND DISCUSSION

MoSe_2/rGO hybrid characterization

The SEM and low magnification TEM images (Fig. 2a, b) show the formation of flower-like morphology of MoSe_2

nanostructures with average diameter of $\sim 100\text{--}150\text{ nm}$. The surface of MoSe_2 nanostructures was investigated by Fourier transform infrared (FTIR) spectroscopy, which indicated the residual OA capping ligands on the MoSe_2 nanostructure surfaces (Fig. S1a, see Supplementary information). The obvious ripples and corrugations suggest the as-obtained MoSe_2 nanoflowers are composed of thin nanosheets, which are also clearly visible in the HAADF-STEM image (inset of Fig. 2b). The thin MoSe_2 nanosheets are composed of ~ 14 layers by estimating the HRTEM image (Fig. S1b). The energy dispersive X-ray spectroscopy (EDX) data (Fig. S1c) verifies that the stoichiometric (the atomic ratio of Mo/Se) of MoSe_2 compound is 1:2.

The SEM and TEM images (Fig. 2c, d and Fig. S1d) illustrate that the MoSe_2 layers nanosheets are fairly uniformly dispersed on the rGO surface and importantly, no free MoSe_2 nanosheets are left in the solvents (Fig. S1e), demonstrating the rGO nanosheets are good substrates for the growth of MoSe_2 nanosheets. The selective growth of MoSe_2 nanostructures on rGO was possibly attributed to the precursors anchored on the surface of GO with functional groups (carboxyl and hydroxyl) [23–25]. While in the absence of GO, the as-formed MoSe_2 are connected with each other (Fig. 2a, b), providing a strong contrast with MoSe_2/rGO hybrid nanostructures (Fig. 2c, d). The obvious difference in configuration changes proves the important role of rGO as the substrate for mediating the growth of MoSe_2 nanostructures [23].

The crystal structure of MoSe_2 was investigated by HRTEM. The HRTEM image in Fig. 2e obviously demonstrates the 3D flower-like MoSe_2 grown on the rGO nanosheets. The crystal lattice fringes with interplanar spacing of $\sim 0.28\text{ nm}$ corresponding to the (100) plane of hexagonal (2H-type) MoSe_2 can be clearly observed in the HRTEM image of Fig. 2f. The (002) plane of MoSe_2 with a lattice spacing of $\sim 0.64\text{ nm}$ is also observed. The SAED pattern (inset of Fig. 2f) reveals that the lattice spacings of the MoSe_2 nanosheets are around ~ 0.28 , 0.25 and 0.16 nm , which match well with the (100), (103) and (110) planes of 2H-type MoSe_2 , respectively. The corresponding atomic structure model (Fig. S2) could provide a deep understanding of the formed MoSe_2 nanostructures.

The XRD patterns of the as-formed MoSe_2 and MoSe_2/rGO hybrid nanostructures are shown in Fig. 3a. The observable peaks can be readily assigned to the (002), (004), (100), (103), (105) and (110) planes in the hexagonal phase MoSe_2 (Drysallite, 2H-type, space group: $P6_3/mmc$, $a=b=0.329\text{ nm}$, $c=1.293\text{ nm}$, JCPDS: 29-0914).

Figure 2 SEM (a, c) and TEM (b, d, e) images of 3D MoSe₂ nanoflowers (a, b) and those grown on rGO to form MoSe₂/rGO hybrid nanostructures (c, d, e). (f) HRTEM image of MoSe₂ nanosheets of the rim of (e) MoSe₂/rGO hybrid nanostructures. The inset of (f) is the corresponding SAED patterns.

Figure 3 (a) XRD patterns of the as-prepared 3D MoSe₂ nanoflowers and MoSe₂/rGO hybrid nanostructures. (b) Raman spectrum and (c–f) XPS spectra of the as-obtained MoSe₂/rGO hybrid nanostructures. (c) XPS survey spectra, (d) Mo 3d, (e) Se 3d, and (f) C 1s signals recorded for MoSe₂/rGO hybrid nanostructures.

The corresponding refined lattice parameters are listed in Table S2. The lattice parameter of 'a' remained constant for MoSe₂ and MoSe₂/rGO while 'c' parameter slightly increased indicating that MoSe₂ coupled with rGO expanded the 'c' parameter. Fig. 3b and Fig. S3a present the Raman spectra of the synthesized pure MoSe₂, graphene nanosheets and MoSe₂/rGO hybrid. Two Raman peaks at 236 and 284 cm⁻¹ can be clearly observed for the pure MoSe₂ (Fig. S3a) and MoSe₂/rGO hybrid (Fig. 3b), which correspond to the characteristic A_{1g} (out-of-plane) and E_{2g} (inplane) modes of MoSe₂, respectively. In the higher wavelength region, the peaks around 1350 and 1580 cm⁻¹ responsible for the characteristic D and G bands of graphene nanosheets (Fig. S3a) can also be observed in the obtained MoSe₂/rGO hybrid (Fig. 3b) [26]. The chemical states of Mo, Se and C in the MoSe₂/rGO hybrid nanostructures were examined by XPS, as shown in Fig. 3c–f. From Fig. 3c, peaks assignable to core levels of Mo 3d, Se 3d, and C 1s are identified. Fig. 3d–f show the XPS spectra taken from the Mo 3d, Se 3d, and C 1s regions of the MoSe₂/rGO hybrid. As shown in Fig. 3d, two intense peaks located at 231.9 and 229.1 eV are attributed to the core levels of Mo 3d_{3/2} and Mo 3d_{5/2} of MoSe₂, respectively, demonstrating that the element chemical state of Mo in MoSe₂/rGO hybrid is mainly quadrivalent [27,28]. Double peaks at 55.0 and 54.1 eV (Fig. 3e) attributable to the core levels of Se 3d_{3/2} and Se 3d_{5/2}, respectively, are the characteristic of Se²⁻ in MoSe₂/rGO hybrid nanostructures [29,30]. From Fig. 3f, only trace amount of oxygen content can be observed, confirming the reduction of GO to rGO [31]. Therefore, the growth of MoSe₂ on graphene nanosheets was verified by the Raman spectra and XPS analysis. TGA was further carried out to determine the ~60.4% loading percentage of MoSe₂ in the MoSe₂/rGO hybrid (Fig. S3b).

In the present synthesis of flower-like MoSe₂ nanostructures, the MoO₄²⁻-(OA)_x intermediate (*x* = number of OA molecules) was first formed by the ligand-exchange reaction between Na₂MoO₄ and OA [32,33]. The sequential selenylation of the Mo–O bond into the Mo–Se bond produced the MoSe₂ nuclei, and then formed MoSe₂ nanoflowers. We found the concentration of (NH₄)₂MoO₄ precursor played a crucial role in the synthesis process of high-quality MoSe₂ nanostructures. For instance, fixing the volume of solvents (9 mL OA/9 mL ethanol (*v/v* = 1:1)) and the mole ratio of (NH₄)₂MoO₄ and Se powder (1:2), when using 0.1 mmol of (NH₄)₂MoO₄ at 180°C for 72 h, only aggregates without 3D flower-like morphologies were obtained (Fig. S4a). However, the same reaction condition but with increasing (NH₄)₂MoO₄ amount to 0.5 mmol, resulted in

MoSe₂ 3D flower-like nanostructure (Fig. S4b). While further increasing (NH₄)₂MoO₄ amount to 0.7 mmol, irregular MoSe₂ was produced (Fig. S4c). On the other hand, the morphology evolution of the final products can be readily controlled by varying the reaction temperature and time, as shown in Figs S5 and S6. Therefore, after a series of optimization of experimental conditions, we found that high-quality MoSe₂ nanostructures can be harvested in 18 mL of mixed OA/ethanol (*v/v* = 1:1) solvent at temperature of 180°C over a reaction time of 72 h, using precursor amounts of 0.5 mmol (NH₄)₂MoO₄ and 1.0 mmol Se powder by maintaining the balance for stages of crystal nucleation and growth (Fig. 2b and Fig. S4b).

Sodium storage performance

To investigate the electrochemical sodium storage behavior of the pure MoSe₂ and MoSe₂/rGO hybrid nanostructures, electrochemical characterization was conducted based on typical coin half cells (metallic sodium served as the counter electrode). Fig. 4a shows the CV curves for the initial three cycles of the MoSe₂/rGO hybrid nanostructure electrode in a voltage ranging from 0 to 3.0 V vs. Na/Na⁺ with a scan rate of 0.5 mV s⁻¹. From the first cathodic sweep, we could see two cathodic peaks at 0.65 and 0.44 V, respectively. The peak at 0.65 V is attributed to the sodium insertion to MoSe₂ to form Na_xMoSe₂ while the next peak at 0.44 V is due to the reduction of Mo⁴⁺ to Mo metal accompanied by the forming of Na₂Se and the irreversible decomposition of the electrolytes [16,34]. During the anodic scan, we could see two oxidation peaks at 0.8 and 1.75 V and this phenomenon is due to the partial oxidation of Mo and Na₂Se [17]. Meanwhile, after the first cycle, one peak at 1.4 V shows up, and the two peaks at 0.44 and 0.65 V in the first cathodic sweep disappear, which may result from the reversible reaction of Mo⁴⁺ + 2Na₂Se ↔ MoSe₂ + 4Na⁺ [16,35]. No obvious changes can be observed for the following redox peaks, demonstrating the excellent stability of the electrode. The electrochemical behavior of pure MoSe₂ electrode is similar to that of the MoSe₂/rGO hybrid nanostructures (Fig. S7a).

Fig. 4b shows the galvanostatic charge/discharge profiles of the MoSe₂/rGO hybrid nanostructure half cell in the 1st, 2nd, 3rd and 10th cycle at a current density of 0.5 A g⁻¹. The anode gave an initial capacity of 1019.8 mA h g⁻¹ calculated based on the mass of the MoSe₂/rGO hybrid nanostructure working electrode. This large discharge capacity was due to the decomposition of the electrolyte and the formation of the solid electrolyte interface (SEI) layer, which was consistent with the CV analysis of the electrode [15]. After the

Figure 4 Electrochemical performance of the MoSe₂/rGO hybrid nanostructures for the half cell test. (a) CV curves at a scan rate of 0.5 mV s⁻¹; (b) charge/discharge curves cycling at 0.5 A g⁻¹; (c) rate performance; (d) cyclic properties at 1 and 5 A g⁻¹.

initial capacity loss, a capacity of 423.4 mA h g⁻¹ could be achieved after 10 cycles, and the discharge/charge pattern almost unchanged thereafter (Fig. S7b). By contrast, pure MoSe₂ was also tested in the half cell system (Fig. S7c). The first discharge and charge capacities for the pure MoSe₂ anode were 895.2 and 438.1 mA h g⁻¹, respectively. However, obvious capacity decrease was observed with cycling and the capacity of the pure MoSe₂ anode decreased to 376.8 mA h g⁻¹ after 10 cycles. Additional charge/discharge curves of the MoSe₂/rGO hybrid for the half cell test at higher rates are shown in Fig. S8a. The reversible capacities are 376, 330, 267, and 198 mA h g⁻¹ at the charge/discharge rates of 1, 2, 4 and 8 A g⁻¹, respectively.

Next, the MoSe₂/rGO hybrid nanostructures and pure MoSe₂ coin half cells were selected for the rate capability test. Specifically these two electrodes were cycled from 0.5 to 8 A g⁻¹ in steps and then returned to 0.5 A g⁻¹. As shown in Fig. 4c, the MoSe₂/rGO hybrid nanostructure electrode exhibits final discharge capacities of 423.4, 384.0, 328.3, 259.4 and 200.2 mA h g⁻¹ at current densities of 0.5, 1, 2, 4, and 8 A g⁻¹, respectively. It should be noted that this reversibility performance was much better than the other previous reports on this material [16,17]. After 60 charge/discharge cycles at different current densities, the

discharge capacity of the MoSe₂/rGO electrode could still achieve 448.2 mA h g⁻¹ at 0.5 A g⁻¹, indicating superior rate capability and resilience ability of the electrode. In comparison, the pure MoSe₂ electrode shows inferior capacities and rate capabilities (Fig. S7d). It gave only 143.4 mA h g⁻¹ at 8 A g⁻¹ and could not achieve its initial capacity when the test current density returned to 0.5 A g⁻¹ after 60 cycles.

Cycling performance of the MoSe₂/rGO hybrid nanostructures and pure MoSe₂ half cells were evaluated by galvanostatic measurement at relative high current densities of 1 and 5 A g⁻¹, respectively. As shown in Fig. 4d, the loss after the first cycle of MoSe₂/rGO hybrid nanostructure electrode could be attributed to the decomposition of the electrolyte. After the first cycle, the MoSe₂/rGO hybrid nanostructure electrode delivered a noticeable capacity of 418.0 mA h g⁻¹ and there was no obvious decay throughout 100 cycles at 1 A g⁻¹. Even at a high current density of 5 A g⁻¹, it still maintained a capacity of 230.1 mA h g⁻¹ after 100 cycles, and kept nearly 100% Coulombic efficiency (Fig. S8b). In contrast, a large capacity decrease was observed for pure MoSe₂ electrode after 100 cycles at 1 and 5 A g⁻¹ (Fig. S7e). The higher reversible capacity of the MoSe₂/rGO hybrid nanostructure electrode could certainly be attributed to the presence of rGO since these rGO nanosheets could buffer

the volume expansions that can cause the pulverization of the active material [34,36].

The high rate and good cycling stability of the MoSe_2/rGO hybrid nanostructures could be attributed to their hybrid structure with conductive rGO. The Nyquist plots of the MoSe_2/rGO hybrid and the MoSe_2 as an anode material for half cell test are shown in Fig. S8c. Compared with the pure MoSe_2 , the diameter of the semi-circle at high frequency range in the Nyquist plot of MoSe_2/rGO hybrid is remarkably decreased, indicating the greatly reduced charge-transfer resistance at the electrode/electrolyte interface due to the combination with conductive rGO. The enhanced conductivity can effectively promote the electron and Na^+ ion transfer in the electrode.

To explain the reaction mechanism of the MoSe_2/rGO hybrid nanostructures, *ex situ* XRD, XPS, SAED and HRTEM were carried out after 20 cycles. Fig. 5a shows the XRD patterns of the MoSe_2/rGO hybrid nanostructure electrode at 0 and 3.0 V state. There are also peaks of current collec-

tor (Cu) in every pattern of the tested samples. At 0 V (Fig. 5a(I)), the peak of Na_2Se is found at about 26.5° [16]. At fully charged state 3.0 V (Fig. 5a(II)), we can clearly observe the reconstruction of MoSe_2 . The XPS and SAED patterns can also be used to confirm the reaction process. When discharged to 0 V, the double peaks of XPS located at 231.2 and 234.8 eV are ascribed to the core levels of Mo $3d_{3/2}$ of Mo(0) and $\text{MoO}_3(+6)$, respectively. The rings of SAED of (200) plane and (110) plane are indexed to metallic Na_2Se and Mo, respectively (Fig. 5c). When fully charged to 3.0 V, the rings of (100), (103) and (110) planes of 2H- MoSe_2 are discovered (Fig. 5d). The TEM and HRTEM images of the fully discharged and charged MoSe_2/rGO hybrid nanostructure electrode are shown in Fig. S9. The final discharge products (Na_2Se) and the reconstruction (MoSe_2) have obvious difference in morphology changes (Fig. S9a, b). And the TEM image of the MoSe_2/rGO hybrid nanostructures after the SIB test (Fig. S9b) reveals that the MoSe_2 nanosheets did not fall off from the surface of rGO, indi-

Figure 5 (a) *Ex situ* XRD patterns of the electrodes at different states (I: state of discharge, II: state of charge). (b) XPS spectra of the electrodes at the fully discharged (0 V) state. SAED patterns of the electrodes at the fully (c) discharged (0 V) state and (d) charged (3.0 V) state.

cating excellent stability of the MoSe_2/rGO hybrid nanostructure electrode in SIBs. In comparison, the morphology of the pure MoSe_2 was destroyed after the SIB test (Fig. S9c, d). When discharged at 0 V, the interplanar spacing of 0.34 nm corresponding to the (200) of Na_2Se is observed (Fig. S9e). When charged to 3.0 V, the lattice fringes with d -space of 0.28 and 0.64 nm are indexed to the (100) and (002) planes of MoSe_2 , respectively (Fig. S9f). Based on the above results, the reaction mechanism of MoSe_2 can be described as follows: $\text{MoSe}_2 + 4\text{Na}^+ + 4\text{e}^- \leftrightarrow \text{Mo} + 2\text{Na}_2\text{Se}$.

Recently, Na-superionic conductor (NASICON)-type NVP has been considered as a promising cathode material for SIBs owing to its fast Na^+ ion diffusion, high voltage plateau and high thermal stability [37,38], so we employed it as a cathode material to couple with the MoSe_2/rGO hybrid nanostructure anode. Physical characterization and electrochemical performance of NVP are shown in Figs S10 and S11. Fig. 6 schematically illustrates the construction of the (NVP)//(MoSe_2/rGO) full cell.

CV studies were conducted from 0 to 4.0 V at a scan rate of 0.5 mV s^{-1} and the result is given in Fig. 7a. In the first cycle, a prominent oxidation peak appears at 2.5 V and the corresponding reduction peak can be seen at 1.6 V. From the second cycle, the original oxidation peak at 2.5 V shifts to 1.9 V and no obvious changes are observed for the following progress.

Galvanostatic charge/discharge tests were also conducted at a current density of 0.5 A g^{-1} (Fig. 7b). The initial charge/discharge capacities were 1052.5 and $363.1 \text{ mA h g}^{-1}$, respectively. The loss of irreversible capacity

may be caused by the reduction of the electrolyte and the formation of an SEI later on the anode surface [39] and this issue can be solved by pre-sodiation of the MoSe_2/rGO hybrid nanostructure anode [40]. After the initial capacity loss, a high capacity retention upon cycling can be observed and a capacity of $320.4 \text{ mA h g}^{-1}$ is achieved after 10 cycles (Fig. S12a).

As displayed in Fig. S12b, the reversible capacities for the full cell test are 298, 236, 123, and 56 mA h g^{-1} at the charge/discharge rates of 1, 2, 5 and 10 A g^{-1} , respectively. Fig. 7c shows the rate ability of the (NVP)//(MoSe_2/rGO) full cell. Specifically, this full cell was cycled from 0.5 to 10 A g^{-1} in steps and then returned to 0.5 A g^{-1} . As shown in Fig. 7c, the MoSe_2/rGO hybrid nanostructure electrode exhibits final discharge capacities of 320.4, 263.0, 200.7, 112.9 and 56.4 mA h g^{-1} at current densities of 0.5, 1, 2, 5 and 10 A g^{-1} , respectively. These results clearly demonstrate the high power capability of the MoSe_2/rGO hybrid nanostructure electrode in the sodium ion full cell system.

Cycling performance of the (NVP)//(MoSe_2/rGO) full cell was evaluated by galvanostatic measurement at a pretty high current density of 1 A g^{-1} . As shown in Fig. 7d, this full cell gave a discharge capacity of $258.8 \text{ mA h g}^{-1}$ based on the mass of MoSe_2/rGO hybrid nanostructures at the first cycle and the discharge capacity could still remain $150.1 \text{ mA h g}^{-1}$ even after 100 cycles, the Coulombic efficiency of the full cell reaches nearly 90% after 40th cycles (it is 40% for the first cycle.) (Fig. S12c), indicating the excellent cyclicity of the (NVP)//(MoSe_2/rGO) full cell.

CONCLUSIONS

In summary, flower-like MoSe_2 nanostructures of $\sim 100\text{--}150 \text{ nm}$ in size were successfully synthesized by a facile one-step solvothermal method and these MoSe_2 nanoflowers were distributed uniformly on rGO nanosheets for the improvement of the electrochemical performance as anode material for SIB. In the half cell test, the MoSe_2/rGO hybrid nanostructure electrode delivered a stable discharge capacity of $230.1 \text{ mA h g}^{-1}$ after 100 cycles at 5 A g^{-1} . Even at 8 A g^{-1} , a high discharge capacity of $200.2 \text{ mA h g}^{-1}$ could still be achieved. The excellent rate and cycling performance were attributed to the presence of rGO which could not only serve as conductive structures to facilitate the electron/ion migration but also buffer the volume expansion that can cause the capacity fading of the active material. The conversion mechanism $\text{MoSe}_2 + 4\text{Na}^+ + 4\text{e}^- \leftrightarrow \text{Mo} + 2\text{Na}_2\text{Se}$ has also been proved. Furthermore, a (NVP)//(MoSe_2/rGO) full cell assembly was carried out with a NASICON-type NVP cathode. It delivered a stable

Figure 6 Schematic illustration of the SIB with the (NVP)//(MoSe_2/rGO) couple.

Figure 7 Electrochemical performance of NVP/(MoSe₂/rGO) for full cell test. (a) CV curves at a scan rates of 0.5 mV s⁻¹, (b) charge/discharge curves cycling at 0.5 A g⁻¹, (c) rate performance, (d) cyclic properties at 1 A g⁻¹.

discharge capacity of 150.1 mA h g⁻¹ after 100 cycles at 1 A g⁻¹. At 10 A g⁻¹, a discharge capacity of 56.4 mA h g⁻¹ could be achieved based on the mass of MoSe₂/rGO hybrid nanostructures in the full cell system. The high rate performance and cycling stability of the MoSe₂/rGO hybrid nanostructure electrode in the full cell test suggest its outstanding performance as the anode of SIBs.

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Author contributions Du YP and Liu ZQ designed and performed the series of synthesis and characterization experiments. Zhang Y preformed the SIBs test. All authors analyzed the experimental results and drafted the manuscript.

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

Supplementary information Experimental details are available in the online version of the paper.

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构建单分散MoSe₂/石墨烯纳米复合材料: 一种优越的钠离子电池材料

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摘要 本文采用一种简单有效的湿化学策略将三维MoSe₂超薄纳米结构均匀分散在石墨烯纳米片上,“一锅法”制备得到了MoSe₂/rGO纳米复合结构. 石墨烯作为支撑,不但能有效防止MoSe₂的团聚,而且使MoSe₂均匀分散在石墨烯纳米片上. 由于这种独特的复合结构, MoSe₂/rGO作为钠离子电池负极材料表现出优异的电化学性能. 在半电池中, MoSe₂/rGO复合纳米材料在8 A g⁻¹电流密度下提供的容量为200.2 mA h g⁻¹,在5 A g⁻¹电流密度下循环100次,其容量可保持在230.1 mA h g⁻¹. 当和Na₃V₂(PO₄)₃正极组成钠离子全电池,在0.5 A g⁻¹的电流密度下提供的容量为200.2 mA h g⁻¹,即使在10 A g⁻¹的高电流密度下, MoSe₂/rGO复合纳米材料仍然可以获得56.4 mA h g⁻¹放电容量,表明MoSe₂/rGO纳米复合材料作为钠离子存储材料具有较高的功率密度.