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Synthesis of a hollow MoSe₂@MXene anode material for sodium-ion batteries†

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MXene and MoSe₂ as a novel two-dimensional transition metal carbide and selenide, respectively, are widely used in battery electrodes. In this study, MoSe₂ nanoflakes were grown *in situ* on hollow MXene spheres *via* a hydrothermal method. The obtained hollow 3D spherical MoSe₂@MXene composite exhibits outstanding rate performance and cycling stability as the sodium-ion battery anode. At a current density of 1 A g⁻¹, it achieves a specific capacity of 350.7 mA h g⁻¹ after 1000 cycles with a retention rate of 93.7%. Even at a high current density of 10 A g⁻¹, the specific capacity remains at 224.2 mA h g⁻¹. The outstanding electrochemical performance of the MoSe₂@MXene composite is primarily attributed to the synergistic interaction between MoSe₂ and the MXene, which significantly reduces the self-aggregation of the MXene and MoSe₂ and effectively enhances the diffusion and migration rates of sodium ions.

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Introduction

With the widespread use of portable electronic devices such as laptops and electric vehicles, lithium-ion batteries as the indispensable technology have experienced rapid development. However, owing to the limited lithium reserves, developing efficient alternatives to lithium-ion batteries has become crucial for the future energy system.^{1–3}

Sodium has the advantages of abundant reserves, cost-effectiveness and physicochemical properties similar to lithium; thus it has great potential applications in energy storage and conversion.⁴ However, the commercialization of sodium-ion batteries still faces certain issues.⁵ First, the larger radius of sodium ions (1.02 Å) than that of lithium ions (0.76 Å) significantly reduces the structural stability and energy density of electrode materials.⁶ Second, graphite, widely used as an anode material in lithium-ion batteries, has been found to be incompatible with sodium-ion batteries because of the larger sodium ions and smaller spacing between graphite layers.^{7–9} Therefore, research and development of anode materials for sodium-ion batteries is of great importance.

In recent years, transition metal chalcogenides (MX₂; M = transition metal and X = S, Se, and Te) have received extensive attention in the field of energy storage owing to their unique

physical structures and chemical properties.^{10–15} Transition metal sulfides (*e.g.* MoS₂) have made significant progress as anode materials for batteries. Selenium and sulfur belong to the same main group; thus, the properties of transition metal selenides and sulfides are similar.^{14,16} Owing to the higher density and conductivity of selenium, the volumetric energy density and rate capability of selenide electrodes may exceed those of sulfides. MoSe₂ is a two-dimensional layered material similar to graphene. The spacing of the Se–Mo–Se interlayer is about 0.65 nm, which is larger than that of sodium ions. Thus, the MoSe₂ electrode can facilitate the rapid insertion and extraction of sodium ions and deliver superior electrochemical performance with a theoretical specific capacity of up to 422 mA h g⁻¹.^{11,17,18} However, because of the inherent low conductivity and agglomeration tendency of MoSe₂, pure MoSe₂ presents poor rate performance and cycling stability. To enhance the conductivity of MoSe₂, researchers have attempted various strategies such as combining selenides with carbon materials or constructing heterojunctions.^{19,20} Zhang²¹ synthesized MoSe₂/rGO composites *via* a hydrothermal method with a reversible capacity of 430 mA h g⁻¹ at a current density of 0.5 A g⁻¹. The synergistic effect between MoSe₂ and graphene significantly improves the sodium storage performance. Chao²² synthesized G-Cu₂Se@MoSe₂ nanosheets with dual heterojunctions by a hydrothermal method. G-Cu₂Se@MoSe₂ with this special structure provides a capacity of 288 mA h g⁻¹ at 50 A g⁻¹ and 89.6% capacity (291 mA h g⁻¹) after 15 000 cycles at 10 A g⁻¹.

MXenes are the novel two-dimensional transition metal carbides, which possess excellent properties such as high metallic conductivity,^{23,24} large specific surface area,²⁵ and abundant

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functional groups.²⁶ The outstanding conductivity facilitates rapid charge transfer, and the unique layered structure promotes the ion diffusion. Additionally, the large specific surface area enhances the interactions with other materials and reveals the significant potential in energy storage applications.²⁵ An MXene/MoSe₂ composite was synthesized by an *in situ* one-step hydrothermal method.²⁷ With the unique heterostructure and large specific area, MXene/MoSe₂ achieved a specific capacitance of 1358.5 F g⁻¹ at 1 A g⁻¹, significantly higher than those of pure MXene and MoSe₂ electrodes. However, similar to other two-dimensional materials, MXene nanosheets tend to stack, restricting the diffusion and transfer of sodium ions. Two-dimensional MXene sheets were synthesized into three-dimensional hollow spheres by a template method.²⁸ The obtained hollow MXene microspheres delivered a reversible capacity of 295 mA h g⁻¹ after 1000 cycles at a charging rate of 2.5 C. Even at a high charging rate of 25 C, the composite retained a discharge capacity of 120 mA h g⁻¹.

The construction of MXenes with hollow spherical structures can effectively improve the structural stability and the electrochemical performance.^{11,19,29} This structure allows the electrolyte to fully penetrate into the hollow cavities and shortens the ion transport path.²⁹ In this study, two-dimensional MXene nanosheets were assembled into hollow MXene spheres using a template method, and then, MoSe₂ was anchored onto the hollow MXene spheres *via* a hydrothermal method, preventing the growth of nanosheets and agglomeration. The obtained MoSe₂@MXene composite demonstrated eminent cycling stability and rate performance for sodium-ion batteries.

Experimental

Chemicals

Titanium aluminum carbide (Ti₂AlC₂, 200 mesh, 98%), sodium molybdate dihydrate (Na₂MoO₄·2H₂O, 98%), methacryloxyethyl trimethyl ammonium chloride (DMC, C₉H₁₈ClNO₂, 75 wt%), 2-methylpropionitrile (AIBN, CH₂N₄, 99%) and glucose (C₆H₁₂O₆, 99%) were purchased from Macklin. Lithium fluoride (LiF, 99%), concentrated hydrochloric acid (HCl, 37%), styrene (C₈H₈, 99.5%), hydrazinium hydrate solution (N₂H₄·xH₂O, 80%) and selenium powder (Se, 99%) were purchased from Aladdin. No further purification was required for these reagents.

Preparation of single-layered MXenes (MXene-SL)

First, 2 g LiF was weighed and dissolved into 120 mL of 9 M HCl solution with stirring at room temperature for 15 minutes. Then, 2 g MAX powder was slowly added into the above solution in small portions to avoid overheating. The mixture was stirred at 55 °C for 48 hours, centrifuged and then washed several times with deionized water at 3500 rpm until the pH value of the supernatant reached approximately 6. The precipitate was redispersed into deionized water, sonicated for 30 minutes, and subsequently centrifuged at 3500 rpm for

1 hour. The resulting suspension was collected with a concentration of approximately 2 mg mL⁻¹ and denoted as MXene-SL.

Preparation of MXene@polystyrene spheres (MXene@PS)

First, 13.6 g styrene was added into a flat-bottom flask containing 120 mL methanol and 30 mL deionized water, and then AIBN and DMC were sequentially mixed with a mass ratio of styrene, AIBN and DMC of about 50/1/1. The mixture was purged with nitrogen gas for 10 minutes to remove dissolved oxygen and then sealed for the reaction in an oil bath at 70 °C for 8 hours. The product was centrifuged and washed to obtain polystyrene (PS) spheres with an approximate diameter of 500 nm. Then 1 g PS spheres were dispersed into 80 mL deionized water, mixed with a 100 mL MXene-SL suspension solution (mass ratio of PS to MXene-SL is 5/1) and then stirred for 30 minutes. Finally, the suspension was centrifuged to remove unbound MXenes, and the product was freeze-dried to obtain greenish-black MXene@PS spheres.

Preparation of the hollow MoSe₂@MXene sphere

The preparation process of hollow-structured MoSe₂@MXene composites is illustrated in Fig. 1. First, 0.4 g MXene@PS spheres, 0.2 g glucose, and different amounts of Na₂MoO₄·2H₂O were ultrasonically dispersed in 30 mL deionized water. Subsequently, Se powder with a Mo-to-Se molar ratio of 1/2.5 was mixed into 15 mL N₂H₄·H₂O solution under constant stirring and heating to obtain a red-brown suspension. The resulting mixture was transferred to a 60 mL polytetrafluoroethylene (PTFE) – lined reactor, sealed in a stainless steel autoclave, and reacted at 200 °C for 24 hours. The black product was washed several times with deionized water and ethanol, vacuum-dried at 60 °C for 12 hours, and finally calcined in a tubular furnace at 550 °C for 1 hour at a heating rate of 5 °C min⁻¹. To investigate the effect of the MXene content on the performance of the composites, the MoSe₂@MXene samples with different mass ratios of MXene to MoSe₂ (10%, 20%, 30%, and 40%) were prepared and labeled as MoSe₂@MXene-10, -20, -30, and -40, respectively.

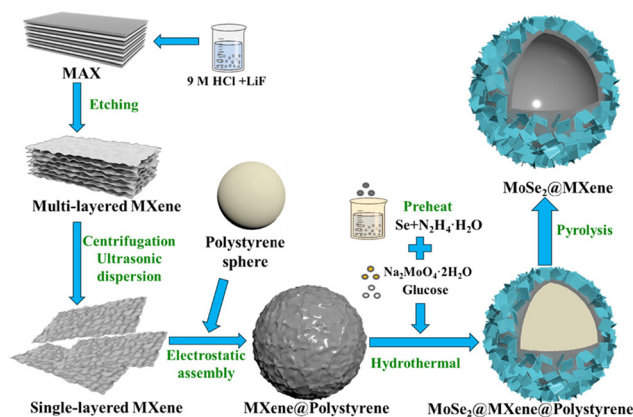


Fig. 1 Schematic of the synthesis of the hollow MoSe₂@MXene spheres.

with obvious self-aggregation (Fig. S1c and d†).³⁶ The addition of MXene@PS spheres effectively suppressed MoSe₂ aggregation and prevented the formation of stacked nanoflower structures. For the MoSe₂@MXene series composites (Fig. S1e–j†), the MoSe₂ layers became thinner and the arrayed structure of MoSe₂ was more pronounced with the gradual increase in MXene content. Notably, the hollow MoSe₂@MXene composites can serve as a container for the electrolyte and offer the buffering space to alleviate the volumetric expansion of MoSe₂ during the charge–discharge processes.³⁴

The microstructure of the MoSe₂@MXene-30 composite was analyzed by transmission electron microscopy (TEM) test. In Fig. 2j–j₃, MoSe₂@MXene-30 displays a clear hollow spherical structure with a particle size of approximately 500 nm. The dark region within the spherical wall corresponds to MXene-SL, which further proves the complete removal of the PS template and the formation of a hollow structure. Additionally, the lattice fringe of 0.95 nm is attributed to the *d*-spacing of the (002) lattice plane for the MXene sample (Fig. 2j₂). It is demonstrated that the interlayer distance of MXene-SL increases during the exfoliation of MXene-ML.³⁷ Fig. 2j₃ shows that the MoSe₂ sheets are grown on the shell of the hollow MXene sphere. The lattice spacing is 0.65 nm corresponding to the (002) crystal plane of hexagonal 2H-MoSe₂.^{11,22} To reveal the elemental distribution of the MoSe₂@MXene composites, energy-dispersive spectroscopy (EDS) analysis was performed, and the patterns are presented in Fig. 2k–k₄. It is shown that Ti and C elements are mainly distributed in the hollow sphere, while Mo and Se are mainly centered in the outer shell. It is illustrated that MoSe₂ is grown uniformly on the surface of hollow MXene sphere. In addition, the contents of Mo and Ti elements in four MoSe₂@MXene composites were measured by ICP-OES. As displayed in Table S1,† the MoSe₂ contents in these composites closely match the theoretical values with minor deviation.

The crystal structures of MAX, MXene-ML, MXene-SL, and MoSe₂@MXene composites were characterized by XRD, and are shown in Fig. 3a. The characteristic diffraction peak (104) of MAX was absent for both MXene and MXene-SL, indicating the complete etching of the Al layer from MAX and the successful synthesis of MXene. Furthermore, the (002) peak located at 9.5° for MAX shifted to 8.7° and 7.4° for MXene-ML and MXene-SL, respectively. Additionally, the diffraction peaks corresponding to the (004) and (006) planes of MXene-SL were observed, which revealed that MXene was successfully prepared²⁹ and the interlayer spacing of MXene increased progressively after the removal and exfoliation of the Al layer.^{19,38} This enlarged interlayer spacing facilitated the rapid insertion and extraction of sodium ions. Fig. 3b presents the XRD patterns of pure MoSe₂ and MoSe₂@MXene composites with different MoSe₂ and MXene ratios. All samples exhibited characteristic peaks centered at 13.7°, 31.56°, 37.88°, and 56.35° attributed to the (002), (100), (103), and (110) planes of hexagonal 2H-MoSe₂ (PDF#29-0914), respectively.^{20,22} It was demonstrated that PS template was removed completely after calcination and no impurity phases were introduced. Notably,

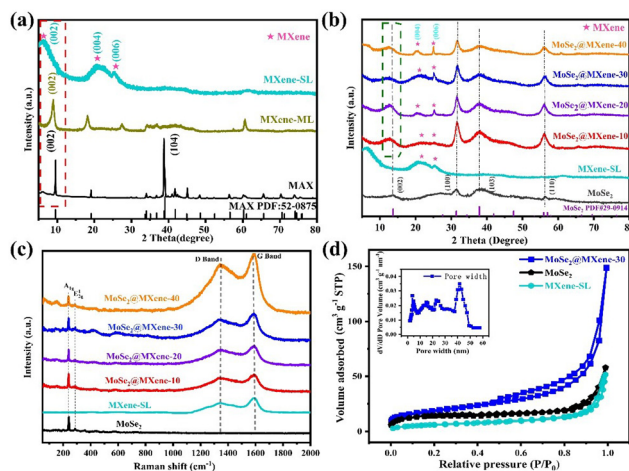


Fig. 3 (a) XRD patterns of MAX, MXene-ML and MXene-SL. (b) XRD patterns of MoSe₂, MXene-SL and MoSe₂@MXene series composites. (c) Raman spectra of the MoSe₂@MXene composites. (d) N₂ adsorption/desorption isotherms of MoSe₂, MXene-SL and MoSe₂@MXene-30 and pore size distribution curve of MoSe₂@MXene-30.

the (002) peak of MoSe₂ for the MoSe₂@MXene samples showed a significant leftward shift compared with that of pure MoSe₂, which indicated that the MoSe₂@MXene samples had larger MoSe₂ layer spacings than those of MoSe₂. The expanded MoSe₂ layers continued to gather into spherical nanoflowers, which is consistent with the above analysis with SEM images. As the MXene-SL ratios of MoSe₂@MXene composites increased, the intensity of the (004) and (006) peaks progressively enhanced.

The Raman spectra of pure MoSe₂, MXene-SL, and MoSe₂@MXene composites are shown in Fig. 3c. Pure MoSe₂ exhibits two distinct peaks at 241.5 cm⁻¹ and 286.8 cm⁻¹, representing the out-of-plane A_{1g} and in-plane E_{12g} vibrational characteristics of Se.¹¹ The Raman peaks of MXene are located at 1344.0 cm⁻¹ and 1591.0 cm⁻¹ corresponding to the D and G bands of carbon vibrations, respectively.³⁹ The four peaks of the MoSe₂@MXene composites attributed to A_{1g} and E_{12g} vibrated peaks of Se element and the D and G vibrated bands of carbon, respectively. The successful *in situ* growth of MoSe₂ on MXene was further confirmed, which is in agreement with the XRD results.

The specific surface area is a crucial factor to the energy storage property of the electrode materials. N₂ adsorption–desorption analyses are performed for pure MoSe₂, MXene-SL and MoSe₂@MXene samples, and the results are displayed in Fig. 3d and Fig. S3.† It is revealed that all MoSe₂@MXene samples exhibit type III hysteresis loops in the curve. The specific surface areas of MoSe₂@MXene-10, -20, -30, and -40 composites are 28.84, 52.37, 71.13, and 37.49 m² g⁻¹, respectively, which are higher than that of pure MoSe₂ and MXene-SL. Notably, the MoSe₂@MXene-30 composite achieved the highest specific surface area, approximately 3.26 times that of pure MoSe₂ (21.8 m² g⁻¹) and 4.9 times that of MXene-SL (14.51 m² g⁻¹), which is due to the vertical growth of MoSe₂

nanoflakes on MXene template spheres and the formation of the unique three-dimensional array structure. The large specific surface area and broad mesoporous distribution (4–50 nm) of MoSe₂@MXene-30 facilitate the rapid transport of Na⁺ ions.

The chemical composition and interfacial characteristics of MoSe₂@MXene-30 composite were characterized by X-ray photoelectron spectroscopy (XPS) analysis. The survey spectrum in Fig. 4a reveals the presence of Mo, Se, Ti, C, and O elements, which is in accordance with the EDS results. As shown in Fig. 4b, the high-resolution Mo 3d spectrum displays three main peaks at 228.4 eV, 231.6 eV, and 234.7 eV, respectively. The first two peaks are attributed to the 3d_{5/2} and 3d_{3/2} peaks of Mo⁴⁺ species, respectively.²⁷ While the last peak at 234.7 eV corresponds to Mo–O bond, which is indicative of the electron exchange between the MXene and MoSe₂.⁴⁰ The Se 3d XPS spectrum shows two distinct peaks at 53.9 eV and 54.9 eV assigned to Se 2d_{5/2} and Se 2d_{3/2}, respectively.^{27,37} Ti 2p XPS spectra, as shown in Fig. 5d, display four distinct peaks located at 457.7, 463.8, 458.4, and 464.7 eV, corresponding to Ti³⁺ 2p_{3/2}, Ti³⁺ 2p_{1/2}, Ti–O 2p_{3/2} and Ti–O 2p_{1/2} orbitals, respectively.¹¹ Notably, it is reported that the characteristic peaks of Ti³⁺ species will vanish from the Ti 2p spectrum if the oxidation of MXene occurred.⁴¹ Thus the presence of Ti³⁺ 2p_{3/2} and 2p_{1/2} peaks authenticates that the MXene nanosheets can still remain unoxidized during the synthesis process. The peaks of Ti–O species arise from the formation of Ti–O bonds between the MXene and oxygen-containing functional groups on the surface.⁴² The C 1s XPS spectrum in Fig. 4e exhibits the characteristic peaks at 280.7, 283.3, and 284.8 eV, assigned to the C–Mo, C–Ti, and C–O bonds, respectively. The presence of C–Mo peak indicates the strong interaction between MoSe₂ and the MXene.⁴³

The electrochemical behavior of the MoSe₂@MXene-30 composite was systematically investigated in sodium-ion batteries. Cyclic voltammetry (CV) measurements were performed in the voltage window of 0.0001–3 V (vs. Na/Na⁺) at a scan rate of 0.1 mV s⁻¹. As shown in Fig. 5a, the CV curves of the MoSe₂@MXene-30 composite for the first two cycles exhibit

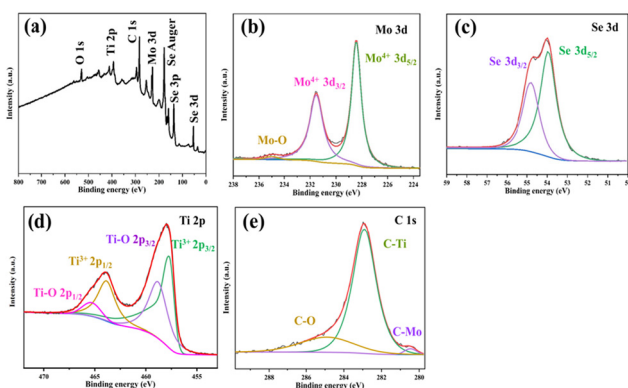


Fig. 4 XPS profiles of MoSe₂@MXene-30 composites: (a) full spectrum, (b) Mo 3d, (c) Se 3d, (d) Ti 2p, and (e) C 1s.

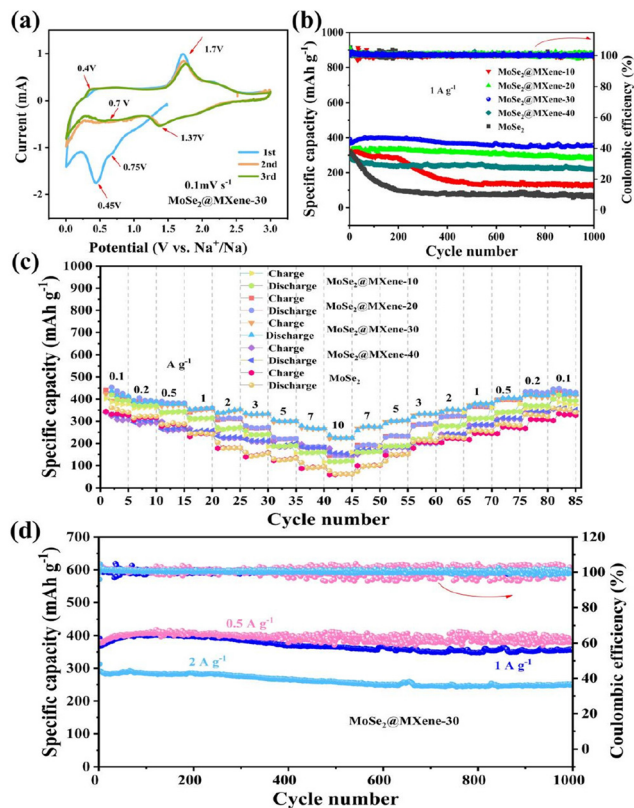


Fig. 5 (a) CV curves of MoSe₂@MXene-30 at a scan rate of 0.1 mV s⁻¹. (b) Cycling performance of MoSe₂ and different MoSe₂@MXene samples at 1 A g⁻¹. (c) Rate performance of MoSe₂ and MoSe₂@MXene composites at different current densities. (d) Long-term cycling discharge capacities and coulombic efficiencies of MoSe₂@MXene-30 at different current densities of 0.5, 1.0, and 2.0 A g⁻¹.

significant differences. The discrepancy is primarily attributed to the formation of SEI films during the first cycle.^{43,44} In the initial cycle, two cathodic peaks are observed at 0.75 V and 0.45 V, respectively. The former peak is ascribed to the initial intercalation of sodium ions into MoSe₂ layers, while the latter peak at 0.45 V is associated with the conversion of Na_xMoSe₂ into metallic Mo and Na₂Se, along with the formation of the SEI layer.^{37,43} Two anodic peaks are observed at 0.4 V and 1.7 V owing to the deinsertion of sodium from Na₂Se and Na_xMoSe₂, respectively.^{27,45} In the second and third cycles, the redox peaks appear nearly at the same positions as the first cycle, indicating the excellent cycling stability of the MoSe₂@MXene-30 composite. Notably, in the second cycle, two additional cathodic peaks emerged at 1.37 V and 0.7 V, corresponding to the intercalation of sodium ions into Se after the formation of SEI layer, namely the reduction of Se to Na₂Se_x and Na₂Se_x to Na₂Se, respectively.^{43,46,47}

The rate performance of pure MoSe₂ and MoSe₂@MXene series composites was evaluated in the current density range of 0.1–10 A g⁻¹ (Fig. 5c). The results demonstrate that MoSe₂@MXene composites exhibit superior rate performance to pure MoSe₂, whether at low or high current densities.

MoSe₂@MXene-30 composite displays the best electrochemical performance. At current densities of 0.1, 0.2, 0.5, 1.0, 2.0, and 3.0 A g⁻¹, it delivers specific capacities of 415, 385, 376, 355, 346, and 332 mA h g⁻¹, respectively. Even at high current densities of 5.0, 7.0, and 10.0 A g⁻¹, the specific capacity can remain 301, 268, and 230 mA h g⁻¹, respectively. Remarkably, when the current density drops back to 0.1 A g⁻¹, the reversible capacity can restore 421 mA h g⁻¹ without any capacity fading. These results further prove that MoSe₂ supported on hollow MXene spheres not only significantly improves the poor electrical conductivity of MoSe₂, but also enhances the structural stability. Thus, MoSe₂@MXene composites show excellent cycling properties and rate performance at high current density.

Fig. 5b manifests the cycling performance of pure MoSe₂ and four different MoSe₂@MXene composites at a current density of 1 A g⁻¹. The initial reversible capacity of the pure MoSe₂ electrode is 319.6 mA h g⁻¹. However, after 1000 cycles, the capacity of the MoSe₂ electrode sharply declines to 41.8 mA h g⁻¹, with only 13.1% retention rate of the initial capacity. The remarkable degradation is attributed to the agglomeration of the flower-like MoSe₂ nanostructures. The edges of MoSe₂ nanoflakes gradually fracture during the cycling, which causes a rapid decrease in electrochemical performance. In contrast, MoSe₂@MXene-10, -20, -30, and -40 electrodes exhibit retention rates of 42.1%, 89.6%, 93.7%, and 80.9%, respectively, after 1000 cycles. Notably, the MoSe₂@MXene-30 electrode demonstrates the best cycling stability, with an initial capacity of 374.3 mA h g⁻¹ and a high reversible capacity of 350.7 mA h g⁻¹ after 1000 cycles.

To further evaluate the cycling stability of MoSe₂@MXene-30 composite, cycling tests are conducted at different current densities (Fig. 5d). At a current density of 0.5 A g⁻¹, the electrode reaches an initial reversible capacity of 386.5 mA h g⁻¹ and maintains the capacity of 367.6 mA h g⁻¹ after 1000 cycles, corresponding to the retention rate of 95.1%. At a higher current density of 2 A g⁻¹, the capacity decreased slightly from the initial 292.3 mA h g⁻¹ to 261.1 mA h g⁻¹ after 1000 cycles, with a retention rate of about 89.1%. Hollow MXene spheres not only serve as a robust bracket to mitigate the agglomeration of MoSe₂ nanoflakes but also reduce the size of the MoSe₂@MXene-30 sample, which can enhance the interaction between the MoSe₂@MXene-30 electrode and the electrolyte and promote exceptional cycling stability.^{37,48} However, MoSe₂@MXene-10 fails to effectively alleviate the agglomeration issues of MoSe₂ due to the low MXene content, resulting in relatively poor cycling stability. Similarly, MoSe₂@MXene-40 composites with low proportion of MoSe₂ possess significantly low capacities due to insufficient active material. The incorporation of MXene substantially enhances the electrochemical performance of MoSe₂-based composites, particularly at high current densities.

To further elucidate the electrochemical behavior of the MoSe₂@MXene-30 composite, the cyclic voltammetry (CV) characteristics were investigated at different scan rates (Fig. 6a). The results indicate that the CV curves of MoSe₂@MXene-30 exhibit similar profiles at a scan rate in the range of 0.2–1 mV s⁻¹. The redox peak intensities gradually

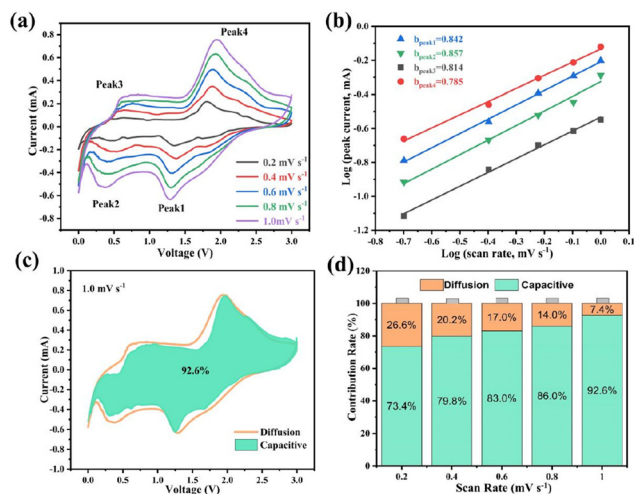


Fig. 6 Electrochemical test of the MoSe₂@MXene-30 composite: (a) CV curves at a scanning rate between 0.2 and 1 mV s⁻¹, (b) relationship between the peak current and the scan rate, (c) capacitive contribution curve at a scan rate of 1 mV s⁻¹, and (d) contribution rates at different scan rates.

increase with the increase in scan rate, accompanied by minor shape deformation. This suggests that the MoSe₂@MXene-30 composite possesses excellent rate performance. At a scan rate of 1 mV s⁻¹, the cathodic peaks (peak 1 and peak 2) are located at 1.3 V and 0.45 V, while the anodic peaks (peak 3 and peak 4) appear at 0.5 V and 2 V, respectively. Moreover, the area under the CV curve reflects the total capacity, which includes the contributions of diffusion-controlled and capacitive processes. The pseudo capacitive behavior of the electrode material can be evaluated using eqn (1) and (2):^{49,50}

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

$$\log i = b \log v + \log a \quad (2)$$

where v represents the scan rate (mV s⁻¹), i denotes the total current (mA), and the characters a and b are adjustable parameters. The value of b was determined by the fitted slope of $\log i$ vs. $\log v$ plot. When the value of b is equal to 0.5 or 1, the electrochemical reaction is regarded as the diffusion-controlled process or surface-controlled pseudocapacitive process, respectively.^{51,52} As shown in Fig. 6b, the values of b obtained from the linear fitting of the cathodic peaks (peak 1 and peak 2) are 0.842 and 0.857, respectively, whereas the values of b are 0.14 and 0.785 acquired from the anodic peaks (peak 3 and peak 4), respectively. These results illustrate that the MoSe₂@MXene-30 composite exhibits a significant pseudocapacitive behavior.⁵³ The proportions of the capacitive effects and diffusion-controlled contributions were calculated using eqn (3) and (4):^{50,54}

$$i = k_1v + k_2v^{1/2} \quad (3)$$

$$i/v^{1/2} = k_1v^{1/2} + k_2 \quad (4)$$

The capacity is composed of diffusion contribution ($k_2v^{1/2}$) and capacitive control (k_1v).⁵⁵ As shown in Fig. 6c, the ratio of

capacitive contribution at a scan rate of 1.0 mV s^{-1} is as high as 92.6%. Moreover, Fig. 6d illustrates that the capacitive contribution gradually increases with the increase in scan rate. It indicates that the $\text{MoSe}_2@MXene-30$ composite exhibits dominant capacitive behavior at higher scan rates, which accounts for its excellent cycling stability and superior rate performance.

To evaluate the reaction kinetics of MoSe_2 and $\text{MoSe}_2@MXene-30$ electrodes, electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of $0.01\text{--}10^5 \text{ Hz}$. Fig. 6a and b present the EIS results of the two electrodes for the third cycle and 1000th cycle, respectively. The Nyquist plots consist of three distinct regions: a semicircle in the high-frequency region representing the solid electrolyte interface (SEI) film resistance (R_f), a semicircle in the mid-frequency region assigned to the charge transfer resistance (R_{ct}) at the interface between the electrode and the electrolyte, and a sloped line in the low-frequency region indicative of ion diffusion resistance, also known as Warburg impedance (Z_w).⁵⁶ Additionally, R_s represents the electrolyte resistance.⁵⁷ The impedance parameters obtained using ZView software are summarized in Table 1.

It is revealed that the R_s values of both MoSe_2 and $\text{MoSe}_2@MXene-30$ remain nearly unchanged before and after the cycles, confirming that no electrolyte decomposition occurs during excessive charge–discharge processes. After 1000 cycles, the value of R_f for pristine MoSe_2 increases from 28.45 to 90.24 Ω , while $\text{MoSe}_2@MXene-30$ retains a relatively constant R_f value. It is suggested that $\text{MoSe}_2@MXene-30$ forms a robust SEI layer, whereas the SEI layer on pristine MoSe_2 tends to rupture and degrade during the cyclic processes.⁵⁸ $\text{MoSe}_2@MXene-30$ has obviously lower R_{ct} values than those of pristine MoSe_2 before and after the cycles, demonstrating that the incorporation of MXenes effectively enhances the conductivity of MoSe_2 . There is a sharp increase in the value of R_{ct} for pristine MoSe_2 after the 1000th cycle, but only a slight increment in the R_{ct} value is seen for the $\text{MoSe}_2@MXene-30$ electrode. It is assumed that the incorporation of MXene relieves the collapse of the structure on account of the volume expansion during the electrochemical cyclings and improves the structural stability.^{59,60} The SEM patterns of $\text{MoSe}_2@MXene-30$ after 1000 cycles are shown in Fig. S1k and l.† It is revealed that $\text{MoSe}_2@MXene-30$ still retains the hollow spherical structure and MoSe_2 is uniformly distributed on the surface of MXene spheres even after 1000 cycles. The highly stable struc-

Table 1 Fitting results of the Nyquist plots of MoSe_2 and $\text{MoSe}_2@MXene-30$ at the 3rd and 1000th cycles

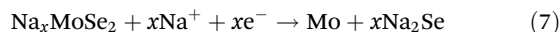
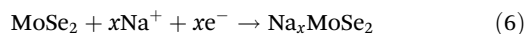
Cycle	MoSe_2		$\text{MoSe}_2@MXene-30$	
	3rd	1000th	3rd	1000th
R_s (Ω)	5.26	6.39	3.71	2.85
R_f (Ω)	28.45	90.24	10.8	15.45
R_{ct} (Ω)	160.6	446.2	96.5	160.1

ture of $\text{MoSe}_2@MXene-30$ not only enhances the cycling performance but also prolongs the lifespan.

The Na^+ diffusion coefficients were obtained from galvanostatic intermittent titration technique (GITT), as shown in Fig. 7c and d. The sodium-ion diffusion coefficient (D_{Na^+}) was calculated using eqn (5):^{61,62}

$$D_{\text{Na}^+} = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (5)$$

where n_m , V_m , and S represent the number of moles (mol), molar volume ($\text{cm}^3 \text{ mol}^{-1}$), and the electrode/electrolyte contact area (cm^2) of the tested sample, respectively. ΔE_s and ΔE_t correspond to the voltage changes (V) during steady-state and constant current discharge, respectively.⁶¹ As shown in Fig. 7d, the value of D_{Na^+} for the MoSe_2 electrode ranges from $10^{-13.09}$ to $10^{-11.37} \text{ cm}^2 \text{ s}^{-1}$ when the discharge voltage is between 0 and 3 V, whereas the diffusion coefficient for the $\text{MoSe}_2@MXene-30$ electrode ranges from $10^{-11.87}$ to $10^{-9.11} \text{ cm}^2 \text{ s}^{-1}$. Both curves exhibit the local minimum value of D_{Na^+} when the discharge voltage is at 0.55 V, 0.8 V, and 1.5 V. Around 1.5 V, some MoSe_2 in the composite undergoes the intercalation reaction with sodium ions to form a Na_xMoSe_2 intermediate. Further intercalations of sodium ions with the Na_xMoSe_2 intermediate are corresponding to the peak at potentials near 0.8 V and 0.55 V.^{22,46} Eqn (6) and (7) describe the intercalation reactions:



This is consistent with the analysis of the cyclic voltammetry (CV) tests discussed above. Clearly, the $\text{MoSe}_2@MXene-30$ electrode shows a higher value of D_{Na^+} than that of the MoSe_2 electrode, indicating that MoSe_2 nanoflakes anchored on

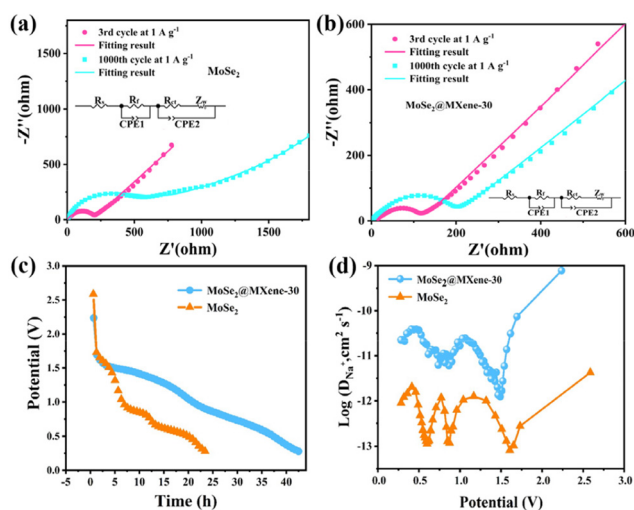


Fig. 7 (a and b) Nyquist plots of MoSe_2 and the $\text{MoSe}_2@MXene-30$ composite after the 3rd and the 1000th cycles; (c) GITT discharge curves and (d) Na^+ diffusion coefficients of MoSe_2 and $\text{MoSe}_2@MXene-30$ electrodes.

MXene spheres provide more active sites for sodium ion reactions and facilitate the faster sodium ion intercalation reaction.

To better understand the impact of MXenes on the properties of MoSe₂, density functional theory (DFT) calculations were performed to simulate the physicochemical properties of the MoSe₂@MXene composite.⁴⁶ As depicted in Fig. 8a, pure MoSe₂ has a clear bandgap of 1.176 eV, indicating that MoSe₂ exhibits a typical semiconducting behavior. However, MXene and MoSe₂@MXene demonstrate a metallic behavior near the Fermi level, with a bandgap of zero, as shown in Fig. 8b and c. It is suggested that the introduction of MXene significantly enhances the electronic conductivity of MoSe₂. The density of states (DOS) for MoSe₂, MXene, and MoSe₂@MXene (Fig. 8d) are consistent with the band structure results. The patterns of the charge density difference for MoSe₂ and MoSe₂@MXene models are depicted in Fig. 8e. The brown and yellow electron clouds reflect the gain and loss of electrons, respectively. It is illustrated that for the MoSe₂@MXene composite, Se atoms in the Na–Se bond accumulate a substantial amount of electrons.⁶³ Furthermore, as shown in Fig. 8f, the adsorption energy of Na⁺ on MoSe₂@MXene is –1.21 eV, which is lower than that of MoSe₂ (–1.16 eV). It is confirmed that the presence of MXenes can thermodynamically favor the adsorption of Na⁺ on MoSe₂, thereby promoting Na⁺ intercalation in the charge and discharge processes.⁶⁴

Conclusions

Hollow MoSe₂@MXene spheres with a unique MoSe₂ array structure were prepared by electrostatic adsorption and hydrothermal methods. The hollow structure not only alleviates structural damage due to volume expansion during cycling, but also enhances the electrolyte penetration and the contact area between the electrolyte and the active material. The presence of MXene and the unique MoSe₂ arrayed structure significantly improve the specific surface area and active sites for sodium-ion storage. Furthermore, the MXene obviously enhances the electrical conductivity of the MoSe₂@MXene series electrodes and accelerates the sodium-ion diffusion. MoSe₂@MXene-30 exhibits superior specific capacity and rate capability. At a current density of 1 A g^{–1}, the composite retained a specific capacity of 350.7 mA h g^{–1} during 1000 cycles with a capacity retention of 93.7%. The specific capacity is 261.1 mA h g^{–1} after 1000 cycles with a retention rate of 89.1% at a current density of 2 A g^{–1}. The specific capacities can still remain at 301, 268, and 230 mA h g^{–1} even at high current densities of 5.0, 7.0, and 10.0 A g^{–1}, respectively. MoSe₂ nanosheets *in situ* supported on the hollow MXene spheres show the potential prospects in sodium-ion battery electrodes.

Data availability

Data will be made available upon request.

Conflicts of interest

The authors declare that they have no conflict of interest.

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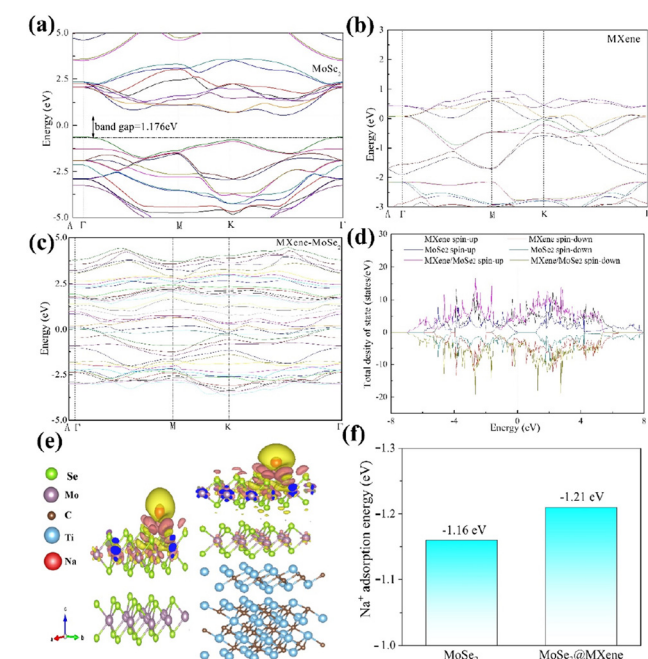


Fig. 8 (a–c) Energy band structure of MoSe₂, MXene, and MoSe₂@MXene; (d) total density of states for MoSe₂, MXene and MoSe₂@MXene; (e) charge density differences of Na⁺ adsorbed on MoSe₂ and MoSe₂@MXene; (f) adsorption energy of Na⁺ adsorbed on the surfaces of MoSe₂ and MoSe₂@MXene models.

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