

Hydrochloric Acid-Assisted Synthesis of Highly Dispersed MoS₂ Nanoflowers as the Cathode Material for Mg-Li Batteries

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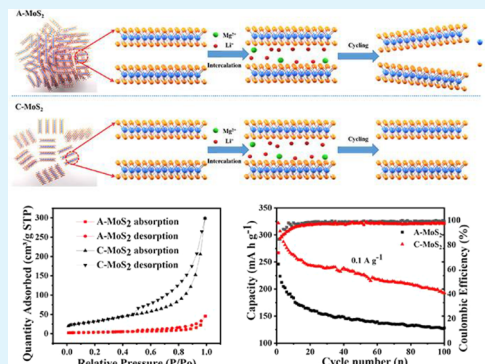
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Supporting Information

ABSTRACT: The layered material MoS₂ has significant potential as a cathode material for hybrid Mg²⁺/Li⁺ batteries (MLIBs) due to its fast two-dimensional ion diffusion channel. However, the low capacity and poor cycling stability limit the practical application of MoS₂. Herein, highly dispersed MoS₂ nanoflowers with a large Brunauer–Emmett–Teller (BET) area of 118.25 m² g⁻¹ and a large lattice spacing of 0.65 nm are synthesized by a one-step hydrothermal method. The obtained MoS₂ nanoflowers deliver a remarkable reversible capacity of 321 mA h g⁻¹ at 0.1 A g⁻¹. Notably, it displays an impressive cycling stability with a reversible capacity of 103 mA h g⁻¹ over 600 consecutive cycles at 1 A g⁻¹. The favorable electrochemical properties of the MoS₂ are attributed to the large BET area and increased lattice spacing that are more conducive to the full contact between the electrolyte and the material, thus promoting the diffusion of ions and improving the reaction kinetics. The results of the present study offer an idea to prepare highly dispersed MoS₂ with enhanced capacity and durability.

KEYWORDS: hybrid Mg²⁺/Li⁺ batteries, MoS₂, nanoflowers, surface area, reaction kinetics



1. INTRODUCTION

Lithium-ion batteries (LIBs) have attracted wide attention due to its high gravimetric energy density, high theoretical capacity, and long-term cycling durability.^{1–3} However, the shortage of lithium resources and the defect of lithium dendrite growth on the anode surface restrict its practical applications.^{4,5} Considering this case, magnesium-ion batteries (MIBs) have aroused wide interest due to the resource abundance and dendrite-free growth on the magnesium anode.⁶ Besides, MIBs have a volumetric capacity of 3833 mA h cm⁻³ and a gravimetric capacity of 2205 mA h g⁻¹ as Mg²⁺ transfers more electrons.^{7,8} However, some grand challenges need to be overcome in order to promote the development of MIBs.⁹ The slow diffusion kinetics can lead to a high polarization during charge–discharge processes.¹⁰ To resolve this obstacle, MLIBs with a dual salt electrolyte were designed.¹¹ The system of hybrid battery comprises the Mg metal as the anode, Mg²⁺/Li⁺ dual salt as the electrolyte, and intercalated materials as cathodes, which can not only take full advantage of the merit of dendrite-free Mg anode, but also realize the rapid kinetic of Li⁺ in the cathode materials.^{12,13} To date, the most reported MLIBs are Daniell-type cells, where only Li⁺ is de-intercalated/intercalated from the cathode materials during charge–discharge process, and the energy density of the battery inevitably depends on the lithium salt solubility in the electrolyte.^{14–17} However, the solubility of lithium salt in the solvent limits the energy density of MLBs in practice.⁶ If the

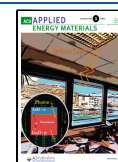
cathode materials can accommodate both Li⁺ and Mg²⁺, the MLIBs will avoid the disadvantages of Daniell-type cells and display a high energy density.¹⁸ Therefore, it is necessary to search for suitable cathode materials to accommodate Mg²⁺/Li⁺.

MX₂ (M = Ti, V, Mo, and W; X = S and Se) have been considered as promising cathode materials for MIBs because they can greatly improve the transport of Mg²⁺ through the unique two-dimensional structure.^{19–22} Molybdenum disulfide (MoS₂), as one typical member of the most classical transition-metal dichalcogenides, has attracted wide concern as the cathode of MLIBs.^{23,24} Although bulk MoS₂ is not conducive to Mg²⁺ intercalation, the exfoliated MoS₂ is more favorable to the diffusion and storage of Mg²⁺.^{25,26} For example, Chang's group reported the Li intercalation-exfoliated MoS₂, which optimized the microstructure of MoS₂ for easier intercalation of various ions.⁵ Furthermore, Jiao and co-workers prepared exfoliated three-dimensional (3D) porous MoS₂ and enlarged the interlayer spacing by intercalating graphene into MoS₂. The flexible electrode showed an initial specific capacity of

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115.9 mA h g⁻¹ at 0.1 A g⁻¹ and high reversible specific capacity of 82.5 mA h g⁻¹ over 50 cycles, which is largely improved compared with bulk MoS₂.²⁷ Although there are many reports on the synthesis of dispersed MoS₂, such as mechanical exfoliation,²⁸ electrochemical exfoliation,²⁷ and liquid exfoliation,²⁹ these methods normally involve complicated synthesis steps or are time- and energy-consuming. Therefore, seeking a simple method to synthesize highly dispersed nano-MoS₂ is of great significance for its application.

In this work, nanostructured MoS₂ with different dispersion degrees was synthesized using hydrochloric acid to control the concentration of sulfur ions in the solution. When the pH of the solution was adjusted to 0.9, the highly dispersed MoS₂ nanoflowers with a large Brunauer–Emmett–Teller (BET) area of 118.25 m² g⁻¹ and large lattice spacing of 0.65 nm are obtained. The dispersed morphology and increased lattice spacing are more conducive to the full contact between electrolyte and material and shorten the ion diffusion path distance in the electrode, which promotes the diffusion of ions and improves the reaction kinetics. As a result, the MoS₂ delivers high initial discharge capacities (321.9 and 200.6 mA h g⁻¹ at 0.1 and 1 A g⁻¹, respectively) and excellent cycling performance (192.8 mA h g⁻¹ over 100 consecutive cycles at 0.1 A g⁻¹ and 102.8 mA h g⁻¹ over 600 consecutive cycles at 1 A g⁻¹, respectively).

2. EXPERIMENTAL SECTION

2.1. Synthesis of MoS₂. The raw materials used in the experiment were all analytically pure and were used without further purification. The MoS₂ with different morphologies were synthesized by a one-step hydrothermal reaction using ammonium molybdate tetrahydrate (H₂₄Mo₇N₆O₂₄·4H₂O) and thiourea (CH₄N₂S) as raw materials, and hydrochloric acid (HCl) was used as a pH regulator of the solution. In a typical synthesis, 1 mM (1.2359 g) H₂₄Mo₇N₆O₂₄·4H₂O and 15 mM (1.1989 g) CH₄N₂S were dissolved in a 60 mL solution with the pH of 7. After stirring for 30 min, it was transferred into a 100 mL Teflon-lined stainless autoclave and kept at 220 °C for 18 h. Then, the obtained product needs to be centrifuged three times with ethanol and deionized water, and the A-MoS₂ sample could be obtained after drying in vacuum kept at 60 °C for 12 h. B-MoS₂, C-MoS₂, and D-MoS₂ were fabricated when the pH of the solution was 4, 0.9, and 0.6, respectively.

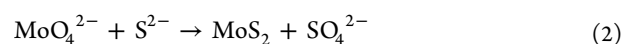
2.2. Materials Characterizations. The as-prepared materials were tested by X-ray diffraction (XRD, Rigaku D/max 2000 diffractometer). The chemical state and element valence of the C-MoS₂ were measured by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha⁺). The morphology was obtained by field-emission scanning electron microscopy (FE-SEM-4800-1, Japan). The microstructure analysis [(transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), and selected area electron diffraction (SAED)] was carried out on the Thermo Fischer Talos F200x. The specific surface area of MoS₂ was recorded by the BET (Tristar II 3020 Version 3.02). Raman spectra of MoS₂ were characterized by the excitation wavelength of 532 nm (XploRA, France).

2.3. Electrochemical Measurements. The electrochemical performance of MoS₂ was characterized by using CR2032 coin cells. The active materials (70 wt %), conductive agent (20 wt %), and binder (10 wt %) were mixed to make a homogeneous slurry. The slurry was coated on stainless steel. The working electrode was obtained after drying at 80 °C for 12 h. The counter electrode and separator are magnesium metal and glass fiber, respectively. The APC electrolyte was synthesized using the method reported by Oren Mizrahi et al.³⁰ 0.25 M aluminum chloride (AlCl₃) was added to 7.5 mL of tetrahydrofuran to form a mixed solution, and then 2.5 mL of phenyl magnesium chloride (MgPhCl) was added. It was magnetically stirred for 24 h, and then lithium chloride (LiCl) of 0.01 M was added

and stirred for 24 h to form the 1 M LiCl/0.25 M APC electrolyte. The whole process was carried out in a glovebox filled with argon gas. The galvanostatic charge and discharge (GCD) test was carried out on the NETWARE BTS-5 V battery test system. Cyclic voltammetry (CV) was carried out on the electrochemical workstation at a scanning rate of 0.1 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) test (frequency from 10⁻² to 10⁵ Hz with voltage amplitude 5 mV) was conducted with an electrochemical workstation.

3. RESULTS AND DISCUSSION

The major steps involved in the synthesis are presented in Figure 1a. The chemical reaction equation of MoS₂ can be described as follows:^{31,32}



As shown in formulas 1 and 2, CH₄N₂S hydrolyzes in solution to produce S²⁻ and MoS₂ is synthesized by the reaction of S²⁻ and MoO₄²⁻. The formulas 3 and 4 indicate that sulfur ions are consumed by electrolysis in the solution. The sulfur concentration is the key parameter that controls the prospects of the material growth.³³

When the concentration of H⁺ was increased, the concentration of S²⁻ would also change, thus affecting the morphologies of MoS₂. Figure 1b–e shows the variations in MoS₂ by adjusting the pH value of the solution. As shown in Figure 1b and c, A-MoS₂ and B-MoS₂ show that the bulk structure is composed of nanosheets. For C-MoS₂, a unique nanoflower structure formed with highly dispersed nanosheets is observed as shown in Figure 1d. D-MoS₂ (Figure 1e) is also composed of nanosheets but tends to aggregate (Figure 1d). Clearly, MoS₂ nanosheets with different dispersion degrees can be synthesized by controlling the concentration of S²⁻ to affect the synthesis rate of MoS₂. The unique structure of highly dispersed nanosheets for C-MoS₂ is more conducive to the full contact between electrolyte and material and shortens the ion diffusion path distance in the electrode, which promotes the diffusion of ions and improves the reaction kinetics.

The as-prepared MoS₂ was characterized by XRD (Figure 2a). All diffraction peaks of the as-prepared MoS₂ index accurately to the MoS₂ with hexagonal structure (PDF#75-1539). Compared with the A-MoS₂, however, the peaks of B-MoS₂/C-MoS₂/D-MoS₂ at the (002) plane shift to a low angle. For example, the diffraction peaks of A-MoS₂ and C-MoS₂ at the (002) plane are observed around 14.3 and 13.7°, respectively. The shift of the diffraction peak indicates an increased interlayer distance from 0.62 nm (A-MoS₂) to 0.65 nm (C-MoS₂), according to Bragg's formula.²⁶ The increase in lattice spacing should be ascribed to the intercalation of NH₄⁺ and the formation of lattice oxygen in the MoS₂ layers during the hydrothermal process.^{34,35} The Raman spectra in Figure 2b further present the structure of A-MoS₂ and C-MoS₂, in which the characteristic peaks observed around 380.2/382.1 and 406.7/406.6 cm⁻¹ are corresponding to E_{2g}¹ and A_{1g} Raman modes, respectively. The phenomenon of the peak shift is mainly attributed to the fact that the interlayer expansion results in a decrease in the interlaminar van der Waals force, which leads to a stronger out-of-plane vibration.^{36,37} Figure 2c shows the N₂ adsorption/desorption isotherm of the as-

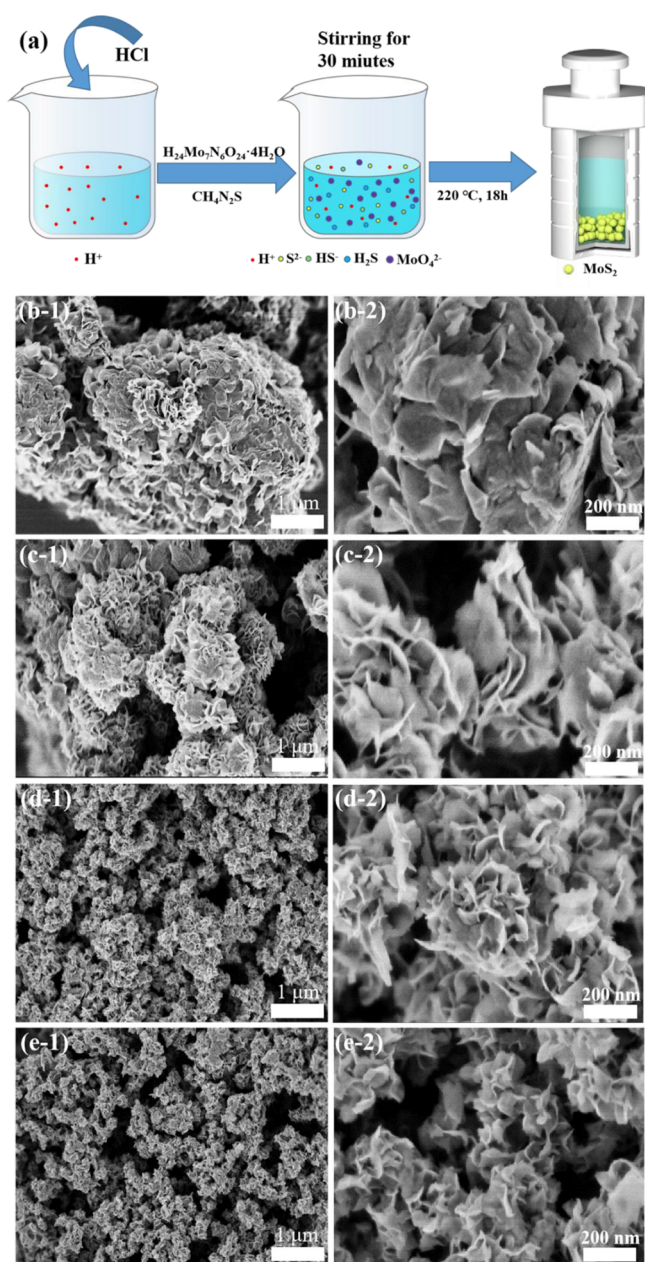


Figure 1. (a) Schematic illustration of the synthesis process of MoS₂. SEM images of (b) A-MoS₂, (c) B-MoS₂, (d) C-MoS₂, and (e) D-MoS₂.

prepared MoS₂ materials. A-MoS₂, B-MoS₂, and D-MoS₂ possess a BET area of 13.27, 18.75, and 102.32 m² g⁻¹, respectively, while the C-MoS₂ possesses a larger BET area of 118.25 m² g⁻¹. It can be seen that there are more abundant interconnected nanostructures in C-MoS₂. XPS was used to investigate the chemical states of Mo and S in the samples with the C-MoS₂, as shown in Figures 2d,e and S1, which indicates the presence of C, O, Mo, and S elements. Figure 2d shows that there are three main characteristic peaks in the spectra of Mo 3d. The peak with a binding energy of 226.9 eV belongs to S 2s, and the other two peaks with binding energies of 229.8 and 233.0 eV are indexed to Mo 3d_{5/2} and Mo 3d_{3/2} of Mo⁴⁺, respectively.³⁸ The characteristic peaks of 162.6 and 163.8 eV displayed in Figure 2e are indexed to S 2P_{3/2} and S 2P_{1/2}, respectively.³⁹

The TEM images of A-MoS₂ show that the material is seriously stacked (Figure 2f), whereas C-MoS₂ has the feature of thin nanosheets in Figure 2g. The highly dispersed morphology of C-MoS₂ affirmed by TEM fits well with the results of SEM and BET. The abovementioned results indicate that by controlling the pH, two-dimensional MoS₂ nanosheets with the larger BET area were successfully synthesized. The HR-TEM images reveal that the interlayer spacing of A-MoS₂ is 0.62 nm, whereas the interlayer distance of C-MoS₂ expands to 0.65 nm (Figure 2h and i), consistent with the XRD results. The uniform distribution of Mo, S, and O elements in the materials could be seen from SEM energy-dispersive mapping images (Figure S2). The presence of the O element evidences the formation of lattice oxygen in the sample.^{34,35} The SAED pattern demonstrates the polycrystalline structure for the C-MoS₂ material (Figure S3). Clearly, the C-MoS₂ material with a larger exposed surface area and interlayer spacing is beneficial to the full contact between electrolyte and material.

The CR2032-type coin cells were assembled to evaluate the electrochemical performance. The redox peaks of the initial three CV curves of C-MoS₂ are around 1.2 and 0.6 V, corresponding to the Mg²⁺/Li⁺ extraction and insertion behavior (Figure 3a). At current densities of 0.1, 0.5, 1, 2, 5, and 10 A g⁻¹, the C-MoS₂ electrode possesses high reversible capacities of 321.2, 218.9, 169.2, 137.3, 105.6, and 80.6 mA h g⁻¹ (Figure 3b and c). For comparison, A-MoS₂ shows reversible capacities of 261.3, 149.8, 121.4, 93.9, 51.4, and 19.4 mA h g⁻¹. Obviously, the C-MoS₂ electrode displays impressive rate performance and higher reversible capacities. The B-MoS₂ and D-MoS₂ electrodes also achieve superior rate ability compared to the A-MoS₂ electrode, indicating that the high dispersion and expanded lattice spacing dominate the electrochemical performance of the MoS₂ electrode (Figure S4).

The cycle stability of MoS₂ was tested. The C-MoS₂ and A-MoS₂ electrodes deliver initial specific capacities of 321.9 and 245.9 mA h g⁻¹ at 0.1 A g⁻¹ (Figure 3d). C-MoS₂ can maintain a specific capacity of 192.8 mA h g⁻¹ after 100 cycles, while the capacity of A-MoS₂ decays to 128.1 mA h g⁻¹. Similarly, the discharge capacity of B-MoS₂/D-MoS₂ is also higher than that of A-MoS₂ (Figure S5), giving the same tendency as observed in rate performance. Figure S6 shows the GCD data of A-MoS₂ and C-MoS₂ cathodes at 0.1 A g⁻¹. The long cycling performance of A-MoS₂ and C-MoS₂ at 1 A g⁻¹ is measured as shown in Figure 3e. It presents that the capacity of A-MoS₂ decreased to 70.1 mA h g⁻¹ over 600 cycles, which shows poor reversible stability. As for C-MoS₂, the reversible capacity is 103 mA h g⁻¹ over 600 cycles, showing excellent stability. We test the electrochemical performance of MoS₂ nanoflowers in pure Li⁺ electrolyte and pure Mg²⁺ electrolyte and compare it with the properties in the Mg²⁺/Li⁺ electrolyte. The Mg²⁺/Li⁺, pure Li⁺, and pure Mg²⁺ electrolytes deliver initial discharge capacities of 321.9, 30.5, and 39.3 mA h g⁻¹, respectively. The Mg²⁺/Li⁺ electrolyte can maintain a specific capacity of 244.25 mA h g⁻¹ over 20 cycles, while that of pure Li⁺ and pure Mg²⁺ electrolyte decays to 11.2 and 36.9 mA h g⁻¹. The favorable cycle performance can be obtained in the Mg²⁺/Li⁺ electrolyte (Figure S7). In addition, the cycle performance of the MoS₂ host reported in the literatures was collected and compared with C-MoS₂ (Table S1). Clearly, C-MoS₂ as the cathode material for MLBs shows a better electrochemical performance. The high capacity of the C-MoS₂ derives from the large BET area and large lattice spacing, which are conducive to the

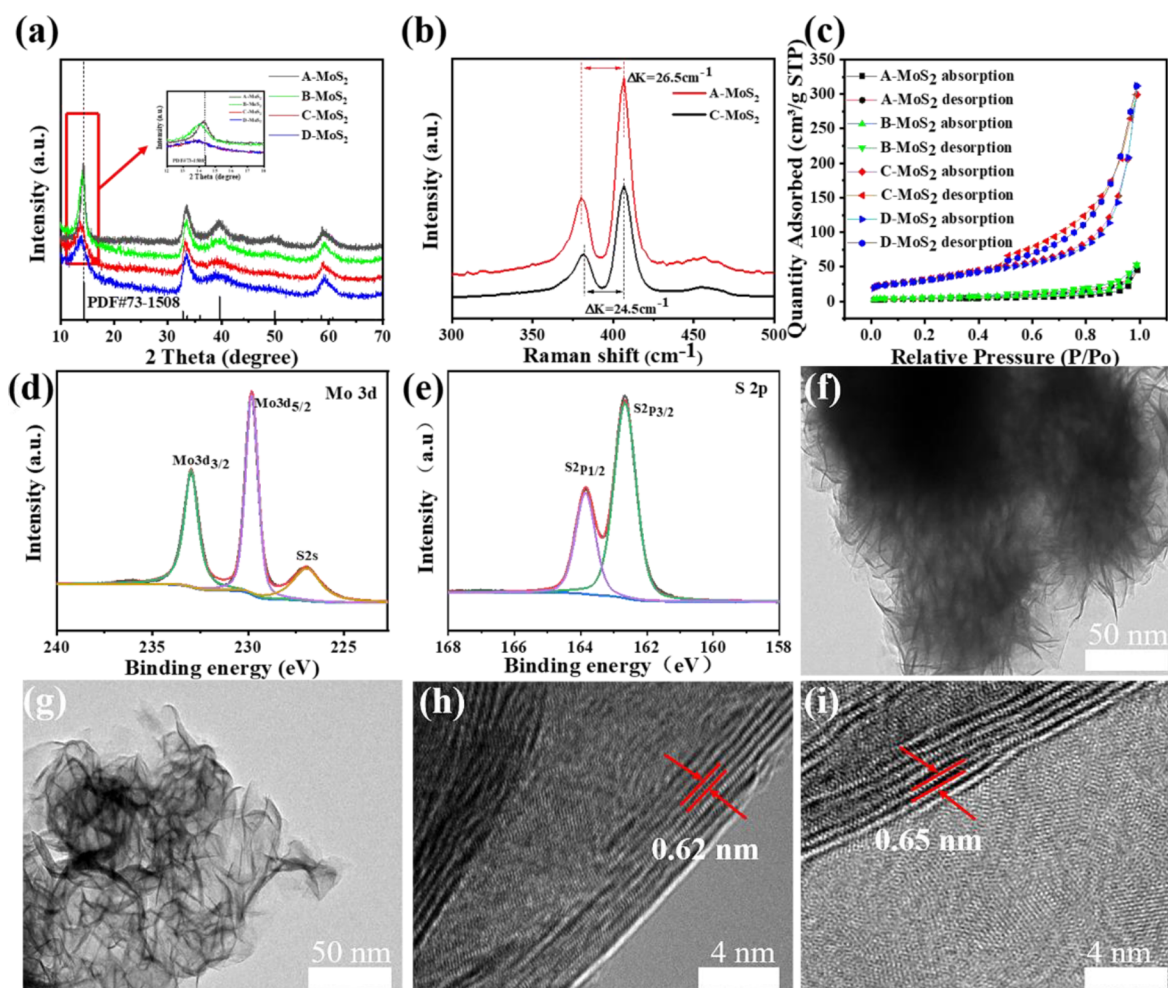


Figure 2. (a) XRD patterns of the as-prepared MoS₂ materials (the inset in the image shows the 12–18° range of MoS₂ materials). (b) Raman spectra of A-MoS₂ and C-MoS₂. (c) Nitrogen adsorption/desorption isotherm of the as-prepared MoS₂. XPS spectra of the C-MoS₂: (d) Mo 3d and (e) S 2p. (f, g) TEM and (h, i) HR-TEM images of A-MoS₂ and C-MoS₂.

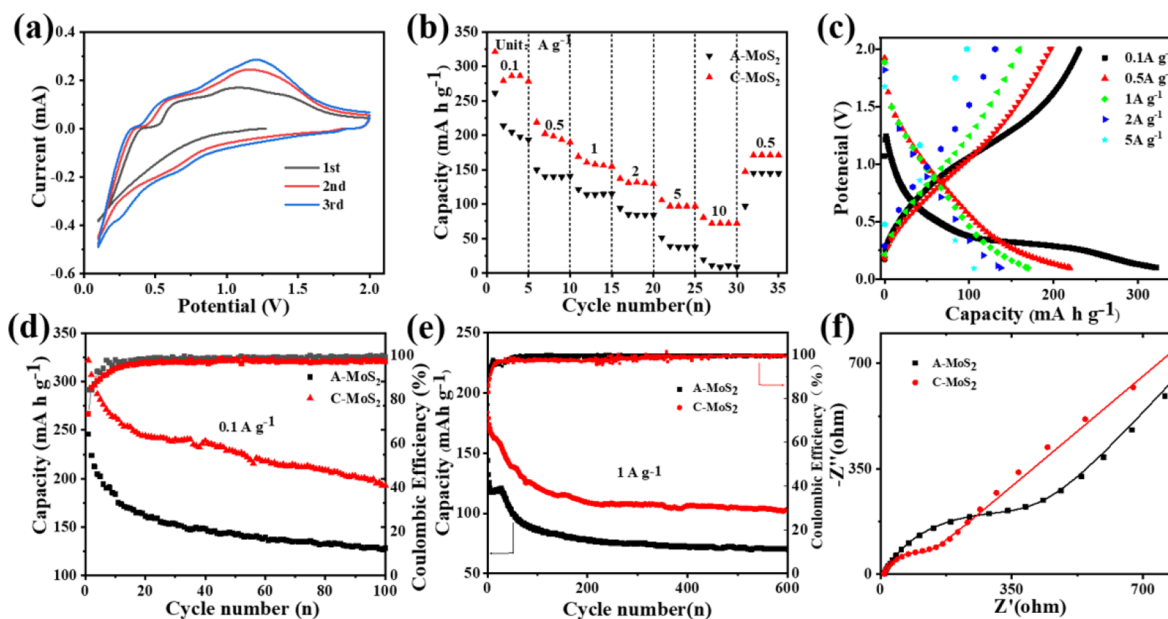


Figure 3. (a) CV profiles at 0.1 mV s⁻¹ of C-MoS₂. (b) Rate capability at 0.1–10 A g⁻¹ of A-MoS₂ and C-MoS₂. (c) Galvanostatic charge/discharge curves of C-MoS₂ batteries at various current densities. (d) Cycling performances of A-MoS₂ and C-MoS₂ at 0.1 A g⁻¹. (e) Long-term cycling stability at 1 A g⁻¹ of A-MoS₂ and C-MoS₂. (f) Nyquist plots of A-MoS₂ and C-MoS₂.

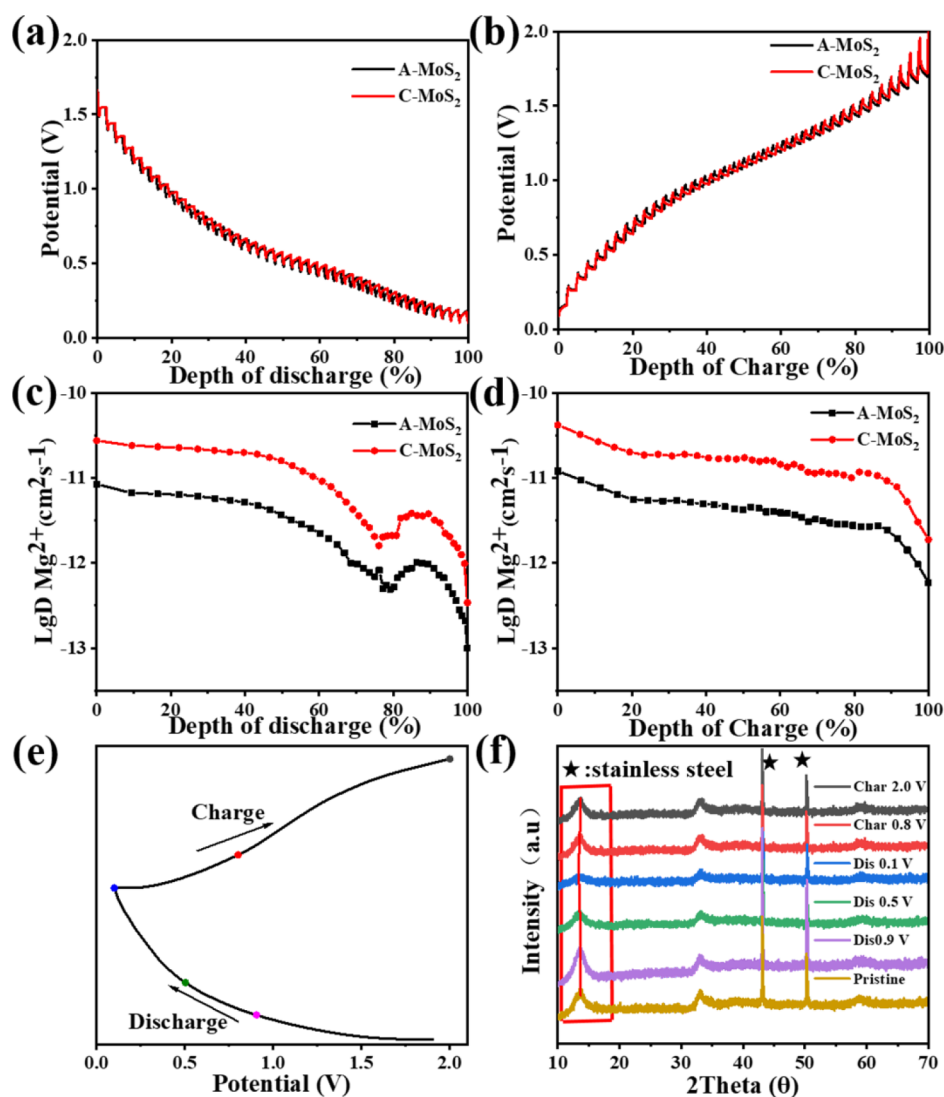


Figure 4. (a, b) GITT curves of A-MoS₂ and C-MoS₂ electrodes. (c, d) Mg²⁺ diffusion coefficient of A-MoS₂ and C-MoS₂ electrodes calculated via GITT curves in the discharged/charged state. (e) Galvanostatic charge and discharge curve of the C-MoS₂ cathode at the second cycle. (f) Ex situ XRD patterns of the C-MoS₂ electrode during the first cycle.

full contact between electrolyte and the material, and shortens the ion diffusion path distance in the electrode. In addition, EIS during the first cycling is carried out to investigate the reaction kinetics of C-MoS₂ and A-MoS₂, and the corresponding Nyquist plots are given in Figure 3f. The Nyquist plots consist of a semicircle at high frequencies and a slash at low frequencies. The semicircle corresponds to charge transfer resistance (R_{ct}), and the slash represents the Warburg impedance (Z_w) related to the Mg-Li ion diffusion.⁴⁰ We have fitted the Nyquist plots, and Figure S8 shows the equivalent circuit diagram. The R_{ct} values of C-MoS₂ and A-MoS₂ are 64.5 and 324.3 Ω , respectively, indicating that C-MoS₂ possesses much lower charge transfer resistance.

To evaluate the effect of interlayer distance and morphology on the diffusivity of ions in MoS₂, the galvanostatic intermittent titration technique (GITT) was employed to probe the diffusivity of ions.⁴¹ Figure 4a and b shows the GITT curves of A-MoS₂ and C-MoS₂. The ion diffusivity D_{GITT} can be obtained via the formula:^{42,43}

$$D_{GITT} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (5)$$

where τ , m_B , M_B , V_M , S , ΔE_t , and ΔE_s correspond to the relaxation time, the mass of active material, molar weight, molar volume, geometric area of the electrode, potential change caused by pulse and constant current charging/discharge, respectively. The calculated diffusion coefficient values of the C-MoS₂ are higher than that of A-MoS₂ (Figure 4c and d), which can be ascribed to the larger layer spacing and the dispersed two-dimensional MoS₂ nanosheets with a larger BET area, which are more conducive to ion transport. To learn the energy storage mechanism of the C-MoS₂ cathode in MLBs, ex situ XPS and ex situ XRD were carried out. Figure S9a and b shows the ex situ XPS spectra of the C-MoS₂ cathode measured at discharge and charge stages. When discharged to 0.1 V, the characteristic peaks of Li 1s and Mg 2p would appear. The characteristic peaks of Li 1s and Mg 2p would disappear and weaken after charging to 2.0 V. Figure 4f displays the ex situ XRD patterns of C-MoS₂ at different discharge/charge stages during the first cycle (marked points

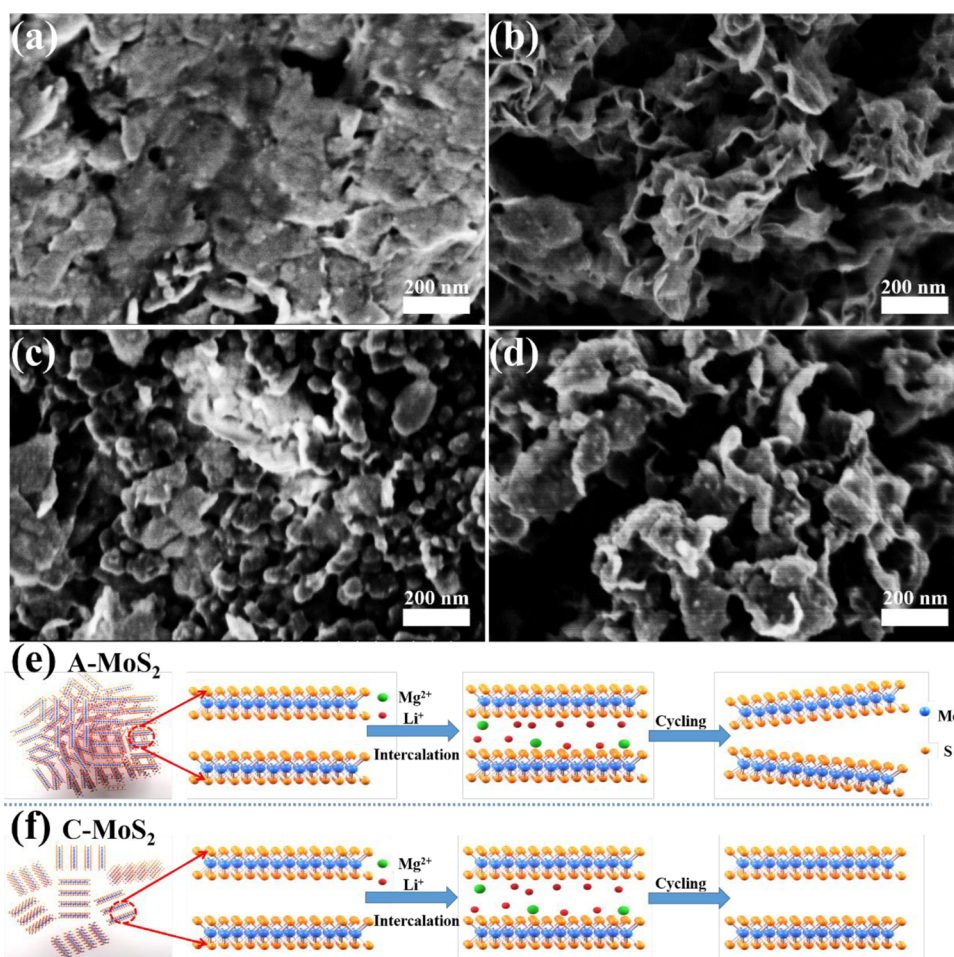


Figure 5. SEM images of A-MoS₂ and C-MoS₂ electrodes in different states. (a, b) Fresh A-MoS₂ and C-MoS₂ electrodes. (c, d) A-MoS₂ and C-MoS₂ electrodes after 50 cycles. Structure evolution scheme of (e) A-MoS₂ and (f) C-MoS₂ during the cycling process.

in Figure 4e). The pristine peak of the (002) plane for the as-prepared C-MoS₂ material is 13.65°. When discharged to 0.1 V, the characteristic peak locked at around 13.43°, which demonstrates that the (002) lattice plane gradually shifts because of the Mg²⁺/Li⁺ insertion. When charged to 2.0 V, the peak of the (002) plane would reversibly recover to 13.65° due to the Mg²⁺/Li⁺ extraction. The reversible intercalation/deintercalation of Mg²⁺/Li⁺ is indicated by the abovementioned results. The schematic illustration of the working mechanism for MLBs is shown in Figure S10. Mg²⁺ are dissolved from the Mg anode into the electrolyte, and Mg²⁺/Li⁺ are inserted into the MoS₂ electrode during the discharging process. Because the diffusion ability of lithium ions is several orders of magnitude stronger than that of magnesium ions, the diffusion of lithium ions is very important in the intercalation process of the cathode.⁴⁴ Mg²⁺ would be deposited on the magnesium anode before lithium ions because magnesium has higher thermodynamic redox potential during the charging process.⁴⁵

The evolution of surface morphologies for the A-MoS₂ and C-MoS₂ electrodes is observed to understand the reasons for the improvement of electrochemical stability. Figure 5a and b shows the surface morphologies of the fresh A-MoS₂ and C-MoS₂ electrodes, respectively. Figure 5c shows the morphology of fine particles for the A-MoS₂ electrode after 50 cycles, presenting that the material is crushed during the cycle process and thus exhibits very poor cyclic stability. Alternatively, the morphology of nanosheets for the C-MoS₂ electrode after 50

cycles is well maintained during the cycle process (Figure 5d) that guarantees the better cyclic stability due to its unique structure and morphology. By analyzing BET, TEM, and SEM data, it can be seen that the highly dispersed nanoflowers significantly improved the structure stability of MoS₂. The bulk A-MoS₂ composed of nanosheets is not conducive to relieving the volume expansion during the cycle, thus resulting in the crushing of the structure (Figure 5e). In contrast, the highly dispersed MoS₂ nanoflowers with a large BET area and lattice spacing are more conducive to the full contact between electrolyte and material and thus sustain its structure after long-term cycling (Figure 5f). The high capacity of the C-MoS₂ derives from the large BET area and large lattice spacing, which improves the diffusion of intercalated Mg²⁺/Li⁺, and thus the material displays an improved electrochemical performance.

4. CONCLUSIONS

In conclusion, highly dispersed MoS₂ nanoflowers were successfully synthesized by using hydrochloric acid to control the concentration of sulfur ions in the solution. The obtained MoS₂ presents a unique structure with a large BET area of 118.25 m² g⁻¹ and large lattice spacing of 0.65 nm, enabling this material to exhibit high capacity, good rate performance, and stable cycling as cathode material for hybrid Mg²⁺/Li⁺ batteries. Benefiting from the unique structure, the reversible capacity of 192.8 mA h g⁻¹ over 100 cycles at 0.1 A g⁻¹ was

obtained. The present study not only furnishes a promising cathode material for MLBs, but also underlines a guide to fabricate highly dispersed MoS₂ materials for other applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.2c00611>.

XPS survey spectrum, elemental mapping images, corresponding SAED pattern, rate capability, cycling performances, charge/discharge curves, equivalent circuit diagram, ex situ XPS spectra, and schematic illustration of the working mechanism for MLBs (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Yu, B.; Chen, Y.; Wang, Z.; Chen, D.; Wang, X.; Zhang, W.; He, J.; He, W. 1T-MoS₂ nanotubes wrapped with N-doped graphene as highly-efficient absorbent and electrocatalyst for Li-S batteries. *J. Power Sources* **2020**, *447*, No. 227364.
- (2) Deng, Z.; Jiang, H.; Hu, Y.; Liu, Y.; Zhang, L.; Liu, H.; Li, C. 3D Ordered Macroporous MoS₂@C Nanostructure for Flexible Li-Ion Batteries. *Adv. Mater.* **2017**, *29*, No. 1603020.
- (3) Tian, C.; Wu, J.; Ma, Z.; Li, B.; Zhang, X.; Zu, X.; Xiang, X.; Li, S. A melt-diffusion strategy for tunable sulfur loading on CC@MoS₂ for lithium-sulfur batteries. *Energy Rep.* **2020**, *6*, 172–180.
- (4) Xu, M.; Bai, N.; Li, H.; Hu, C.; Qi, J.; Yan, X. Synthesis of MXene-supported layered MoS₂ with enhanced electrochemical performance for Mg batteries. *Chinese Chem. Lett.* **2018**, *29*, 1313–1316.
- (5) Hsu, C. J.; Chou, C. Y.; Yang, C. H.; Lee, T. C.; Chang, J. K. MoS₂/graphene cathodes for reversibly storing Mg²⁺ and Mg²⁺/Li⁺ in rechargeable magnesium-anode batteries. *Chem. Commun.* **2016**, *52*, 1701–1704.
- (6) Yu, X.; Zhao, G.; Liu, C.; Wu, C.; Huang, H.; He, J.; Zhang, N. A MoS₂ and Graphene Alternately Stacking van der Waals Heterostructure for Li⁺/Mg²⁺ Co-Intercalation. *Adv. Funct. Mater.* **2021**, *31*, No. 2103214.
- (7) Venkateswarlu, G.; Madhu, D.; Rani, J. V. Electroanalytical characterization of F-doped MoS₂ cathode material for rechargeable magnesium battery. *Funct. Mater. Lett.* **2019**, *12*, No. 19S0041.
- (8) Liu, Y.; Jiao, L.; Wu, Q.; Zhao, Y.; Cao, K.; Liu, H.; Wang, Y.; Yuan, H. Synthesis of rGO-supported layered MoS₂ for high-performance rechargeable Mg batteries. *Nanoscale* **2013**, *5*, 9562–9567.
- (9) Sun, Y.; Chen, H.; Xing, Y.; Mao, X.; Wang, M.; Li, H.; Guo, P.; Zhao, X. S. Synthesis of MnO₂ nanowires and their capacitive behavior in aqueous electrolytes containing magnesium ions. *Colloids Surf., A* **2018**, *553*, 539–545.
- (10) Liang, Y. L.; Feng, R.; Yang, S.; Ma, H. M.; Liang, J. L.; Chen, J. Rechargeable Mg Batteries with Graphene-like MoS₂ Cathode and Ultrasmall Mg Nanoparticle Anode. *Adv. Mater.* **2010**, *23*, 640–643.
- (11) Zhang, Z.; Zhao, H.; Teng, Y.; Chang, X.; Xia, Q.; Li, Z.; Fang, J.; Du, Z.; Świerczek, K. Carbon-Sheathed MoS₂ Nanothorns Epitaxially Grown on CNTs: Electrochemical Application for Highly Stable and Ultrafast Lithium Storage. *Adv. Energy Mater.* **2018**, *8*, No. 1700174.
- (12) Hou, X.; Shi, H.; Chang, T.; Hou, K.; Feng, L.; Suo, G.; Ye, X.; Zhang, L.; Zhang, Y.; Wang, W. Hollow opening nanoflowers MoS₂-CuS-EG cathodes for high-performance hybrid Mg/Li-ion batteries. *Chem. Eng. J.* **2021**, *409*, No. 128271.
- (13) Huang, H.; Zhao, G.; Zhang, N.; Sun, K. Two-dimensional Nb₂O₅ holey nanosheets prepared by a graphene sacrificial template method for high performance Mg²⁺/Li⁺ hybrid ion batteries. *Nanoscale* **2019**, *11*, 16222–16227.
- (14) Cho, J. H.; Aykol, M.; Kim, S.; Ha, J. H.; Wolverton, C.; Chung, K. Y.; Kim, K. B.; Cho, B. W. Controlling the intercalation chemistry to design high-performance dual-salt hybrid rechargeable batteries. *J. Am. Chem. Soc.* **2014**, *136*, 16116–16119.
- (15) Liu, C.; Zhao, G.; Zhang, L.; Lyu, P.; Yu, X.; Huang, H.; Maurin, G.; Sun, K.; Zhang, N. Self-supported PPy-encapsulated CoS₂ nanosheets anchored on the TiO_{2-x} nanorod array supported by Ti-S bonds for ultra-long life hybrid Mg²⁺/Li⁺ batteries. *J. Mater. Chem. A* **2020**, *8*, 22712–22719.
- (16) Wang, Y.; Wang, C.; Yi, X.; Hu, Y.; Wang, L.; Ma, L.; Zhu, G.; Chen, T.; Jin, Z. Hybrid Mg/Li-ion batteries enabled by Mg²⁺/Li⁺ co-intercalation in VS₄ nanodendrites. *Energy Storage Mater.* **2019**, *23*, 741–748.

- (17) Yu, X.; Zhao, G.; Huang, H.; Liu, C.; Lyu, P.; Zhang, N. Interlayer-expanded MoS₂ nanoflowers anchored on the graphene: A high-performance Li⁺/Mg²⁺ co-intercalation cathode material. *Chem. Eng. J.* **2022**, *428*, No. 131214.
- (18) Vincent, M.; Avvaru, V. S.; Rodríguez, M. C.; Haranczyk, M.; Etacheri, V. High-rate and ultralong-life Mg-Li hybrid batteries based on highly pseudocapacitive dual-phase TiO₂ nanosheet cathodes. *J. Power Sources* **2021**, *506*, No. 230118.
- (19) Shen, Y.; Wang, Y.; Miao, Y.; Yang, M.; Zhao, X.; Shen, X. High-Energy Interlayer-Expanded Copper Sulfide Cathode Material in Non-Corrosive Electrolyte for Rechargeable Magnesium Batteries. *Adv. Mater.* **2020**, *32*, No. 1905524.
- (20) Byeon, A.; Zhao, M. Q.; Ren, C. E.; Halim, J.; Kota, S.; Urbankowski, P.; Anasori, B.; Barsoum, M. W.; Gogotsi, Y. Two-Dimensional Titanium Carbide MXene As a Cathode Material for Hybrid Magnesium/Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2017**, *9*, 4296–4300.
- (21) Truong, Q. D.; Kempaiah Devaraju, M.; Nakayasu, Y.; Tamura, N.; Sasaki, Y.; Tomai, T.; Honma, I. Exfoliated MoS₂ and MoSe₂ Nanosheets by a Supercritical Fluid Process for a Hybrid Mg-Li-Ion Battery. *ACS Omega* **2017**, *2*, 2360–2367.
- (22) Xu, J.; Wei, Z.; Zhang, S.; Wang, X.; Wang, Y.; He, M.; Huang, K. Hierarchical WSe₂ nanoflower as a cathode material for rechargeable Mg-ion batteries. *J. Colloid Interface Sci.* **2021**, *588*, 378–383.
- (23) Tan, Y.; Zhou, F.; Huang, Z.; Yao, W.; Zhang, T.; Yao, H.; Lu, L.; Yu, S. MoS₂-Nanosheet-Decorated Carbon Nanofiber Composites Enable High-Performance Cathode Materials for Mg Batteries. *ChemElectroChem* **2018**, *5*, 996–1001.
- (24) Zhang, H.; Cong, L.; Wang, J.; Wang, X.; Liu, G.; Yu, W.; Zhang, H.; Dong, X.; Fan, W. Impact of CTAB on morphology and electrochemical performance of MoS₂ nanoflowers with improved lithium storage properties. *J. Mater. Sci.: Mater. Electron.* **2018**, *29*, 3631–3639.
- (25) Kun Chang, W. C.; Ma, L.; Li, H.; Li, H.; Huang, F.; Xu, Z.; Zhang, Q.; Leed, J. Y. Graphene-like MoS₂ amorphous carbon composites with high capacity and excellent stability as anode materials for lithium ion batteries. *J. Mater. Chem. A* **2011**, *21*, 6521.
- (26) Fan, X.; Gaddam, R. R.; Kumar, N. A.; Zhao, X. S. A Hybrid Mg²⁺/Li⁺ Battery Based on Interlayer-Expanded MoS₂/Graphene Cathode. *Adv. Energy Mater.* **2017**, *7*, No. 1700317.
- (27) Liu, Y.; Fan, L.; Jiao, L. Graphene intercalated in graphene-like MoS₂: A promising cathode for rechargeable Mg batteries. *J. Power Sources* **2017**, *340*, 104–110.
- (28) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-dimensional atomic crystals. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 10451–10453.
- (29) Yan, J.; Li, H.; Wang, K.; Jin, Q.; Lai, C.; Wang, R.; Cao, S.; Han, J.; Zhang, Z.; Su, J.; Jiang, K. Ultrahigh Phosphorus Doping of Carbon for High-Rate Sodium Ion Batteries Anode. *Adv. Energy Mater.* **2021**, *11*, No. 2003911.
- (30) Mizrahi, O.; Amir, N.; Pollak, E.; Chusid, O.; Marks, V.; Gottlieb, H.; Larush, L.; Zinigrad, E.; Aurbach, D. Electrolyte Solutions with a Wide Electrochemical Window for Rechargeable Magnesium Batteries. *J. Electrochem. Soc.* **2008**, *155*, A103–A109.
- (31) Sun, P.; Zhang, W.; Hu, X.; Yuan, L.; Huang, Y. Synthesis of hierarchical MoS₂ and its electrochemical performance as an anode material for lithium-ion batteries. *J. Mater. Chem. A* **2014**, *2*, 3498–3504.
- (32) Göde, F.; Gümüş, C.; Zor, M. Investigations on the physical properties of the polycrystalline ZnS thin films deposited by the chemical bath deposition method. *J. Cryst. Growth* **2007**, *299*, 136–141.
- (33) Najmaei, S.; Liu, Z.; Zhou, W.; Zou, X.; Shi, G.; Lei, S.; Yakobson, B. I.; Idrobo, J. C.; Ajayan, P. M.; Lou, J. Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nat. Mater.* **2013**, *12*, 754–759.
- (34) Li, S.; Liu, Y.; Zhao, X.; Cui, K.; Shen, Q.; Li, P.; Qu, X.; Jiao, L. Molecular Engineering on MoS₂ Enables Large Interlayers and Unlocked Basal Planes for High-Performance Aqueous Zn-Ion Storage. *Angew. Chem. Int. Ed.* **2021**, *60*, 20286–20293.
- (35) Hu, Z.; Wang, L.; Zhang, K.; Wang, J.; Cheng, F.; Tao, Z.; Chen, J. MoS₂ Nanoflowers with Expanded Interlayers as High-Performance Anodes for Sodium-Ion Batteries. *Angew. Chem. Int. Ed.* **2014**, *53*, 12794–12798.
- (36) Wu, C.; Zhao, G.; Gong, S.; Zhang, N.; Sun, K. PVP incorporated MoS₂ as a Mg ion host with enhanced capacity and durability. *J. Mater. Chem. A* **2019**, *7*, 4426–4430.
- (37) Wu, C.; Zhao, G.; Yu, X.; Liu, C.; Lyu, P.; Maurin, G.; Le, S.; Sun, K.; Zhang, N. MoS₂/graphene heterostructure with facilitated Mg-diffusion kinetics for high-performance rechargeable magnesium batteries. *Chem. Eng. J.* **2021**, *412*, No. 128736.
- (38) Yang, W.; Han, L.; Liu, X.; Hong, L.; Wei, M. Template-free fabrication of 1D core-shell MoO₂@MoS₂/nitrogen-doped carbon nanorods for enhanced lithium/sodium-ion storage. *J. Colloid Interface Sci.* **2021**, *588*, 804–812.
- (39) Ma, C.; Xu, Z.; Jiang, J.; Ma, Z.; Olsen, T.; Xiong, H.; Wang, S.; Yuan, X. Tailored nanoscale interface in a hierarchical carbon nanotube supported MoS₂@MoO₂-C electrode toward high performance sodium ion storage. *J. Mater. Chem. A* **2020**, *8*, 11011–11018.
- (40) Yang, J.; Yu, L.; Zheng, B.; Li, N.; Xi, J.; Qiu, X. Carbon Microtube Textile with MoS₂ Nanosheets Grown on Both Outer and Inner Walls as Multifunctional Interlayer for Lithium-Sulfur Batteries. *Adv. Sci.* **2020**, *7*, No. 1903260.
- (41) Li, Y.; Liang, Y.; Robles Hernandez, F. C.; Deog Yoo, H.; An, Q.; Yao, Y. Enhancing sodium-ion battery performance with interlayer-expanded MoS₂-PEO nanocomposites. *Nano Energy* **2015**, *15*, 453–461.
- (42) Li, D.; Zhang, Y.; Sun, Q.; Zhang, S.; Wang, Z.; Liang, Z.; Si, P.; Ci, L. Hierarchically porous carbon supported Sn₄P₃ as a superior anode material for potassium-ion batteries. *Energy Storage Mater.* **2019**, *23*, 367–374.
- (43) Huang, H.; Zhao, G.; Yu, X.; Shen, X.; Wang, M.; Bai, X.; Zhang, N. V-doped T-Nb₂O₅ toward high-performance Mg²⁺/Li⁺ hybrid ion batteries. *J. Mater. Chem. A* **2022**, *10*, 577–584.
- (44) Li, X.; Tang, Y.; Liu, L.; Gao, Y.; Zhu, C.; NuLi, Y.; Yang, T. 2D Ti₃C₂ MXene embedded with Co(II)(OH)_n nanoparticles as the cathode material for hybrid magnesium-lithium-ion batteries. *J. Mater. Sci.* **2021**, *56*, 2464–2473.
- (45) Yoo, H. D.; Liang, Y.; Li, Y.; Yao, Y. High areal capacity hybrid magnesium-lithium-ion battery with 99.9% Coulombic efficiency for large-scale energy storage. *ACS Appl. Mater. Interfaces* **2015**, *7*, 7001–7007.