

Highly Ambient-Stable 1T-MoS₂ and 1T-WS₂ by Hydrothermal Synthesis under High Magnetic Fields

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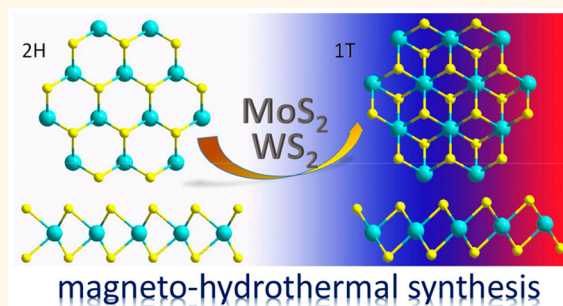
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Supporting Information

ABSTRACT: The phase-controlled synthesis of metallic and ambient-stable 2D MX₂ (M is Mo or W; X is S) with 1T octahedral coordination will endow these materials with superior performance compared with their semiconducting 2H coordination counterparts. We report a clean and facile route to prepare 1T-MoS₂ and 1T-WS₂ through hydrothermal processing under high magnetic fields. We reveal that the as-synthesized 1T-MoS₂ and 1T-WS₂ are ambient-stable for more than 1 year. Electrochemical measurements show that 1T-MoS₂ performs much better than 2H-MoS₂ as the anode for sodium ion batteries. These results can provide a clean and facile method to prepare ambient-stable 1T-phase MX₂.

KEYWORDS: MoS₂, nanosheets, metallic 1T phase, high magnetic fields, hydrothermal



Controllable phase synthesis of materials is desired because the crystal structure can obviously affect the properties.^{1–5} Transition-metal dichalcogenides (TMDs) MX₂ (M = Mo, W; X = S, Se, Te), as representative 2D materials, have been widely investigated recently because of their potential interesting applications.^{5–23} Importantly, the polymorphs of the MX₂ compounds such as MoS₂ and WS₂ usually show several types, including 1T and 2H phases, based on the different coordinating modes of M and X atoms. The 2H phase can be described as consisting of two S–M–S layers made up of edge-sharing MS₆ trigonal prisms, and the 1T phase is characterized in terms of one S–M–S layer built from edge-sharing MS₆ octahedra.^{24–28} Compared with its 2H phase counterpart with semiconducting characteristics, the 1T phase shows metallic behavior and has superior performances due to its high electrical conductivity.^{29–36}

From the thermodynamic viewpoint, the 1T polymorph is metastable, and the 2H phase is favored.^{7,37–39} Recently, several methods have been reported to synthesize 1T-MX₂,

such as alkali metal intercalation,^{8,35,36,40–44} mechanical exfoliation,^{45,46} plasma hot electron transfer,⁴⁷ electron-beam irradiation,²⁵ mechanical strains,^{48–51} and hydrothermal reaction.^{31,52} However, the as-synthesized 1T-MX₂ is easily converted into the 2H phase by contamination, the occurrence of intermediary phases, and oxidation.^{38,39,53} There has been no efficient route to synthesize clean and ambient-stable 1T-MX₂. Magnetic fields as a type of important thermodynamic parameters in materials processing could transfer high energy on an atomic scale of substances, resulting in the expected atomic and molecular alignments.^{54–56} Besides the manipulation of the morphology, the product phases can be tuned by applied magnetic fields in processing.⁵⁷ Even metastable phases could be induced or stabilized by applied magnetic fields

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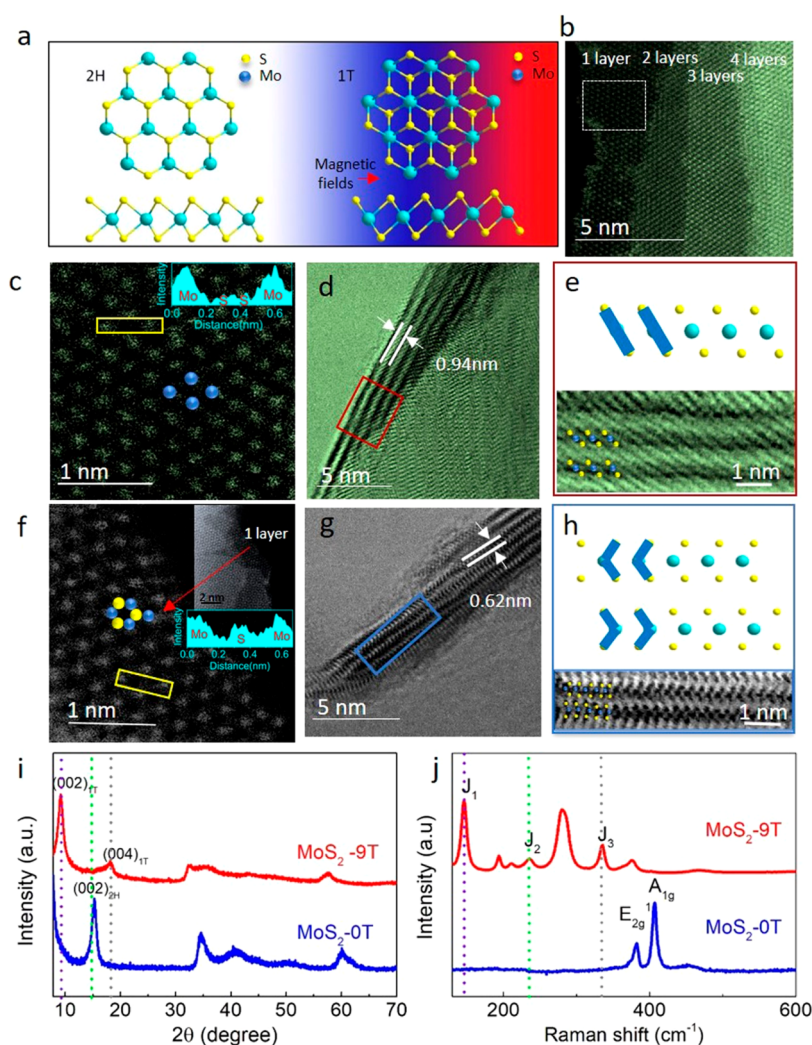


Figure 1. Crystal structure of MoS₂. (a) Schematic of MoS₂ structures. (b) Top-view HAADF-STEM image of MoS₂-9T. (c) Magnified top-view HAADF-STEM image from the area inside the white rectangle in panel b, indicating the 1T phase lattice arrangement. (The insert image gives the intensity profiles to show the atomic ratio between S and Mo from the area labeled with the yellow rectangle.) (d) Side-view annular bright-field (ABF) image of MoS₂-9T. (e) Magnified side-view ABF image from the area inside the red rectangle in panel d; the side-view structure of 1T MoS₂ is also shown. (f) Magnified top-view HAADF-STEM image of MoS₂-0T nanosheets indicating coordination around S and Mo atoms. (The insert images are the original top-view HAADF-STEM image of MoS₂-0T and the intensity profiles from the area labeled with the yellow rectangle.) (g) Side-view ABF image of the MoS₂-0T nanosheets. (h) Magnified side-view ABF image from the area inside the blue rectangle of panel g; the side-view structures of 2H MoS₂ are also shown. (i) XRD and (j) Raman spectra of MoS₂-9T and MoS₂-0T. The blue dots indicate Mo atoms, and the yellow dots indicate S atoms in panels c, e, f, and h.

during synthesis processing, such as successful achievements of γ -Fe₂O₃, Fe₃S₄, and α -Co(OH)₂.^{57–59} Because of the importance of magnetic fields in phase engineering, it is supposed that phase manipulation could be realized in MX₂ by magnetic fields.

We provide a facile strategy for the synthesis of 1T-MoS₂ and 1T-WSe₂ by hydrothermal processing on a high-magnetic-field hydrothermal apparatus. Pure 1T-MoS₂ and 1T-WSe₂, showing high ambient-stability, were successfully synthesized by hydrothermal processing under high magnetic fields named as magneto-hydrothermal processing. Then, the synthesized products were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, aberration-corrected scanning transmission electron microscopy (STEM), photoluminescence (PL), and X-ray photoelectron spectroscopy (XPS). Furthermore, as the proof of suitability for applications, the ambient-stable 1T-MoS₂

nanosheets were employed as the anode for sodium ion batteries, showing excellent electrochemical performance as well as high stability after cycling with retention of the 1T crystal structure. We believe that magneto-hydrothermal processing will provide a clean route to synthesize ambient-stable 1T-MX₂.

RESULTS AND DISCUSSION

Sample Preparation and Characterization. 1T-MoS₂ and 1T-WSe₂ were synthesized using a homemade magneto-hydrothermal apparatus, (Figure S1), in which the magnetic field can reach as high as 10 T. The scanning electron microscope (SEM) images and the selected area electron diffraction (SAED) patterns (Figures S2 and S3) reveal that the as-synthesized MoS₂ is composed of nanosheets with excellent crystalline quality. Meanwhile, the MoS₂ nanosheets show graphene-like morphologies with ripples and corruga-

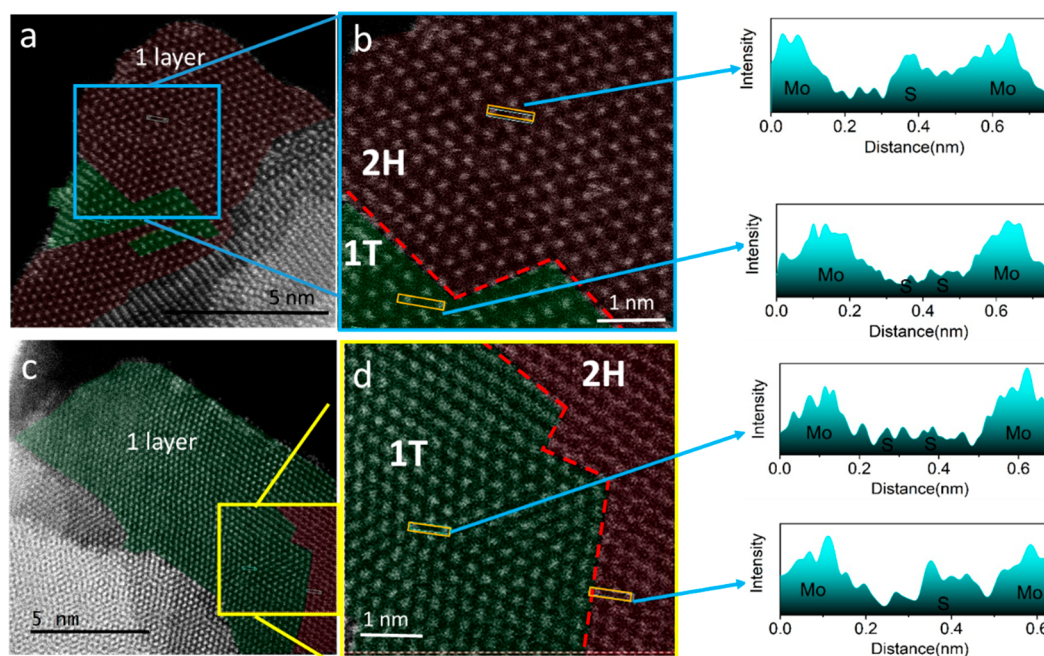


Figure 2. (a) HAADF-STEM image of MoS₂-0T. (b) Magnified top-view HAADF-STEM image from the area inside the blue rectangle in panel a, from which a small fraction of 1T phase is observed and the intensity profiles from the selected areas confirm the 2H and 1T phases. (c) HAADF-STEM image of MoS₂-8T. (d) Magnified top-view HAADF-STEM image from the area inside the yellow rectangle in panel c, from which a high fraction of 1T phase is observed and the intensity profiles from the selected areas confirm the 2H and 1T phases. The green area indicates the 1T phase, and the red area indicates the 2H phase.

tions, and their thickness was reduced with increasing the applied magnetic fields during processing (Figures S3 and S4). This tendency can be also observed from the atomic force microscopy (AFM) images (Figure S5).

The symmetry difference between the octahedral coordinated 1T-MoS₂ and the trigonal coordinated 2H-MoS₂ crystal structures (Figure 1a) can be directly identified by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM).^{5,23–26,60} The HAADF-STEM images from the single-layer of the 9 T (Figure 1b–e and Figure S6) and 0 T magneto-hydrothermally synthesized MoS₂ (Figure 1f–h) directly show the differences in atomic arrangements. For the former one (MoS₂-9T), the HAADF-STEM image (Figure 1b) shows a multilayered microstructure, as judged from the intensity profile (Figure S7), and the S atoms are dispersed uniformly around the Mo atoms, leading to a strong contrast between S and Mo sites (Figure 1c). In addition, the intensity ratio of S/Mo is ~ 0.2 , as shown in the inset image of Figure 1c.^{23,24} The diagonal atomic-scale edge structure (Figure 1d) and the crystalline ordering (Figure 1e) confirm the 1T octahedral lattice.^{12,24–26} In the latter one (MoS₂-0T), honeycomb lattice intensity variations of the 2H phase are observed (Figure 1f and Figure S8), in which the two overlapping sulfur atoms can enhance the signal along the electron beam direction. As a result, the contrast of the S sites is close to that of the Mo sites, even though the atomic number (*Z*) of sulfur is lower. The intensity ratio of 2S/Mo is ~ 0.7 , as depicted in the inset image of Figure 1f.^{12,22,24} The chevron-shaped atomic-scale edge structure (Figure 1g) and the crystalline ordering (Figure 1h) give evidence of the 2H trigonal lattice.^{12,24–26}

The crystal structures of the as-produced MoS₂ samples were investigated through XRD (Figure 1i). The MoS₂-0T shows a strong 2H-MoS₂ (002) peak at $2\theta = 14.38^\circ$, which is

attributed to the interplanar spacing of 6.15 Å, and it is consistent with the STEM data (Figure 1g). Interestingly, for the MoS₂-9T, the (002) and (004) diffraction peaks with interplanar distance of 9.4 and 4.7 Å are observed, respectively, agreeing with the crystal structure of 1T-MoS₂.^{23,61,62} As seen from the Raman spectra (Figure 1j), for the MoS₂-0T nanosheets, two typical Raman peaks at wavelength of ~ 378 and 404 cm^{-1} are evident from the E_{2g} and A_{1g} modes, respectively, confirming the 2H crystal structure.³ Interestingly, additional peaks centered at 146 (J₁), 234 (J₂), and 335 (J₃) cm^{-1} can be clearly observed, which are believed to be from 1T-MoS₂, indicating the 1T crystal structure of the MoS₂-9T.³⁰ Because of the semiconductor-like characterization of 2H-MoS₂ and the metallic behavior of 1T-MoS₂, a PL peak is observed for the former one, whereas no such PL peak appears for the latter one. The PL spectra (Figure S9) show an obvious PL peak for the MoS₂-0T, but no such PL peak is seen for the MoS₂-9T, further confirming the 1T crystal structure of the MoS₂-9T.^{41,63} From the aforementioned results, it is interesting to observe that 1T-MoS₂ can be successfully synthesized by magneto-hydrothermal processing. Additionally, 1T-WS₂ can also be synthesized by magneto-hydrothermal processing (Figures S10–S14), suggesting the validity of magneto-hydrothermal processing for the preparation of 1T-MX₂.

Phase Engineering and Stability. As has been seen, 1T-MX₂ can be synthesized through magneto-hydrothermal processing, and it is interesting to investigate the function of the magnetic field strength in processing. HAADF-STEM observations from the single-layer of the MoS₂ prepared under different magnetic fields in magneto-hydrothermal processing were therefore carried out (Figure S15). The as-synthesized MoS₂ under zero magnetic field processing is also composed of a small fraction of 1T phase (Figure 2a,b), which can be

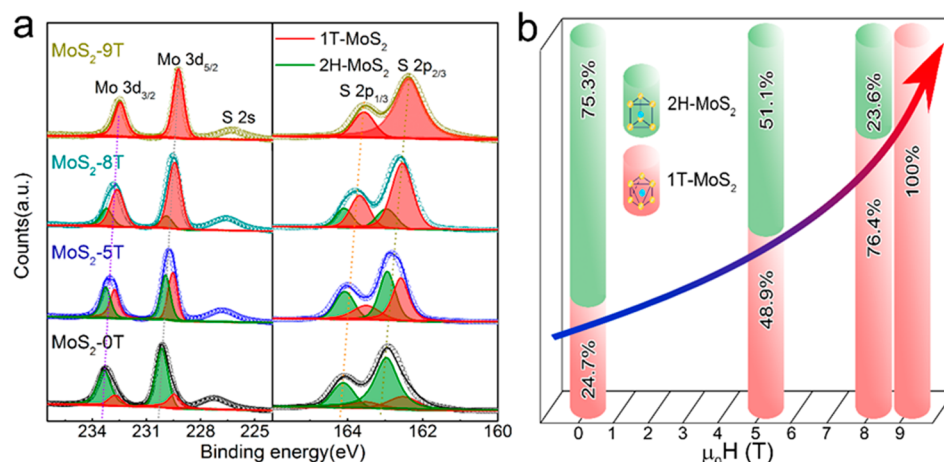


Figure 3. (a) XPS results of the as-synthesized MoS₂ processed under different magnetic fields in magneto-hydrothermal processing. (b) Phase percentage of MoS₂ from deconvolution of XPS spectra.

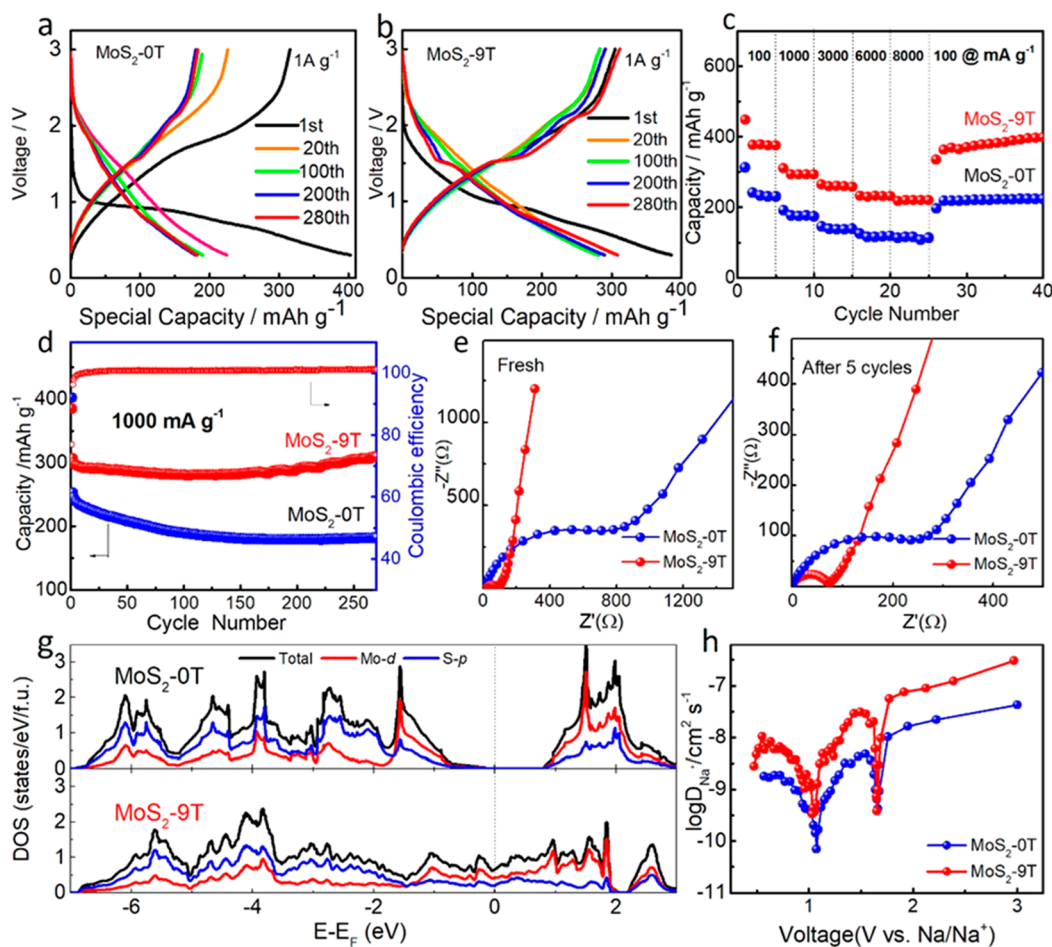


Figure 4. Electrochemical measurements: Discharge/charge curves of (a) MoS₂-0T and (b) MoS₂-9T electrode. (c) Rate performance for MoS₂-0T and MoS₂-9T. (d) Cycling performance for MoS₂-0T and MoS₂-9T at 1 A g⁻¹. (e,f) AC impedance plots for fresh and after five cycles at 1 A g⁻¹ from 0.1 Hz to 100 kHz, respectively. (g) Electronic density of states (DOS) for MoS₂-0T and MoS₂-9T, in which the Fermi level is set to zero (dashed line). (h) Chemical diffusion coefficient of sodium ions as a function of voltage calculated by GITT.

attributed to some content of S vacancies in the as-synthesized nanosheets (Figure S16 and Table S1).⁶⁴ Interestingly, the 1T phase is obviously expanded by increasing the applied magnetic fields in magneto-hydrothermal processing, such as for the MoS₂-8T (Figure 2c,d), and pure 1T phase is obtained under 9T (Figure 1c). The percentage of 1T phase in the as-

synthesized 1T-MX₂ can be calculated from the XPS spectra because the binding energy of the 1T phase is lower than that of the 2H counterpart by ~0.8 eV.^{23,41,65} By deconvoluting the XPS peaks (Figure 3a), the percentage of 1T-MoS₂ synthesized under 0, 5, 8, and 9 T is, respectively, estimated to be 24.7, 48.9, 76.4, and 100% (Figure 3b). Similarly, the percentage of

1T-WS₂ synthesized under 0 and 8 T is estimated to be ~60 and 100%, respectively (Figure S14).

The stability of 1T-MX₂ is very important for applications. In general, 1T MX₂ is metastable, and it is usually observed that 1T phase is gradually converted into 2H phase.^{38,39} The XRD (Figure S17), HAADF-STEM (Figure S18), and XPS (Figure S19) results for the magneto-hydrothermally synthesized 1T-MoS₂ and 1T-WS₂ after aging for 1 year reveal no obvious changes. It is surprising to observe that the 1T-MoS₂ and 1T-WS₂ obtained by magneto-hydrothermal processing show high ambient stability, confirming the advantages of magneto-hydrothermal processing for the preparation of 1T-MX₂. In general, the formation energy of 2H-MoS₂ is ~0.5 eV lower than that of the stoichiometric 1T-MoS₂ phase, leading to the thermodynamically preferred 2H phase.⁵¹ Interestingly, with the appearance of S vacancies, the difference in formation energy between 2H and 1T phase decreases due to the extra electrons induced by S vacancies, so that it can be close to zero but still above zero when the vacancy concentration reaches 8 at % in MoS₂.⁶⁴ It is worth noting that pure 1T-MX₂ cannot be directly obtained through simple S-vacancy manipulation in our processing because large amounts of S vacancies will lead to the collapse of the crystal structure. Here the ratios of Mo/S and W/S are determined to be 1:1.89 and 1:1.75 for the synthesized 1T-MoS₂ and 1T-WS₂, respectively (Table S1). The 4d electrons in the trigonal prismatic crystal field of 2H-MoS₂ are split into $d_{x^2-y^2}/d_{xy}$, d_{yz}/d_{xz} , and d_z^2 orbitals, showing no unpaired spins and diamagnetism. On the contrary, the 4d electrons in the octahedral prismatic crystal field of 1T-MoS₂ are split into d_{xy} , d_{yz} , and d_{xz} degenerate orbitals and d_z^2 and $d_{x^2-y^2}$ degenerate orbitals, leading to a net magnetic moment on Mo atoms.⁶⁶ In magneto-hydrothermal processing, with the introduction of magnetic fields, an extra free energy, called magnetic free energy, $E_M = -\frac{1}{2}\mu_0\chi VH^2$, will be induced, in which μ_0 is the permeability of vacuum, χ is the volumetric magnetic susceptibility, V is the volume, and H is the magnetic field strength.^{56,58} Because the 1T-MoS₂ shows a higher χ than that of 2H-MoS₂ (Figure S20),⁶⁶ the ground-state energy of 1T-MoS₂ will be lowered in magneto-hydrothermal processing compared with the 2H phase. Additionally, the E_M will be decreased with B^2 , resulting in the gradual enhancement of the concentration of 1T-MoS₂ with increasing magnetic field in magneto-hydrothermal processing; finally, nearly pure 1T-MoS₂ can be obtained, as confirmed by the PL result without PL emission peaks due to the metallic characteristic (Figure S9). As for the long-time stability of the synthesized 1T-MoS₂, the magnetostatic energy should be considered. The magnetostatic energy μ is described as $\mu = -\frac{\mu_0}{2}NM^2$, where μ_0 is the vacuum magnetic permeability, N is the demagnetization factor, and M is the magnetic moment.⁶⁷ The magnetic moment is enhanced with increasing magnetic field in magneto-hydrothermal processing, resulting in the decreased magnetostatic energy (Figure S20), which will lead to the long-time stability for the synthesized 1T-MoS₂ samples.

Electrochemical Measurements. As a proof of suitability for electrochemical applications, the as-synthesized 1T-MoS₂ and 2H-MoS₂ were used to construct half cells using sodium metals as the counter electrodes, respectively. The capacity versus voltage (*C-V*) measurements of the MoS₂-0T and the MoS₂-9T were carried out in the potential window of 0.3–3 V at a current density of 1 A g⁻¹. The MoS₂-0T electrode delivered the initial discharge and charge capacities with 401

and 314 mA h g⁻¹, respectively. The shapes of the *C-V* profiles, however, obviously changed during the following cycling (Figure 4a), suggesting lower reversibility and structural stability during the processes of sodiation and desodiation. As for the MoS₂-9T electrode, the first discharge and charge capacities are 385 and 304 mA h g⁻¹, respectively. (Figure 4b). Interestingly, the shapes of the charge/discharge profiles are similar to each other after the first cycle, indicating highly reversible sodium storage. Moreover, the MoS₂-9T exhibits more excellent rate performance (Figure 4c), showing reversible discharge capacity with 293 mA h g⁻¹ at a current density of 1 A g⁻¹. Even when cycled at 8 A g⁻¹, the specific capacity reached 224 mA h g⁻¹. In addition, to investigate the high-rate cycling performance, the MoS₂-0T and MoS₂-9T anodes were subjected to prolonged cycling at 1 A g⁻¹ (Figure 4d). The MoS₂-9T reaches the initial discharge capacity with 385 mA h g⁻¹ and retains a high discharge capacity with 310 mA h g⁻¹ after 280 cycles, which is higher than that of the MoS₂-0T with the discharge capacity of 182 mA h g⁻¹ after 280 cycles.

To reveal the electrochemical performance, electrochemical impedance spectra (EIS) measurements were carried out using the cells at the stable state. The plots consist of a straight line at low frequency relative to the Na⁺ diffusion and a high-frequency semicircle depending on the charge-transfer resistance at the electrode and electrolyte interface (R_{ct}).⁶⁸ From the EIS plots of the cells before (Figure 4e) and after five cycles (Figure 4f), one can see that the semicircles of the MoS₂-9T electrode are much smaller than those of the MoS₂-0T electrode, indicating lower charge-transfer resistance for the former one for both the fresh and the cycled conditions.⁶⁹ For further illustration, the electronic densities of states (DOS) of MoS₂-0T and MoS₂-9T were carried out using first-principles density functional theory (DFT) (Figure 4g). It is seen that the MoS₂-0T is a semiconductor with a band gap of ~1 eV, whereas the MoS₂-9T is metallic. It is well known that the electronic conductivity is the most important factor influencing the rate capability of the anode material for sodium-ion batteries (SIBs). The small resistance will lead to a small amount of heat during the charging and discharging process, which is beneficial for the long life and safety of the batteries. To further investigate the kinetics, galvanostatic intermittent titration technique (GITT) measurements within the voltage window of 0.3–3 V were performed (Figure S21).⁷⁰ Accordingly, the Na⁺ diffusion coefficient, D , can be calculated as $D = \frac{4L^2}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \left(\tau \ll \frac{L^2}{D} \right)$, where τ is the titration time, L is the thickness of the electrode, ΔE_s is the difference between two consecutive stabilized open-circuit voltages, and ΔE_t is the total change in the cell voltage during a constant current pulse excluding the IR drop (Figure S22).⁷⁰ It is observed that the diffusion coefficient of MoS₂-9T is significantly higher than that of the MoS₂-0T (Figure 4h). The enhanced D of the MoS₂-9T electrode is ascribed to a lower barrier for the Na⁺ insertion/extraction because of the bigger d spacing of the 1T-MoS₂,⁶⁸ resulting in the improved electrochemical performance.

Furthermore, to give a clear picture of the 1T structural stability after cycling, HAADF-STEM observations were carried out on the discharged MoS₂-9T electrode after the 125th cycle at 1 A g⁻¹. The elemental mapping results revealed that Mo and S coexist, and they are distributed uniformly after 125 cycles (Figure 5a–d). The multilayered structure is

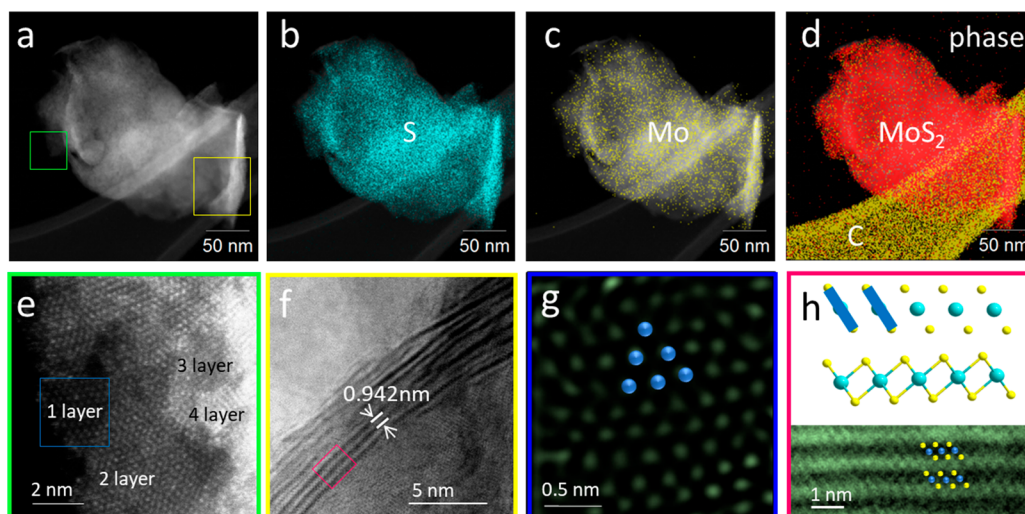


Figure 5. STEM observations of the MoS₂-9T electrode after 125 cycles at 1 A g^{−1}: (a) STEM image. (b–d) Energy-dispersive spectroscopy (EDS) elemental mappings. (e) Typical top-view HAADF-STEM image from the area inside the green rectangle of panel a. (f) Typical side-view annular bright-field (ABF) image from the area inside the yellow rectangle of panel a. (g) Magnified top-view HAADF-STEM image for a single layer from the area inside the blue circles of panel e, showing coordination around the Mo and S atoms. (h) Magnified side-view ABF image indicated by the area in the red rectangle in panel f, with the coordination of atoms around Mo and S shown at the top. (Yellow and blue dots, respectively, indicate the S and Mo atoms in panels g and h.)

effectively maintained (Figure 5e), and the *d* spacing between the layers is also maintained as 0.942 nm (Figure 5f). The magnified top-view (Figure 5g) and side-view HAADF-STEM (Figure 5h) images clearly show that the 1T octahedral lattice arrangements are conserved, further confirming the high structural stability of the 1T-MoS₂. Additionally, the measurements of the electrochemical properties for the synthesized MoS₂-9T electrodes aged for 1 year have been carried out, and the results show that the electrochemical properties are slightly degraded, confirming the long-time stability of the magneto-hydrothermal synthesized MoS₂ samples (Figure S23). As for the MoS₂-0T electrode, the nanosheets are broken into small fragments after 125 cycles at 1 A g^{−1}, which is similar to previous reports due to the small interlayer spacing of the 2H phase (Figure S24).^{68,71}

CONCLUSIONS

Magneto-hydrothermal processing as a facile and clean route to synthesize 1T-MoS₂ and 1T-Ws₂ was developed. The 1T octahedral coordination structure was confirmed by XRD, XPS, PL, Raman spectroscopy, and STEM. The as-synthesized 1T-MoS₂ and 1T-Ws₂ samples are ambient-stable, showing long-time stability for more than 1 year. A superior electrochemical performance of 1T-MoS₂ as the anode in sodium ion batteries was observed with a specific capacity of 224 mAh g^{−1} at a high current density of 8 A g^{−1}. This excellent performance originates from its enhanced kinetics and stable 1T octahedral coordination, as confirmed by GITT and STEM measurements. Our findings will open up a clean and facile way to synthesize ambient-stable 2D 1T-MX₂ materials for applications in electrochemical devices.

EXPERIMENTAL METHODS

Preparation of MoS₂ Nanosheets. (NH₄)₆Mo₇O₂₄·4H₂O (CAS number 12027-67-7) and thiourea (CAS number 62-56-6) were purchased from Alfa Aesar. All chemicals were used without any further purification. 1.4209 g thiourea and 0.7242 g (NH₄)₆Mo₇O₂₄·4H₂O were dissolved in deionized water (21.8 mL) and stirred

vigorously for 30 min to get a homogeneous solution. After the mixture was transferred to a Teflon-lined stainless-steel autoclave (28 mL capacity), a magnetic field was applied. Then, it was heated to 210 °C in 40 min and kept for 18 h under different magnetic fields. After synthesis, when the temperature was decreased to 80 °C, the magnetic field was then removed and the reaction system was naturally cooled to room temperature. The resulting product was filtered, washed several times by deionized water and ethanol, and finally dried at 70 °C in a vacuum oven.

Preparation of WS₂ Nanosheets. WCl₆ (CAS number 13283-01-7) and thioacetamide (TAA, CAS number 62-55-5) were purchased from Sigma-Aldrich. All chemicals were used without any further purification. 0.61 g tungsten chloride and 1.17 g TAA were dissolved in deionized water (20.5 mL) and stirred vigorously for 30 min. After the mixture was transferred to a Teflon-lined stainless-steel autoclave (26 mL capacity), a magnetic field was applied. Then, it was heated to 210 °C in 40 min and kept for 24 h under different magnetic fields. When the temperature was decreased to 80 °C, the magnetic field was removed, and the reaction system was naturally cooled to room temperature. The product was filtered, washed several times by deionized water and absolute ethanol, and finally dried at 70 °C in a vacuum oven.

Electrochemical Characterization. The electrochemical tests were carried out with CR2032 cells assembled in a glovebox filled with argon. The MoS₂ electrodes were produced by mixing active material (80 wt %), Super P (10 wt %), and carboxymethyl cellulose (CMC) (10 wt %) in deionized water. The resultant slurry was coated on Cu foil and dried at 80 °C for overnight in vacuum, which was followed by pressing under 20 MPa in a table compression machine. Electrochemical measurements were conducted with coin half cells. Glass fiber was used as the separator, and sodium foil served as the counter electrode. The electrolyte was a solution of 1 M sodium trifluoromethane-sulfonate in diethylene glycol dimethyl ether (DEGDME), which was free from H₂O. A Landt CT2001 cell testing system was used for galvanostatic charge–discharge tests between 0.3 and 3 V. A VMP-3 electrochemical workstation was used for in situ EIS measurement.

Characterization. Field-emission scanning electron microscope (FE-SEM) images were collected on a JEOL JSM-6700F SEM. High-resolution transmission electron microscope (HRTEM) images were collected on a JEOL-2011 TEM operated at an acceleration voltage of 200 kV. HAADF-STEM images were collected on a JEOL JEM-

ARM200F at an acceleration voltage of 80 kV. Specimens for STEM characterization were prepared by dropping an ethanol suspension of the as-prepared MoS₂/WS₂ onto amorphous carbon-coated copper grids. For top-view images, the edge regions of horizontally placed nanosheets were searched for single-layer regions. Nanosheets placed vertically were searched to get the side-view images (Figure S25). The XPS was obtained on an ESCALAB MK II device with Mg K α as the excitation source. Raman spectroscopy was carried out by a LabRAM HR800 UV NIR spectrometer with 532 nm laser excitation. XRD was carried out on a Philips X'Pert Pro Super diffractometer with Cu K α radiation (λ = 1.54178 Å). Magnetization studies were performed using a superconducting quantum interference device (SQUID) magnetometer. The PL spectra were obtained with a Nd:YAG laser (λ = 532 nm).

Density Functional Theory Calculations. The DFT calculations were carried out by Quantum ESPRESSO⁷² with ultrasoft pseudopotentials.⁷³ The exchange and correlation effects were processed within the generalized gradient approximation (GGA).⁷⁴ Deficient MoS₂-9T was simulated using a 2 × 2 × 4 supercell with two S vacancies. In the irreducible Brillouin zone, we used the plane-wave cutoff energy of 60 Ry and 16 × 16 × 8 *k*-point mesh in the irreducible Brillouin zone for stoichiometric MoS₂-0T, along with a 16 × 16 × 1 *k*-point mesh for the MoS₂-9T (1T-MoS_{1.875}) supercell. The van der Waals interaction correction DFT-D₂^{75,76} was used to avoid overestimation of the interlayer distance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b07744.

Schematic illustration of homemade magneto-hydrothermal apparatus, SEM and TEM images of MoS₂ nanosheets obtained under different high magnetic fields, AFM and STEM images of MoS₂-0T and MoS₂-9T, STEM elemental mapping images of MoS₂-9T, PL spectra of MoS₂-0T and MoS₂-9T nanosheets, SEM, TEM, STEM images, XRD spectra, Raman spectra, and XPS of WS₂ nanosheets obtained with (8T) and without high magnetic fields, HAADF-STEM images of MoS₂-0T and MoS₂-8T, XRD patterns after 1 year of aging for 1T-MoS₂ and 1T-WS₂ samples, HAADF-STEM images of MoS₂-9T aging for 1 year, XPS patterns after a half year of aging of MoS₂-8T and MoS₂-9T samples, *M*–*H* curves of MoS₂ nanosheets obtained using different magnetic fields during processing, GITT measurement of MoS₂-9T and MoS₂-0T, cycling and rate performance results for the MoS₂-9T sample after 1 year, and HRTEM images of the MoS₂0T samples after 125 cycles (PDF)

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W.D. and L.H. contributed equally. W.D., L.H., X.Z., and J.D. designed the experiments. All experimental work was conducted by W.D. with L.H., X.T., R.W., X.Z., Q.L. M.C. Z.S., W.S., and C.L. All data were analyzed by W.D. and L.H.. W.D. and X.Z. wrote the paper based on the opinion of all authors. D.S. did the theoretical calculations. S.C., Q.C. Y.S., and S.X.D. provided constructive discussion on the experiments and writing. All authors participated in the discussion of the results.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Sun, S. C.; Murray, B.; Weller, D.; Folks, L.; Moser, A. Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices. *Science* **2000**, *287*, 1989–1992.
- (2) Park, C. H.; Cheong, B.-H.; Lee, K.-H.; Chang, K. J. Structural and Electronic Properties of Cubic, 2H, 4H, and 6H SiC. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *49*, 4485–4493.
- (3) Yu, Y.; Nam, G. H.; He, Q.; Wu, X. J.; Zhang, K.; Yang, Z.; Chen, J.; Ma, Q.; Zhao, M.; Liu, Z.; Ran, F. R.; Wang, X.; Li, H.; Huang, X.; Li, B.; Xiong, Q.; Zhang, Q.; Liu, Z.; Gu, L.; Du, Y.; et al. High Phase-Purity 1T'-MoS₂- and 1T'-MoSe₂-Layered Crystals. *Nat. Chem.* **2018**, *10*, 638–643.
- (4) Fan, Z.; Luo, Z.; Huang, X.; Li, B.; Chen, Y.; Wang, J.; Hu, Y.; Zhang, H. Synthesis of 4H/fcc Noble Multimetallic Nanoribbons for Electrocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 1414–1419.
- (5) Chhowalla, M.; Liu, Z.; Zhang, H. Two-Dimensional Transition Metal Dichalcogenide (TMD) Nanosheets. *Chem. Soc. Rev.* **2015**, *44*, 2584–2586.
- (6) Butler, S. Z.; Hollen, S. M.; Cao, L.; Cui, Y.; Gupta, J. A.; Gutierrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J.; Ismach, A. F.; Johnston-Halperin, E.; Kuno, M.; Plashnitsa, V. V.; Robinson, R. D.; Ruoff, R. S.; Salahuddin, S.; Shan, J.; Shi, L.; Spencer, M. G.; Terrones, M.; et al. Progress, Challenges, and Opportunities in Two-Dimensional Materials beyond Graphene. *ACS Nano* **2013**, *7*, 2898–2926.
- (7) Chia, X.; Eng, A. Y. S.; Ambrosi, A.; Tan, S. M.; Pumera, M. Electrochemistry of Nanostructured Layered Transition-Metal Dichalcogenides. *Chem. Rev.* **2015**, *115*, 11941–11966.
- (8) Coleman, J. N.; Lotya, M.; O'Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J.; Shvets, I. V.; Arora, S. K.; Stanton, G.; Kim, H. Y.; Lee, K.; Kim, G. T.; Duesberg, G. S.; Hallam, T.; Boland, J. J.; Wang, J. J.; et al. Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* **2011**, *331*, 568–571.
- (9) Karunadasa, H. I.; Montalvo, E.; Sun, Y. J.; Majda, M.; Long, J. R.; Chang, C. J. A Molecular MoS₂ Edge Site Mimic for Catalytic Hydrogen Generation. *Science* **2012**, *335*, 698–702.
- (10) Eda, G.; Maier, S. A. Two-Dimensional Crystals: Managing Light for Optoelectronics. *ACS Nano* **2013**, *7*, 5660–5665.
- (11) Botello-Méndez, A. R.; López-Urías, F.; Terrones, M.; Terrones, H. Metallic and Ferromagnetic Edges in Molybdenum Disulfide Nanoribbons. *Nanotechnology* **2009**, *20*, 325703.

- (12) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L. J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.
- (13) Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. Engineering the Surface Structure of MoS₂ to Preferentially Expose Active Edge Sites for Electrocatalysis. *Nat. Mater.* **2012**, *11*, 963–969.
- (14) Kuc, A.; Heine, T. The Electronic Structure Calculations of Two-Dimensional Transition-Metal Dichalcogenides in the Presence of External Electric and Magnetic Fields. *Chem. Soc. Rev.* **2015**, *44*, 2603–2614.
- (15) Lee, Y. H.; Zhang, X. Q.; Zhang, W.; Chang, M. T.; Lin, C. T.; Chang, K. D.; Yu, Y. C.; Wang, J. T.; Chang, C. S.; Li, L. J.; Lin, T. W. Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition. *Adv. Mater.* **2012**, *24*, 2320–2325.
- (16) Voiry, D.; Fullon, R.; Yang, J.; de Carvalho Castro e Silva, C.; Kappera, R.; Bozkurt, I.; Kaplan, D.; Lagos, M. J.; Batson, P. E.; Gupta, G.; Mohite, A. D.; Dong, L.; Er, D.; Shenoy, V. B.; Asefa, T.; Chhowalla, M. The Role of Electronic Coupling between Substrate and 2D MoS₂ Nanosheets in Electrocatalytic Production of Hydrogen. *Nat. Mater.* **2016**, *15*, 1003–1009.
- (17) Wang, Z.; Dong, Z.; Zhu, H.; Jin, L.; Chiu, M. H.; Li, L. J.; Xu, Q. H.; Eda, G.; Maier, S. A.; Wee, A. T. S.; Qiu, C. W.; Yang, J. K. W. Selectively Plasmon-Enhanced Second-Harmonic Generation from Monolayer Tungsten Diselenide on Flexible Substrates. *ACS Nano* **2018**, *12*, 1859–1867.
- (18) Xie, J.; Zhang, H.; Li, S.; Wang, R.; Sun, X.; Zhou, M.; Zhou, J.; Lou, X. W.; Xie, Y. Defect-Rich MoS₂ Ultrathin Nanosheets with Additional Active Edge Sites for Enhanced Electrocatalytic Hydrogen Evolution. *Adv. Mater.* **2013**, *25*, 5807–5813.
- (19) Zhang, G.; Liu, H.; Qu, J.; Li, J. Two-Dimensional Layered MoS₂ Rational Design, Properties and Electrochemical Applications. *Energy Environ. Sci.* **2016**, *9*, 1190–1209.
- (20) Xie, J.; Zhang, J.; Li, S.; Grote, F.; Zhang, X.; Zhang, H.; Wang, R.; Lei, Y.; Pan, B.; Xie, Y. Controllable Disorder Engineering in Oxygen-Incorporated MoS₂ Ultrathin Nanosheets for Efficient Hydrogen Evolution. *J. Am. Chem. Soc.* **2013**, *135*, 17881–17888.
- (21) Voiry, D.; Yamaguchi, H.; Li, J.; Silva, R.; Alves, D. C.; Fujita, T.; Chen, M.; Asefa, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. Enhanced Catalytic Activity in Strained Chemically Exfoliated WS₂ Nanosheets for Hydrogen Evolution. *Nat. Mater.* **2013**, *12*, 850–855.
- (22) Kappera, R.; Voiry, D.; Yalcin, S. E.; Branch, B.; Gupta, G.; Mohite, A. D.; Chhowalla, M. Phase-Engineered Low-Resistance Contacts for Ultrathin MoS₂ Transistors. *Nat. Mater.* **2014**, *13*, 1128–1134.
- (23) Acerce, M.; Voiry, D.; Chhowalla, M. Metallic 1T Phase MoS₂ Nanosheets as Supercapacitor Electrode Materials. *Nat. Nanotechnol.* **2015**, *10*, 313–318.
- (24) Eda, G.; Fujita, T.; Yamaguchi, H.; Voiry, D.; Chen, M.; Chhowalla, M. Coherent Atomic and Electronic Heterostructures of Single-Layer MoS₂. *ACS Nano* **2012**, *6*, 7311–7317.
- (25) Lin, Y. C.; Dumcenco, D. O.; Huang, Y. S.; Suenaga, K. Atomic Mechanism of the Semiconducting-to-Metallic Phase Transition in Single-Layered MoS₂. *Nat. Nanotechnol.* **2014**, *9*, 391–396.
- (26) Voiry, D.; Mohite, A.; Chhowalla, M. Phase Engineering of Transition Metal Dichalcogenides. *Chem. Soc. Rev.* **2015**, *44*, 2702–2712.
- (27) Xia, M.; Li, B.; Yin, K.; Capellini, G.; Niu, G.; Gong, Y.; Zhou, W.; Ajayan, P. M.; Xie, Y. H. Spectroscopic Signatures of AA' and AB Stacking of Chemical Vapor Deposited Bilayer MoS₂. *ACS Nano* **2015**, *9*, 12246–12254.
- (28) Wu, R. J.; Odlyzko, M. L.; Mkhoyan, K. A. Determining the Thickness of Atomically Thin MoS₂ and WS₂ in the TEM. *Ultramicroscopy* **2014**, *147*, 8–20.
- (29) Kim, J. S.; Kim, J.; Zhao, J.; Kim, S.; Lee, J. H.; Jin, Y.; Choi, H.; Moon, B. H.; Bae, J. J.; Lee, Y. H.; Lim, S. C. Electrical Transport Properties of Polymorphic MoS₂. *ACS Nano* **2016**, *10*, 7500–7506.
- (30) Cheng, P.; Sun, K.; Hu, Y. H. Memristive Behavior and Ideal Memristor of 1T Phase MoS₂ Nanosheets. *Nano Lett.* **2016**, *16*, 572–576.
- (31) Geng, X.; Zhang, Y.; Han, Y.; Li, J.; Yang, L.; Benamara, M.; Chen, L.; Zhu, H. Two-Dimensional Water-Coupled Metallic MoS₂ with Nanochannels for Ultrafast Supercapacitors. *Nano Lett.* **2017**, *17*, 1825–1832.
- (32) Kappera, R.; Voiry, D.; Yalcin, S. E.; Branch, B.; Gupta, G.; Mohite, A. D.; Chhowalla, M. Phase-Engineered Low-Resistance Contacts for Ultrathin MoS₂ Transistors. *Nat. Mater.* **2014**, *13*, 1128–1134.
- (33) Qi, Y.; Xu, Q.; Wang, Y.; Yan, B.; Ren, Y.; Chen, Z. CO₂-Induced Phase Engineering: Protocol for Enhanced Photoelectrocatalytic Performance of 2D MoS₂ Nanosheets. *ACS Nano* **2016**, *10*, 2903–2909.
- (34) Tan, S. J. R.; Sarkar, S.; Zhao, X.; Luo, X.; Luo, Y. Z.; Poh, S. M.; Abdelwahab, I.; Zhou, W.; Venkatesan, T.; Chen, W.; et al. Temperature- and Phase-Dependent Phonon Renormalization in 1T'-MoS₂. *ACS Nano* **2018**, *12*, 5051–5058.
- (35) Chen, W.; Gu, J.; Liu, Q.; Luo, R.; Yao, L.; Sun, B.; Zhang, W.; Su, H.; Chen, B.; Liu, P.; Zhang, D. Quantum Dots of 1T Phase Transitional Metal Dichalcogenides Generated via Electrochemical Li Intercalation. *ACS Nano* **2018**, *12*, 308–316.
- (36) Zhang, R.; Tsai, I. L.; Chapman, J.; Khestanova, E.; Waters, J.; Grigorieva, I. V. Superconductivity in Potassium-Doped Metallic Polymorphs of MoS₂. *Nano Lett.* **2016**, *16*, 629–636.
- (37) Jiménez Sandoval, S.; Yang, D.; Frindt, R. F.; Irwin, J. C. Raman Study and Lattice Dynamics of Single Molecular Layers of MoS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1991**, *44*, 3955–3962.
- (38) Calandra, M. Chemically Exfoliated Single-Layer MoS₂ Stability, Lattice Dynamics, and Catalytic Adsorption from First Principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, 245428.
- (39) Shi, S.; Sun, Z.; Hu, Y. H. Synthesis, Stabilization and Applications of 2-Dimensional 1T Metallic MoS₂. *J. Mater. Chem. A* **2018**, *6*, 23932–23977.
- (40) Fan, X.; Xu, P.; Li, Y. C.; Zhou, D.; Sun, Y.; Nguyen, M. A.; Terrones, M.; Mallouk, T. E. Controlled Exfoliation of MoS₂ Crystals into Trilayer Nanosheets. *J. Am. Chem. Soc.* **2016**, *138*, 5143–5149.
- (41) Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from Chemically Exfoliated MoS₂. *Nano Lett.* **2011**, *11*, 5111–5116.
- (42) Py, M. A.; Haering, R. R. Structural Destabilization Induced by Lithium Intercalation in MoS₂ and Related Compounds. *Can. J. Phys.* **1983**, *61*, 76–84.
- (43) Wang, L.; Xu, Z.; Wang, W.; Bai, X. Atomic Mechanism of Dynamic Electrochemical Lithiation Processes of MoS₂ Nanosheets. *J. Am. Chem. Soc.* **2014**, *136*, 6693–6697.
- (44) Zheng, J.; Zhang, H.; Dong, S.; Liu, Y.; Tai Nai, C.; Suk Shin, H.; Young Jeong, H.; Liu, B.; Ping Loh, K. High Yield Exfoliation of Two-Dimensional Chalcogenides Using Sodium Naphthalenide. *Nat. Commun.* **2014**, *5*, 2995.
- (45) Benameur, M. M.; Radisavljevic, B.; Héron, J. S.; Sahoo, S.; Berger, H.; Kis, A. Visibility of Dichalcogenide Nanolayers. *Nanotechnology* **2011**, *22*, 125706.
- (46) Lee, C.; Li, Q. Y.; Kalb, W.; Liu, X. Z.; Berger, H.; Carpick, R. W.; Hone, J. Frictional Characteristics of Atomically Thin Sheets. *Science* **2010**, *328*, 76–80.
- (47) Kang, Y.; Najmaei, S.; Liu, Z.; Bao, Y.; Wang, Y.; Zhu, X.; Halas, N. J.; Nordlander, P.; Ajayan, P. M.; Lou, J.; Fang, Z. Plasmonic Hot Electron Induced Structural Phase Transition in a MoS₂ Monolayer. *Adv. Mater.* **2014**, *26*, 6467–6471.
- (48) Johari, P.; Shenoy, V. B. Tuning the Electronic Properties of Semi-Conducting Transition Metal Dichalcogenides by Applying Mechanical Strains. *ACS Nano* **2012**, *6*, 5449–5456.
- (49) Dybala, F.; Polak, M. P.; Kopaczek, J.; Scharoch, P.; Wu, K.; Tongay, S.; Kudrawiec, R. Pressure Coefficients for Direct Optical Transitions in MoS₂MoSe₂WS₂ and WSe₂ Crystals and Semiconductor to Metal Transitions. *Sci. Rep.* **2016**, *6*, 26663.
- (50) Nayak, A. P.; Bhattacharyya, S.; Zhu, J.; Liu, J.; Wu, X.; Pandey, T.; Jin, C.; Singh, A. K.; Akinwande, D.; Lin, J. F. Pressure-Induced Semiconducting to Metallic Transition in Multilayered Molybdenum Disulfide. *Nat. Commun.* **2014**, *5*, 3731.

- (51) Duerloo, K. A. N.; Li, Y.; Reed, E. J. Structural Phase Transitions in Two-Dimensional Mo- and W-Dichalcogenide Monolayers. *Nat. Commun.* **2014**, *5*, 4214.
- (52) Geng, X.; Sun, W.; Wu, W.; Chen, B.; Al-Hilo, A.; Benamara, M.; Zhu, H.; Watanabe, F.; Cui, J.; Chen, T. P. Pure and Stable Metallic Phase Molybdenum Disulfide Nanosheets for Hydrogen Evolution Reaction. *Nat. Commun.* **2016**, *7*, 10672.
- (53) Chou, S. S.; Huang, Y. K.; Kim, J.; Kaehr, B.; Foley, B. M.; Lu, P.; Dykstra, C.; Hopkins, P. E.; Brinker, C. J.; Huang, J.; Dravid, V. P. Controlling the Metal to Semiconductor Transition of MoS₂ and WS₂ in Solution. *J. Am. Chem. Soc.* **2015**, *137*, 1742–1745.
- (54) Wang, J.; Chen, Q.; Zeng, C.; Hou, B. Magnetic-Field-Induced Growth of Single-Crystalline Fe₃O₄ Nanowires. *Adv. Mater.* **2004**, *16*, 137–140.
- (55) Hu, L.; Zhang, R.; Chen, Q. Synthesis and Assembly of Nanomaterials under Magnetic Fields. *Nanoscale* **2014**, *6*, 14064–14105.
- (56) De Rango, P.; Lees, M.; Lejay, P.; Sulpice, A.; Tournier, R.; Ingold, M.; Germin, P.; Pernet, M. Texturing of Magnetic Materials at High Temperature by Solidification in a Magnetic Field. *Nature* **1991**, *349*, 770–772.
- (57) He, Z.; Yu, S. H.; Zhou, X.; Li, X.; Qu, J. Magnetic-Field-Induced Phase-Selective Synthesis of Ferrosulfide Microrods by a Hydrothermal Process: Microstructure Control and Magnetic Properties. *Adv. Funct. Mater.* **2006**, *16*, 1105–1111.
- (58) Wang, J.; Ma, Y.; Watanabe, K. Magnetic-Field-Induced Synthesis of Magnetic γ -Fe₂O₃ Nanotubes. *Chem. Mater.* **2008**, *20*, 20–22.
- (59) Dai, P.; Yan, T.; Hu, L.; Pang, Z.; Bao, Z.; Wu, M.; Li, G.; Fang, J.; Peng, Z. Phase Engineering of Cobalt Hydroxides Using Magnetic Fields for Enhanced Supercapacitor Performance. *J. Mater. Chem. A* **2017**, *5*, 19203–19209.
- (60) Hartel, P.; Rose, H.; Dinges, C. Conditions and Reasons for Incoherent Imaging in STEM. *Ultramicroscopy* **1996**, *63*, 93–114.
- (61) Geng, X.; Jiao, Y.; Han, Y.; Mukhopadhyay, A.; Yang, L.; Zhu, H. Freestanding Metallic 1T MoS₂ with Dual Ion Diffusion Paths as High Rate Anode for Sodium-Ion Batteries. *Adv. Funct. Mater.* **2017**, *27*, 1702998.
- (62) Wang, D.; Zhang, X.; Bao, S.; Zhang, Z.; Fei, H.; Wu, Z. Phase Engineering of a Multiphasic 1T/2H MoS₂ Catalyst for Highly Efficient Hydrogen Evolution. *J. Mater. Chem. A* **2017**, *5*, 2681–2688.
- (63) Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C. Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275.
- (64) Cai, L.; He, J.; Liu, Q.; Yao, T.; Chen, L.; Yan, W.; Hu, F.; Jiang, Y.; Zhao, Y.; Hu, T.; Sun, Z.; Wei, S. Vacancy-Induced Ferromagnetism of MoS₂ Nanosheets. *J. Am. Chem. Soc.* **2015**, *137*, 2622–2627.
- (65) Papageorgopoulos, C. A.; Jaegermann, W. Li Intercalation across and along the Van Der Waals Surfaces of MoS₂(0001). *Surf. Sci.* **1995**, *338*, 83–93.
- (66) Yan, S.; Qiao, W.; He, X.; Guo, X.; Xi, L.; Zhong, W.; Du, Y. Enhancement of Magnetism by Structural Phase Transition in MoS₂. *Appl. Phys. Lett.* **2015**, *106*, 012408.
- (67) O'Handley, R. C. *Modern Magnetic Materials Principle and Applications*; Wiley-Interscience: New York, 1999; pp 48–50.
- (68) 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.
- (69) Tan, G.; Xu, R.; Xing, Z.; Yuan, Y.; Lu, J.; Wen, J.; Liu, C.; Ma, L.; Zhan, C.; Liu, Q.; Wu, T.; Jian, Z.; Shahbazian-Yassar, R.; Ren, Y.; Miller, D. J.; Curtiss, L. A.; Ji, X.; Amine, K. Burning Lithium in CS₂ for High-Performing Compact Li₂S-Graphene Nanocapsules for Li-S Batteries. *Nat. Energy* **2017**, *2*, 17090.
- (70) Zheng, W.; Shui, M.; Shu, J.; Gao, S.; Xu, D.; Chen, L. L.; Feng, L.; Ren, Y. GITT Studies on Oxide Cathode LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ Synthesized by Citric Acid Assisted High-Energy Ball Milling. *Bull. Mater. Sci.* **2013**, *36*, 495–498.
- (71) Gao, P.; Wang, L.; Zhang, Y.; Huang, Y.; Liu, K. Atomic-Scale Probing of the Dynamics of Sodium Transport and Intercalation-Induced Phase Transformations in MoS₂. *ACS Nano* **2015**, *9*, 11296–11301.
- (72) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
- (73) Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *41*, 7892–7895.
- (74) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (75) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (76) Barone, V.; Casarin, M.; Forrer, D.; Pavone, M.; Sami, M.; Vittadini, A. Role and Effective Treatment of Dispersive Forces in Materials: Polyethylene and Graphite Crystals as Test Cases. *J. Comput. Chem.* **2009**, *30*, 934–939.