Robust synthesis of two-dimensional metal dichalcogenides and their alloys by active chalcogen monomer supply

Kaihui Liu (✉ khliu@pku.edu.cn)

State Key Laboratory for Mesoscopic Physics, Frontiers Science Center for Nano-optoelectronics, School of Physics, Peking University, Beijing 100871 <https://orcid.org/0000-0002-8781-2495>

Yonggang Zuo

Institute of Physics, Chinese Academy of Sciences <https://orcid.org/0000-0003-1262-6767>

Can Liu

State Key Laboratory for Mesoscopic Physics, Frontiers Science Centre for Nanooptoelectronics, School of Physics, Peking University, Beijing, China <https://orcid.org/0000-0001-5451-4144>

Liping Ding

Institute for Basic Science

Ruixi Qiao

Peking University

Chang Liu

Peking University

Ying Fu

Institute of Physics, Chinese Academy of Sciences

Kehai Liu

Institute of Physics, Chinese Academy of Sciences

Xu Zhou

South China Normal University <https://orcid.org/0000-0003-3318-8735>

Qinghe Wang

Peking University

Quanlin Guo

Peking University

Guodong Xue

Peking University

Jinhuan Wang

Beijing Institute of Technology

Hao Hong

State Key Laboratory for Mesoscopic Physics, Collaborative Innovation Centre of Quantum Matter, School of Physics, Peking University

Muhong Wu

Peking University <https://orcid.org/0000-0003-3607-8945>

Dapeng Yu

Institute for Quantum Science and Engineering and Department of Physics, South University of Science and Technology of China

Enge Wang

Peking University

Xuedong Bai

Institute of Physics, Chinese Academy of Sciences <https://orcid.org/0000-0002-1403-491X>

Feng Ding

Institute for Basic Science <https://orcid.org/0000-0001-9153-9279>

Physical Sciences - Article

Keywords: Two-dimensional transition metal dichalcogenides, alloys, chalcogen monomers supply

Posted Date: April 21st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-411823/v1>

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Robust synthesis of two-dimensional metal dichalcogenides and their alloys by active chalcogen monomer supply

Yonggang Zuo^{1,2#}, Can Liu^{1#}, Liping Ding^{3#}, Ruixi Qiao^{4#}, Chang Liu⁴, Ying Fu⁵, Kehai Liu⁵, Xu Zhou⁶, Qinghe Wang¹, Quanlin Guo¹, Guodong Xue¹, Jinhuan Wang¹, Hao Hong¹, Muhong Wu^{4,7}, Dapeng Yu⁸, Enge Wang^{4,5,9}, Xuedong Bai^{2,5*}, Feng Ding^{3*}, Kaihui Liu^{1,4*}

¹ State Key Laboratory for Mesoscopic Physics, Frontiers Science Centre for Nano-optoelectronics, School of Physics, Peking University, Beijing, China

² Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, China

³ Centre for Multidimensional Carbon Materials, Institute for Basic Science, Ulsan, South Korea

⁴ International Centre for Quantum Materials, Collaborative Innovation Centre of Quantum Matter, Peking University, Beijing, China

⁵ Songshan Lake Materials Laboratory, Institute of Physics, Chinese Academy of Sciences, Dongguan, China

⁶ School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou, China

⁷ Interdisciplinary Institute of Light-Element Quantum Materials and Research Center for Light-Element Advanced Materials, Peking University, Beijing, China

⁸ Shenzhen Institute for Quantum Science and Engineering, Southern University of Science and Technology, Shenzhen, China

⁹ School of Physics, Liaoning University, Shenyang, China

These authors contributed equally to this work

* Correspondence: khliu@pku.edu.cn, f.ding@unist.ac.kr, xdbai@iphy.ac.cn

Two-dimensional (2D) transition metal dichalcogenides (TMDs), with their atomic thicknesses, high carrier mobility, fast charge transfer, and intrinsic spin-valley couplings, have been demonstrated one of the most appealing candidates for next-generation electronic and optoelectronic devices¹⁻³. The synthesis of TMDs with well-controlled crystallinity, quality and composition is essential to fully realize their promising applications⁴⁻¹³. Similar to that in III-V semiconductor synthesis, the precise precursor supply is a precondition for controllable growth of TMDs. Although great efforts have been devoted to modulate the transition metal supply, few effective methods of chalcogen feeding control were developed¹⁴⁻²¹. Herein we report a strategy of using active chalcogen monomer supply to grow TMDs and their alloys in a robust and controllable manner. It is found that at a high temperature, the active chalcogen monomers (such as S, Se, Te atoms or their mixtures) can be controllably released from metal chalcogenides and, thus, enable the synthesis of TMDs (MX_2 , $\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}, \text{Te}$) with very high quality, e.g., MoS_2 monolayers exhibit photoluminescent circular helicity of $\sim 92\%$, comparable to the best exfoliated single-crystal flakes and close to the theoretical limit of unity. More intriguingly, a uniform quaternary TMD alloy with three different anions, i.e., $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$, was accomplished for the first time. Our mechanism study revealed that the active chalcogen monomers can bind and diffuse freely on a TMD surface, which enables the effective nucleation and reaction, quick chalcogen vacancy healing, and alloy formation during the growth. The chalcogen monomer supply strategy offers more degrees of freedom for the controllable synthesis of 2D compounds and their alloys, which will greatly benefit the development of high-end devices with desired 2D materials.

It is well known that the controllable growth of multi-element bulk materials is generally much more challenging than that of single-element ones. For example, the synthesized first-generation semiconductor, silicon, can have the extremely low impurity of $\sim 10^{-11}$ and is nearly threading dislocation free, but the synthesized third-generation semiconductor, GaN, generally have a much higher impurity, $\sim 10^{-4}$, and a threading dislocation density of $\sim 10^4$ - 10^5 cm⁻² (ref²²). Analogously for the growth of 2D materials, the as-grown graphene already has excellent properties, which is comparable to the samples exfoliated from natural crystals, and the measured carrier mobilities are close to the theoretical limit²³, while the as-grown 2D compounds, such as TMDs, typically have lower quality than the natural crystals or the theoretical expectations²⁴. The main difficulty in controllable compounds' growth lies in the complicated feeding of several elements simultaneously during the growth process. Therefore, in the semiconductor industry, advanced and expensive techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapour deposition (MOCVD) have been developed to realize the precise control of multi-element supplies for the compound film growth.

The synthesis of high-quality TMD materials requires the precise feeding control of both the transition metal and chalcogen precursors as well. In the past decade, intensive efforts have been devoted to optimizing the feeding of metal precursors by thermal evaporation or molten-salt-assisted evaporation of metal oxide¹⁴, decomposition of metal-organic precursor¹⁵, direct deposition of metal layers, and others¹⁶⁻¹⁸. Although some methods for controllable chalcogen feeding, such as using either elemental chalcogen or chalcogen compounds (i.e., heating sulfur powder, using H₂S gas and ammonium sulphide¹⁹⁻²¹), have also been developed, it turns out that the chalcogen feeding control is much less effective than metal feeding control, as indicated by the most challenging problem in TMD quality control that the most synthesized TMDs are rich with chalcogen vacancies²⁵. Therefore, developing more effective chalcogen supply methods to enable the growth of high-quality TMDs is of critical importance.

In this work, we propose to use a chalcogen monomer feeding method in controllable TMD growth because of the following advantages: (i) the chalcogen monomers or atoms are generally very active than corresponding dimers or bulk and thus they can quickly react with metal precursors to form TMDs, (ii) the active chalcogen monomers can bind and quickly diffuse on a TMD surface to scavenge the vacancy defects effectively, which will greatly improve the quality of the TMDs and (iii) an active chalcogen monomer can react with a TMD and easily substitute a chalcogen atom and, thus, allow the synthesis of uniform TMD chalcogen alloys. However, as chalcogen of monomer state only exists at very high temperature (>2500 K) under normal circumstance²⁶, the most used methods can't produce enough chalcogen monomers at the typical TMD growth temperature, which is generally less than 1273 K. Herein, we developed an effective route to provide chalcogen monomer by heating a metal chalcogenide. The success of this approach lies in that the dangling bonds on the surface of metal chalcogenides are unstable and can be easily broken to release chalcogen atoms (monomers) under a relatively low temperature²⁷,²⁸, and the slowly released chalcogen atoms have a very low probability to react with each other to form dimers.

In our design, metal chalcogenide plate, ZnS, which served as the source for S monomers, was directly placed above the growth substrates of sapphire or SiO₂/Si (see Methods for details). The substrates were precoated with a thin layer of Na₂MoO₄ precursor to provide Mo source for MoS₂ growth (Fig. 1a, left panel). A confined space with a narrow gap of ~ 20 μm was naturally formed between the ZnS and the growth substrates. At an elevated growth temperature (750-950 $^{\circ}\text{C}$), S monomers slowly released from the ZnS surface can quickly reach the substrate surface and the possibility of their combination into dimers or polymers in the gas phase is very low (Fig. 1a, middle panel). These S monomers will react with melted Na₂MoO₄ pellets on the substrate to form monolayer MoS₂ (Fig. 1a, right panel). Indeed, the release of S monomers from the metal sulphide surface was observed long time ago²⁹, and was unambiguously revealed by the in-situ mass spectroscopy in our experiment (Fig. 1b). It is important to note that the S

monomers can't be obtained by sublimation of sulfur powders, where S_2 dimers are the dominating species at thermal equilibrium³⁰.

Since 2D materials are atomic thick and their growth only needs a trace amount of chalcogen atoms, the slowly released S monomers are sufficient for the successful synthesis of uniform monolayer MoS_2 with typical domain sizes of 50-80 μm and continuous film (Fig. 1c and Extended Data Fig. 1). A series of characterizations unequivocally reveal the high quality of MoS_2 fed by S monomer supply. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image exhibited the perfect hexagonal honeycomb lattice with both Mo and S atoms (Fig. 1d). The low-temperature photoluminescence (PL) spectra of the S-monomer-feeding-grown MoS_2 (Fig. 1e, orange curve) has a characteristic neutral exciton (X^0) emission peak accompanied with a trion (X^T) peak (believed to be caused by the n-type doping from substrate³¹), but the X^D peak (believed to be caused by S vacancy³² and was obvious in S-powder-feeding-grown samples, Fig. 1e, dark yellow curve) is nearly invisible, which clearly proves the high quality of the S-monomer-feeding-grown MoS_2 samples.

In addition, its high quality can be further confirmed by the measured optical circular helicity, which was detected to be as high as 92% (Fig. 1f) and comparable with the best exfoliated flakes from high-quality natural crystals³³. The circular helicity is directly related to the scattering between K and K' valleys in the Brillouin zone of MoS_2 whilst the defects will greatly enhance the inter-valley scattering and decrease circular helicity value. Thus, the near-unity circular helicity strongly proves the high quality of the as-grown MoS_2 samples. Here, we would like to note that intrinsic quality information of MoS_2 accessed by the optical helicity measurement is more reliable than that via electronic device measurements, where the device fabrication process, contact quality and device configuration will all bring great uncertainties in quality assessment³⁴.

Our strategy on MoS_2 growth by monomer feeding has also been proved to be applicable for the growth of other high-quality TMD materials. Six typical monolayer TMDs (Fig. 2a) have

been successfully synthesized by simply replacing the transition metal sources (e.g., Na_2MoO_4 and Na_2WO_4) and chalcogenide plates (e.g., ZnS , ZnSe , and ZnTe) (see Methods). The Raman and PL spectra of these obtained TMD samples demonstrated the successful synthesis of the 2H phase MoS_2 , WS_2 , MoSe_2 , WSe_2 , MoTe_2 and the 1T' phase WTe_2 and MoTe_2 (Fig. 2c-e and Extended Data Fig. 2). It's worth noting that the formation of transition metal tellurides, e.g., MoTe_2 and WTe_2 , are usually less favourable when chalcogen bulks applied³⁵, due to their higher formation energy compared to the corresponding sulphide and selenide (Fig. 2b). Thanks to the introduction of active Te monomers, the synthesis of WTe_2 and MoTe_2 turns to be much easier because of the greatly reduced formation energy.

The chalcogen monomer feeding method has a unique advantage in the growth of TMD chalcogen alloys. Since the evaporation temperatures, saturated vapour pressures and reaction energies of S, Se and Te are significantly different, it is nearly impossible to form high-quality TMD alloys with more than two anion elements by traditional approaches³⁶. Till now, there is no report on the successful growth of $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ alloy. In our experiment, we applied a compressed plate mixed with different metal chalcogenide powders, i.e., ZnS , ZnSe , and ZnTe , to supply three kinds of chalcogen monomers (S, Se, and Te) simultaneously (Fig. 3a). The as-grown alloy of $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ has a triangular domain similar to 2H phase TMDs (Fig. 3b). The X-ray photoelectron spectroscopy (XPS) unambiguously revealed the coexistence of S, Se, and Te atoms in the synthesized TMD alloy (Extended Data Fig. 3), and the energy dispersive X-ray spectroscopy (EDS) as well as the STEM measurements further demonstrated the homogenous element distribution throughout the TMD alloy in both macro- and micro-scales, with no observable phase separation (Fig. 3e and Extended Data Fig. 4). Enlarged STEM image (Fig. 3f) further demonstrated the high crystallinity of the TMD alloy, and the distinct intensity distribution revealed the Mo, S, Se, and Te site occupancies according to the Z-contrast nature of HAADF image (Fig. 3g). Quantitative analysis of the doped Te and Se distribution was evaluated in a 32×32 nm STEM image, and the statistical results match well with the binomial distribution

model (Fig. 3h,i, Extended Data Fig. 5 and Methods), suggesting the random distribution of S, Se and Te atoms in the TMD alloy.

Furthermore, one can easily tune the composition of the TMD alloys by controlling the growth temperature to vary the fluxes of S, Se and Te from the ZnS, ZnSe and ZnTe composite. As the growth temperature increased, the PL peak shifted to longer wavelength (Fig. 3c), revealing the concentration of Se and Te atoms became higher in the alloy (MoSe₂ and MoTe₂ have smaller bandgaps than MoS₂). Meanwhile, in the Raman spectra, the MoS₂-featured peaks gradually attenuated and the MoTe₂-featured peaks gradually enhanced, while the MoSe₂-featured peaks enhanced first and then attenuated (Fig. 3d), which indicates that the heavy chalcogen atoms are being doped more into the MoS₂ at higher temperature.

Finally, we try to understand the unique role of chalcogen monomer supply in the synthesis of high-quality TMDs and their complex alloys theoretically. We firstly explore the reactions of Na₂MoO₄ with sulfur monomers and dimers, respectively, by first-principles molecular dynamic (MD) simulations (Extended Data Fig. 6). The simulation results clearly demonstrated that sulfur monomers are more reactive to substitute the oxygen atoms in a MoO₄ group of Na₂MoO₄ while most dimers are desorbed from the Na₂MoO₄ surface due to their less activity. By adding more S and MoS₃ clusters to the Na₂MoO₄, the nucleation of Mo_xS_y clusters can also be clearly seen (Extended Data Fig. 7).

In compare with the bond-saturated S₂/Se₂/Te₂ dimers, S/Se/Te monomers possess much higher adsorption energies on a TMD surface (for dimers $E_b < 0.8$ eV, for monomers $E_b > 1.5$ eV) (Fig. 4b and Extended Data Fig. 8a). Therefore, one can expect a large number of S/Se/Te monomers to diffuse on the TMD surface during the whole growth process and the growth of TMD is in a chalcogen monomer rich environment. Once a chalcogen monomer diffuse to the vicinal area of a vacancy, the vacancy can be quickly healed by a highly exothermic reaction (Fig. 4a, Fig. 4c and Extended Data Fig. 8b). Therefore, the chalcogen vacancy density is greatly

reduced as has been shown in the experimental results. To address the capacity of forming TMD chalcogen alloys, we calculated the reaction energy of substituting a chalcogen atom in a TMD by using chalcogen monomer, dimer, and bulk as references (Extended Data Fig. 9). It is clearly shown that doping of Te dimer or bulk into MoS₂/MoSe₂, S bulk into MoSe₂, Se bulk into MoS₂ are all difficult because of the near-zero or positive reaction energies. While, if chalcogen monomer is used as the source of dopant, all doping reactions become more exothermic with negative reaction energies, which implies the greatly improved capacity of forming chalcogen TMD alloys.

This study clearly demonstrated that the high reactivity of chalcogen monomers can significantly facilitate the TMD nucleation, chalcogen defects healing in the growth to greatly improve the samples' quality and allow the formation of various chalcogen TMDs and their alloys. The monomer supply should provide a new degree of freedom in modulating compound materials and high-entropy 2D alloys, thus widening their potential applications in electronic, optoelectronic and valleytronic devices.

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Acknowledgements: This work was supported by the National Natural Science Foundation of China (52025023, 51991342, 52021006, 51991344 and 11888101), The Key R&D Program of Guangdong Province (2020B010189001, 2019B010931001 and 2018B030327001), the Pearl River Talent Recruitment Program of Guangdong Province (2019ZT08C321), the Strategic Priority Research Program of Chinese Academy of Sciences (XDB33000000 and XDB33030200), Beijing Natural Science Foundation (JQ19004), Beijing Excellent Talents Training Support (2017000026833ZK11), National Postdoctoral Program for Innovative Talents (BX20190016) and China Postdoctoral Science Foundation (2019M660280, 2019M660281 and 2020T130022). We acknowledge the Electron Microscopy Laboratory in Peking University for the use of electron microscopy.

Methods:

Growth of TMDs and their alloys.

The substrate of sapphire or SiO₂/Si was first pretreated by O₂ plasma, followed by the spin-coating process of Na₂MoO₄ or Na₂WO₄ aqueous solution with optimized concentrations (Na₂MoO₄ of 12, 18, and 6 mg/mL for MoS₂, MoSe₂, and MoTe₂ growth, Na₂WO₄ of 20, 30 and 12 mg/mL for WS₂, WSe₂, and WTe₂ growth, respectively). After dried in Ar atmosphere, the chalcogenide crystal plate (ZnS, ZnSe, or ZnTe) was placed directly above the substrate and then loaded into the CVD furnace together. The chamber of furnace was flushed with Ar (100 sccm) and heated to the optimized growth temperature (~780 °C, ~930 °C, ~800 °C, ~820 °C, ~750-800 °C, ~800 °C and ~780 °C for MoS₂, WS₂, MoSe₂, WSe₂, 2H-MoTe₂, 1T'-MoTe₂ and 1T'-WTe₂, respectively). During the growth process, the system pressure was kept at ~120 Pa and the growth duration was set as 10-60 minutes. After growth, the system was naturally cooled down to room temperature. Similar growth conditions were applied to the TMD alloy growth, wherein the major difference lies in the use of a chalcogenide mixture plate.

Characterizations of TMDs and their alloys.

Optical measurements. Optical images were taken with an Olympus BX51M microscope. Raman and PL spectra were measured by a customer-designed optical system with the excitation wavelength of 532 nm and the power of ~1 mW. Low-temperature PL spectra were obtained at 10 K by optical cryostat (Montana Instruments) with the laser excitation wavelength of 532 nm. Circular-polarization-resolved PL measurements were performed under near-resonant excitation of 633 nm at 10 K. The circularly polarized light was generated by using a super-achromatic quarter-wave plate (Thorlabs SAQWP05M-1700) and the photoluminescence was analyzed through the same quarter-wave plate and a linear-polarizer. We define the degree of PL circular helicity (η), which reflects the valley polarization, as $\eta = (\text{PL}(\sigma^+) - \text{PL}(\sigma^-)) / (\text{PL}(\sigma^+) + \text{PL}(\sigma^-))$.

XPS, MS, EDS, STEM characterizations. XPS measurements were performed using an ESCALAB 250X system (Thermo Fisher Scientific) and excited by monochromatic Al K α radiation. Mass spectrometer (Hiden HR20) attached with temperature-programmed decomposition (TPD) was used to in-situ detect and analyze the released gas in inert atmosphere. EDS and STEM experiments were performed in FEI Titan Themis G2 300 operated at 300 kV and in Nion U-HERMES200 at 60 kV for element analysis and characterizing atomic structures of samples.

Statistical Se and Te atoms distribution in the quaternary MoS_{2(1-x-y)}Se_{2x}Te_{2y} alloy.

To evaluate the distribution of Se and Te atoms in our quaternary alloy, statistical analysis was conducted in a 32 × 32 nm STEM image (Extended Data Fig. 5a). The atoms in the image were sorted into metal atom (M) sites and chalcogen atom (X₂) sites. The intensity histogram of all X₂ sites shows three peaks, which are assigned to be “S site”, “Se site” and “Te site” regions, respectively, according to the Z-contrast nature of STEM image (Extended Data Fig. 5b). Note that every X₂ site in STEM image is actually a projection of two overlapped X atoms along the electron beam direction, “S site” denotes both X atoms are S, “Se site” means two possible configurations: Se-S or Se-Se, while “Te site” stands for Te-S, Te-Se, or Te-Te. According to the overall statistical result, $P(S)$, the probability for an X₂ site to be “S site”, is

9122/(9122+2417+771) = 0.741. Similarly, the probability of “Se site” and “Te site” denoting as $P(Se)$ and $P(Te)$, are 0.196 and 0.063, respectively.

Assume that Se and Te are randomly distributed in the X₂ sites, the overall probability of $P(Se)$ and $P(Te)$ will also be valid to every X₂ site. Thus, the probability of Se distribution could be calculated by the binomial distribution

$$f(k; N, P(Se)) = \frac{N!}{k! (N-k)!} P(Se)^k (1 - P(Se))^{N-k} \quad (1)$$

where N is the total X₂ site number of a region and k is the “Se site” number found in it. The same analysis can be applied to the Te case. To verify this random-distribution assumption, the entire image was cut into identical 30 × 30 parts, each of which comprised about 14 X₂ sites. The statistical histogram of “Te site” and “Se site” for these 900 parts are shown in Fig. 3i and Extended Data Fig. 5d), which match well with the purple dotted lines calculated by the binomial distribution, suggesting the random distribution of Te and Se atoms in our quaternary alloy.

In addition, there is a relationship between the probability P and the atom concentration c :

$$P(S) = c(S)^2 \quad (2)$$

$$P(Se) = 2c(Se)c(S) + c(Se)^2 \quad (3)$$

$$c(S) + c(Se) + c(Te) = 1 \quad (4)$$

from the probability data and these equations, the concentrations of S, Se and Te were extracted to be 86.1%, 10.7%, 3.2%, respectively, which is very close to the concentrations extracted from the preceding EDS spectrum (84.0%, 12.7%, and 3.3%, respectively, as mentioned in Extended Data Fig. 4) and confirms our statistical conclusion.

Computational details.

All the density functional theory (DFT) calculations were implemented by the Vienna Ab Initio Simulation Package (VASP)^{37, 38}, with projector-augmented wave (PAW)³⁹ method describing the interaction between valence electrons and ion cores. The Perdew-Burke-Ernzerhof (PBE)⁴⁰,⁴¹ exchange-correlation functional was used to describe the interaction between electrons. A plane

wave basis set with a cutoff energy of 450 eV was adopted. All the structures were fully relaxed, and the convergence criteria for energy and force were set at 10^{-5} eV and 10^{-2} eV/Å, respectively. The Brillion zone is sampled by $1\times 1\times 1$ grid meshes. A vacuum spacing larger than 15 Å was set to avoid the interaction between neighboring images along the non-periodic direction. The energy barriers were calculated by using the climbing image nudged elastic band (CI-NEB) method⁴² with a force threshold of -0.02 eV/Å.

Theoretical calculations on initiated nucleation of MoS₂ by sulfur monomer or dimer supply.

Based on the MD simulations, the sulfidation processes of Na₂MoO₄ are analyzed at atomic-level. Here we consider the sulfur source in the form of S monomers and S₂ dimers respectively. As shown in Extended Data Fig. 6, eight S monomers and four S₂ dimers were deposited on the NaMoO₄ surface during the MD trajectories. The MD simulations clearly showed that S monomers are more active and can easily substitute the oxygen atoms of Na₂MoO₄, resulting in SO or SO₂ molecules in gas phase and Mo-S bond formation in the liquid Na₂MoS_xO_{4-x} (green circle). This proves that S monomers released from the ZnS surface are more reactive in the growth of TMDs. Adding more S monomers to the Na₂MoO₄ surface (Extended Data Fig. 7a-b), the aggregation of Mo and S atoms during the MD simulation is clearly seen and the clusters of MoS₃O_x are formed on the surface (Extended Data Fig. 7c-d). To demonstrate the nucleation of MoS₂, we added a few MoS₃ molecules on the substrate and large Mo_xS_y clusters (green circle) were formed during the MD simulation (Extended Data Fig. 7e-f). In summary, we have demonstrated the mechanism of TMD growth by the density-functional-theory-based MD simulations. Firstly, the active S monomers replace O atoms in Na₂MoO₄. Then, the high concentration of S substitutes in the Na₂MoO₄ will lead to the formation of Mo_xS_y clusters on the surface of the substrate. Finally, the aggregation of Mo_xS_y clusters results in the nucleation of MoS₂ on the Na₂MoO₄ surface.

Calculations of formation energies of different transition metal dichalcogenides.

To understand the relative stability of these TMDs (MX_2 , $\text{M} = \text{Mo, W}$; $\text{X} = \text{S, Se, Te}$), the formation energies of these TMDs were calculated by using

$$E_f = E_{\text{MX}_2} - \mu_{\text{M}} - 2\mu_{\text{X}}, \quad (5)$$

where E_{MX_2} is the energy of the MX_2 , μ_{M} and μ_{X} are the energies of M in the form of bulk and X atoms using monomer or bulk as references, respectively. These results on formation energies (Fig. 2b) clearly show that MS_2 and MSe_2 are highly stable, while MTe_2 might hardly to be synthesized due to the high formation energies, which agree well with the most experimental results of TMD synthesis.

Reaction energies of ternary TMD alloys obtained by X (X = S, Se, Te) doped MoX_2 .

In order to confirm the possibility of forming $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ alloy, we calculated the reaction energy (E_R) of X (X = S, Se, Te) doped MoX_2 (X = S, Se, Te). Here, we take ternary alloy $\text{MoSe}_x\text{S}_{2-x}$ as an example. Its reaction energy can be calculated by using

$$E_R = E_{\text{MoSe}_x\text{S}_{2-x}} - E_{\text{MoS}_2} + x\mu_{\text{S}} - x\mu_{\text{Se}}, \quad (6)$$

Where $E_{\text{MoSe}_x\text{S}_{2-x}}$ and E_{MoS_2} are the energies of ternary alloy $\text{MoSe}_x\text{S}_{2-x}$ and perfect MoS_2 , respectively. μ_{S} and μ_{Se} are the energies of S and Se atoms which are in the form of bulk, dimer and monomer, respectively. The obtained different formation energies are shown in Extended Data Fig. 9. It is found that the monomers of S, Se and Te monomers can be easily doped into MoX_2 with reaction energies less than -2.0 eV. While the Te_2 could hardly be used to dope MoS_2 or MoSe_2 because of the near zero reaction energy. If bulk dopants are employed, only S/Se can easily dope the MoTe_2 . This result further confirms the advantage of using S/Se/Te monomer to grow $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ alloys.

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Figures and captions:

Figure 1 | Growth of high-quality monolayer MoS₂ by sulfur monomer supply. **a**, Schematic of sulfur (S) monomer supply for the growth of MoS₂. S monomers are released from the surface of ZnS under high temperature, then confined in the narrow space and react with Na₂MoO₄ to form MoS₂. **b**, In-situ mass spectrum of ZnS annealed at 1000 °C. The intense peak at the mass of 32 clearly proves the dominating release of S monomers. The measurements were carried out with carrier gas of He and the data was subtracted by background. **c**, Optical image of as-grown monolayer MoS₂ domain on sapphire. **d**, Atomic-resolved HAADF-STEM image of the prepared MoS₂, revealing the high crystallinity of MoS₂ without detectable S vacancies. **e**, Low-temperature (10 K) PL spectra of MoS₂ samples fed by S monomer (orange curve) and S powder (dark yellow curve), respectively. Three typical features, X⁰, X^T, and X^D peaks assign to neutral exciton, trion, and defect state emission peaks, respectively. The absence of X^D peak confirmed the high quality of MoS₂ grown by S monomer supply. **f**, The circular dichroism PL spectrum measured at 10 K. The near-unity polarization of MoS₂ on sapphire indicates the high optical quality.

Figure 2 | Universal growth of diverse TMDs by chalcogen monomer supply. **a**, Optical images of the representative TMDs, including 2H phase MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂ and 1T' phase WTe₂. **b**, The calculated formation energy (E_f) of the six representative TMDs. When chalcogen bulks are supplied as precursors, the formation of transition metal tellurides in relative to their corresponding sulphide and selenide are less favourable due to their high formation energy (-0.73 and -0.68 eV/unit for MoTe₂ and WTe₂, respectively). While it becomes highly favourable when Te monomers are applied. **c-e**, The corresponding Raman (c,d) and PL (e) spectra of TMDs in (a). All spectra were vertically shifted for clarity.

Figure 3 | Growth and characterization of quaternary TMD alloy. **a**, Schematic diagram of quaternary alloy growth using a compressed plate mixed with chalcogenide powders of ZnS, ZnSe, and ZnTe. **b**, Optical image of $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ domain on SiO_2/Si substrate. **c,d**, PL (**c**) and Raman (**d**) spectra of the $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ sample grown at different temperatures. As the growth temperature increased, the PL peak position showed a clear red shift. The intensity of MoS_2 -like E_{2g} ($\sim 380 \text{ cm}^{-1}$) and A_{1g} ($\sim 400 \text{ cm}^{-1}$) was reduced while the MoTe_2 -like A_{1g} ($\sim 150 \text{ cm}^{-1}$) increased and MoSe_2 -like A_{1g} ($\sim 240 \text{ cm}^{-1}$) increased first and then reduced. **e,f**, STEM images of the $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$, demonstrating the high crystallinity of quaternary alloy. **g**, Intensity profiles along the labeled orange dotted box in (f), which highlights the occupancies of Mo, S, Se, and Te sites. **h**, The Te-site distribution in a $32 \times 32 \text{ nm}$ STEM image of the quaternary alloy. The image was divided into 30×30 parts. **i**, The corresponding statistical histogram of Te-site counts in each parts of the image. It shows a well binomial distribution feature (purple dotted line), revealing the random distribution of Te atoms.

448

449 **Figure 4 | Growth Mechanism with chalcogen monomer supply in MoX₂ (X = S, Se, Te).** **a**,
 450 Schematic diagram of adsorption, diffusion, and vacancy healing of chalcogen monomer on
 451 MoX₂ surface. **b**, The binding energies of monomers and dimers on MoX₂ surface. The much
 452 higher energy of monomers facilitates their better adsorption on the TMD surface than dimers. **c**,
 453 The energy profiles of vacancy healing for MoX₂ surface by using chalcogen monomers. The
 454 relatively small energy barriers of chalcogen monomer diffusion and the highly exothermic
 455 reaction at the vacancy both accelerate the self-healing of MoX₂.

Extended Data Fig. 1 | Characterization of the as-grown monolayer MoS₂ domain and film.

a,b, The PL mapping image (a) and a representative PL spectrum (b) of MoS₂ domain grown by S monomer supply. **c,** The optical image of MoS₂ film grown on sapphire by S monomer supply. The green region on upper right of (c) indicates the bare sapphire substrate.

461

462 **Extended Data Fig. 2 | 1T' phase MoTe₂ sample prepared by Te monomer supply. a,** Optical

463 **image of 1T'-MoTe₂. b,** Raman spectrum of 1T'-MoTe₂ flake.

Extended Data Fig. 3 | XPS of quaternary 2D $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ alloy. a-d, XPS spectra of as-grown $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ sample, showing binding energy states of Se 3p and S 2p (a), Se 2p (b), Te 3d (c), and Mo 3d (d), respectively.

Extended Data Fig. 4 | EDS characterization of quaternary monolayer $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ alloy. **a**, EDS spectrum of $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ sample transferred onto TEM Cu grid. The peaks of S, Se, and Te were clearly observed, and their atomic concentrations were quantitatively extracted to be 84.0%, 12.7%, and 3.3%, respectively. **b**, The scanning transmission electron microscopy (STEM) image of the as-grown monolayer alloy film. **c-f**, EDS mapping of Mo (c), S (d), Se (e), and Te (f) corresponding to the area in (b), showing the uniform element distribution.

475

476 **Extended Data Fig. 5 | STEM analysis of quaternary 2D $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ alloy.** **a**, 32×32
 477 nm STEM image of $\text{MoS}_{2(1-x-y)}\text{Se}_{2x}\text{Te}_{2y}$ quaternary alloy. The Te-occupied sites in the image
 478 exhibit the brightest contrast and uniform distribution. **b**, Intensity histogram of the chalcogen
 479 atom (X_2) sites in (a). Due to the Z-contrast nature of STEM image, X_2 sites occupied by different
 480 atoms show distinct intensity ranges. The three peaks are assigned to be “S site”, “Se site” and
 481 “Te site” regions as marked by yellow, green, and blue, respectively. The statistical result shows
 482 9122 S sites, 2417 Se sites, and 771 Te sites from the total 12310 X_2 sites in (a). **c**, The Se-site
 483 distribution in the divided 30×30 parts of (a). **d**, The corresponding statistical histogram of Se-
 484 site counts in each parts of (a).

Extended Data Fig. 6 | Snapshots taken during the MD simulation of sulfidation of liquid Na_2MoO_4 and the corresponding energy profiles. a,b, Snapshots taken during the MD simulation of sulfidation with eight sulfur monomers and the corresponding energy profiles at t_1 (0 ps), t_2 (1.69 ps), t_3 (6.27 ps) and t_4 (7.94 ps), respectively. It shows that S monomers can easily substitute the oxygen atoms of Na_2MoO_4 . **c,d,** Snapshots taken during the MD simulation of sulfidation with four sulfur dimers and the corresponding energy profiles at t_1 (0 ps), t_2 (1.12 ps), t_3 (5.97 ps) and t_4 (8.00 ps), respectively. The structures inside green circle present the $\text{MoS}_x\text{O}_{4-x}$ cluster, the ones inside blue circle indicate that S dimers disappears in the form of gas. The yellow, red, violet, and blue spheres represent sulfur, oxygen, sodium and molybdenum atoms, respectively.

Extended Data Fig. 7 | Snapshots taken during the MD simulation on nucleation process with S monomers supply and their corresponding energy profiles. **a,b**, Snapshots taken during the MD simulation when some sulfur monomers exist on the Na_2MoO_4 surface in the first stage and the corresponding energy profiles at t_1 (0 ps), t_2 (1.05 ps), t_3 (5.14 ps) and t_4 (8.00 ps), respectively. **c,d**, Snapshots taken during the MD simulation when $\text{MoS}_x\text{O}_{4-x}$ clusters (green circle) formed on the Na_2MoO_4 surface in the second stage and the corresponding energy profiles at t_5 (0 ps), t_6 (0.62 ps), t_7 (1.92 ps) and t_8 (3.50 ps), respectively. **e,f**, Snapshots taken during the MD simulation when Mo_xS_y clusters (green circle) result in the nucleation of MoS_2 (black circle) in the finally stage and the corresponding energy profiles at t_9 (0 ps), t_{10} (1.0 ps), t_{11} (1.50 ps) and t_{12} (2.48 ps), respectively. The yellow, red, violet, and blue spheres represent sulfur, oxygen, sodium, and molybdenum atoms, respectively.

508

509 **Extended Data Fig. 8 | Proposed mechanism of chalcogen monomer modulated WX₂ (X =**
 510 **S, Se, Te) growth. a,** The binding energies of monomer and dimer on MoX₂ surface. **b,** The
 511 energy profiles of vacancy healing on WX₂ surface by using chalcogen monomer.

Extended Data Fig. 9 | Calculated reaction energies of ternary TMD alloys. **a**, The schematic diagram of substituting a chalcogen atom in a TMD by using chalcogen monomer, dimer and bulk as references. **b**, The reaction energies to form ternary TMD alloys. It can be clearly seen that the S, Se, and Te monomers can be easily doped into MoX₂ with reaction energies less than -2.0 eV, while doping of Te dimer or bulk into MoS₂/MoSe₂, S bulk into MoSe₂, Se bulk into MoS₂ are all difficult because of the near-zero or high reaction energies. These results further emphasize the advantage of S/Se/Te monomer supply to grow MoS₂(1-x-y)Se_{2x}Te_{2y} alloy.

Figures

Figure 1

Growth of high-quality monolayer MoS₂ by sulfur monomer supply. a, Schematic of sulfur (S) monomer supply for the growth of MoS₂. S monomers are released from the surface of ZnS under high temperature, then confined in the narrow space and react with Na₂MoO₄ to form MoS₂. b, In-situ mass spectrum of ZnS annealed at 1000 °C. The intense peak at the mass of 32 clearly proves the dominating release of S monomers. The measurements were carried out with carrier gas of He and the data was subtracted by background. c, Optical image of as-grown monolayer MoS₂ domain on sapphire. d, Atomic-resolved HAADF-STEM image of the prepared MoS₂, revealing the high crystallinity of MoS₂ without detectable S vacancies. e, Low temperature (10 K) PL spectra of MoS₂ samples fed by S monomer (orange curve) and S powder (dark yellow curve), respectively. Three typical features, X₀, X_T, and X_D peaks assign to neutral exciton, trion, and defect state emission peaks, respectively. The absence of X_D peak confirmed the high quality of MoS₂ grown by S monomer supply. f, The circular dichroism PL spectrum measured at 10 K. The near-unity polarization of MoS₂ on sapphire indicates the high optical quality.

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