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

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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 devices\cite{1-3}. The synthesis of TMDs with well-controlled crystallinity, quality and composition is essential to fully realize their promising applications\cite{4-13}. 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 developed\cite{14-21}. 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$_2$, M = Mo, W; X = S, Se, Te) with very high quality, e.g., MoS$_2$ monolayers exhibit photoluminescent circular helicity of ~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., MoS$_{2(1-x-y)}$Se$_{2x}$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\(^{-2}\) (ref \(^{22}\)). 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 limit\(^ {23}\), while the as-grown 2D compounds, such as TMDs, typically have lower quality than the natural crystals or the theoretical expectations\(^ {24}\). 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 oxide\(^ {14}\), decomposition of metal-organic precursor\(^ {15}\), direct deposition of metal layers, and others\(^ {16-18}\). Although some methods for controllable chalcogen feeding, such as using either elemental chalcogen or chalcogen compounds (i.e., heating sulfur powder, using H\(_2\)S gas and ammonium sulphide\(^ {19-21}\)), 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 vacancies\(^ {25}\). 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 circumstance, 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 temperature, 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 °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 ago, 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 S₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ (Fig. 1e, orange curve) has a characteristic neutral exciton (X⁰) emission peak accompanied with a trion (X³⁺) peak (believed to be caused by the n-type doping from substrate³¹), but the X⁰ 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 MoS₂ 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 MoS₂ 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 MoS₂ samples. Here, we would like to note that intrinsic quality information of MoS₂ 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 MoS₂ 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$_2$MoO$_4$ and Na$_2$WO$_4$) 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 applied$^{35}$, 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 approaches$^{36}$. Till now, there is no report on the successful growth of MoS$_{2(1-x-y)}$Se$_{2x}$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 MoS$_{2(1-x-y)}$Se$_{2x}$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 (MoSe$_2$ and MoTe$_2$ have smaller bandgaps than MoS$_2$). Meanwhile, in the Raman spectra, the MoS$_2$-featured peaks gradually attenuated and the MoTe$_2$-featured peaks gradually enhanced, while the MoSe$_2$-featured peaks enhanced first and then attenuated (Fig. 3d), which indicates that the heavy chalcogen atoms are being doped more into the MoS$_2$ 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 Na$_2$MoO$_4$ 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 MoO$_4$ group of Na$_2$MoO$_4$ while most dimers are desorbed from the Na$_2$MoO$_4$ surface due to their less activity. By adding more S and MoS$_3$ clusters to the Na$_2$MoO$_4$, the nucleation of Mo$_x$S$_y$ clusters can also be clearly seen (Extended Data Fig. 7).

In compare with the bond-saturated S$_2$/Se$_2$/Te$_2$ 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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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 ($\eta$), 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 Kα 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$_x$Te$_y$ alloy.

To evaluate the distribution of Se and Te atoms in our quaternary alloy, statistical analysis was conducted in a $32 \times 32$ nm STEM image (Extended Data Fig. 5a). The atoms in the image were sorted into metal atom (M) sites and chalcogen atom (X$_2$) sites. The intensity histogram of all X$_2$ 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 X$_2$ 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 X$_2$ 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

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

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 $c$:

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

$$P(Se) = 2c(Se)c(S) + c(Se)^2$$

$$c(S) + c(Se) + c(Te) = 1$$

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)\textsuperscript{37, 38}, with projector-augmented wave (PAW)\textsuperscript{39} method describing the interaction between valence electrons and ion cores. The Perdew-Burke-Ernzerhof (PBE)\textsuperscript{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) method with a force threshold of -0.02 eV/Å.

Theoretical calculations on initiated nucleation of MoS$_2$ by sulfur monomer or dimer supply. Based on the MD simulations, the sulfidation processes of Na$_2$MoO$_4$ are analyzed at atomic-level. Here we consider the sulfur source in the form of S monomers and S$_2$ dimers respectively. As shown in Extended Data Fig. 6, eight S monomers and four S$_2$ dimers were deposited on the NaMoO$_4$ surface during the MD trajectories. The MD simulations clearly showed that S monomers are more active and can easily substitute the oxygen atoms of Na$_2$MoO$_4$, resulting in SO or SO$_2$ molecules in gas phase and Mo-S bond formation in the liquid Na$_2$MoS$_x$O$_{4-x}$ (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 Na$_2$MoO$_4$ surface (Extended Data Fig. 7a-b), the aggregation of Mo and S atoms during the MD simulation is clearly seen and the clusters of MoS$_3$O$_x$ are formed on the surface (Extended Data Fig. 7c-d). To demonstrate the nucleation of MoS$_2$, we added a few MoS$_3$ molecules on the substrate and large Mo$_x$S$_y$ 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 Na$_2$MoO$_4$. Then, the high concentration of S substitutes in the Na$_2$MoO$_4$ will lead to the formation of Mo$_x$S$_y$ clusters on the surface of the substrate. Finally, the aggregation of Mo$_x$S$_y$ clusters results in the nucleation of MoS$_2$ on the Na$_2$MoO$_4$ surface.

Calculations of formation energies of different transition metal dichalcogenides.
To understand the relative stability of these TMDs (MX$_2$, M = Mo, W; X = S, Se, Te), the formation energies of these TMDs were calculated by using

$$E_f = E_{MX_2} - \mu_M - 2\mu_X,$$

where $E_{MX_2}$ is the energy of the MX$_2$, $\mu_M$ and $\mu_X$ 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 MoS$_2$($1-x-y$)Se$_x$Te$_y$ 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 MoSe$_x$S$_{2-x}$ as an example. Its reaction energy can be calculated by using

$$E_R = E_{MoSe_xS_{2-x}} - E_{MoS_2} + x\mu_S - x\mu_{Se},$$

Where $E_{MoSe_xS_{2-x}}$ and $E_{MoS_2}$ are the energies of ternary alloy MoSe$_x$S$_{2-x}$ and perfect MoS$_2$, respectively. $\mu_S$ and $\mu_{Se}$ 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 MoS$_2$($1-x-y$)Se$_x$Te$_y$ alloys.
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**Figures and captions:**

**Figure 1 | Growth of high-quality monolayer MoS\(_2\) by sulfur monomer supply.**

- **a**, Schematic of sulfur (S) monomer supply for the growth of MoS\(_2\). S monomers are released from the surface of ZnS under high temperature, then confined in the narrow space and react with Na\(_2\)MoO\(_4\) to form MoS\(_2\).
- **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 MoS\(_2\) domain on sapphire.
- **d**, Atomic-resolved HAADF-STEM image of the prepared MoS\(_2\), revealing the high crystallinity of MoS\(_2\) without detectable S vacancies.
- **e**, Low-temperature (10 K) PL spectra of MoS\(_2\) samples fed by S monomer (orange curve) and S powder (dark yellow curve), respectively. Three typical features, \(X^0\), \(X^T\), 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 MoS\(_2\) grown by S monomer supply.
- **f**, The circular dichroism PL spectrum measured at 10 K. The near-unity polarization of MoS\(_2\) 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 MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$, WSe$_2$ and 1T’ phase WTe$_2$. 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 MoTe$_2$ and WTe$_2$, 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 MoS$_{2(1-x-y)}$Se$_{2x}$Te$_{2y}$ domain on SiO$_2$/Si substrate. c,d, PL (c) and Raman (d) spectra of the MoS$_{2(1-x-y)}$Se$_{2x}$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$_{2g}$ (~380 cm$^{-1}$) and A$_{1g}$ (~400 cm$^{-1}$) was reduced while the MoTe$_2$-like A$_{1g}$ (~150 cm$^{-1}$) increased and MoSe$_2$-like A$_{1g}$ (~240 cm$^{-1}$) increased first and then reduced. e,f, STEM images of the MoS$_{2(1-x-y)}$Se$_{2x}$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 × 32 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.
**Figure 4** | Growth Mechanism with chalcogen monomer supply in MoX$_2$ (X = S, Se, Te). a, Schematic diagram of adsorption, diffusion, and vacancy healing of chalcogen monomer on MoX$_2$ surface. b, The binding energies of monomers and dimers on MoX$_2$ surface. The much higher energy of monomers facilitates their better adsorption on the TMD surface than dimers. c, The energy profiles of vacancy healing for MoX$_2$ surface by using chalcogen monomers. The relatively small energy barriers of chalcogen monomer diffusion and the highly exothermic reaction at the vacancy both accelerate the self-healing of MoX$_2$. 
Extended Data Fig. 1 | Characterization of the as-grown monolayer MoS$_2$ domain and film.

a,b, The PL mapping image (a) and a representative PL spectrum (b) of MoS$_2$ domain grown by S monomer supply. c, The optical image of MoS$_2$ film grown on sapphire by S monomer supply. The green region on upper right of (c) indicates the bare sapphire substrate.
Extended Data Fig. 2 | 1T’ phase MoTe₂ sample prepared by Te monomer supply. 

a, Optical image of 1T'-MoTe₂. b, Raman spectrum of 1T'-MoTe₂ flake.
**Extended Data Fig. 3 | XPS of quaternary 2D MoS$_{2(1-x-y)}$Se$_{2x}$Te$_{2y}$ alloy.** a-d, XPS spectra of as-grown MoS$_{2(1-x-y)}$Se$_{2x}$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 Mo$_{2(1-x-y)}$Se$_{2x}$Te$_{2y}$ alloy. 

**a**, EDS spectrum of Mo$_{2(1-x-y)}$Se$_{2x}$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.
Extended Data Fig. 5 | STEM analysis of quaternary 2D MoS$_{2(1-x-y)}$Se$_{2x}$Te$_{2y}$ alloy. a, 32 × 32 nm STEM image of MoS$_{2(1-x-y)}$Se$_{2x}$Te$_{2y}$ quaternary alloy. The Te-occupied sites in the image exhibit the brightest contrast and uniform distribution. b, Intensity histogram of the chalcogen atom (X$_2$) sites in (a). Due to the Z-contrast nature of STEM image, X$_2$ sites occupied by different atoms show distinct intensity ranges. The three peaks are assigned to be “S site”, “Se site” and “Te site” regions as marked by yellow, green, and blue, respectively. The statistical result shows 9122 S sites, 2417 Se sites, and 771 Te sites from the total 12310 X$_2$ sites in (a). c, The Se-site distribution in the divided 30 × 30 parts of (a). d, The corresponding statistical histogram of Se-site counts in each parts of (a).
Extended Data Fig. 6 | Snapshots taken during the MD simulation of sulfidation of liquid Na$_2$MoO$_4$ 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$_2$MoO$_4$. **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 MoS$_{x}$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 Na₂MoO₄ surface in the first stage and the corresponding energy profiles at t₁ (0 ps), t₂ (1.05 ps), t₃ (5.14 ps) and t₄ (8.00 ps), respectively. 

c,d, Snapshots taken during the MD simulation when MoSₓO₄₋ₓ clusters (green circle) formed on the Na₂MoO₄ surface in the second stage and the corresponding energy profiles at t₅ (0 ps), t₆ (0.62 ps), t₇ (1.92 ps) and t₈ (3.50 ps), respectively. 

e,f, Snapshots taken during the MD simulation when MoₓSᵧ clusters (green circle) result in the nucleation of MoS₂ (black circle) in the finally stage and the corresponding energy profiles at t₉ (0 ps), t₁₀ (1.0 ps), t₁₁ (1.50 ps) and t₁₂ (2.48 ps), respectively. The yellow, red, violet, and blue spheres represent sulfur, oxygen, sodium, and molybdenum atoms, respectively.
**Extended Data Fig. 8** | Proposed mechanism of chalcogen monomer modulated WX₂ (X = S, Se, Te) growth. a, The binding energies of monomer and dimer on MoX₂ surface. b, The 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)Se₂xTe₂y alloy.