

Materials Science

Special Topic: Two-dimensional Materials and Devices

Iodine-assisted ultrafast growth of high-quality monolayer MoS₂ with sulfur-terminated edges

Qinke Wu^{1, #}, Jialiang Zhang^{1, #}, Lei Tang^{1, #}, Usman Khan^{1, 2}, Huiyu Nong¹, Shilong Zhao¹, Yujie Sun¹, Rongxu Zheng¹, Rongjie Zhang¹, Jingwei Wang¹, Junyang Tan¹, Qiangmin Yu¹, Liqiong He¹, Shisheng Li³, Xiaolong Zou¹, Hui-Ming Cheng^{4, 5, 6} & Bilu Liu^{1, *}

¹Shenzhen Geim Graphene Center, Tsinghua-Berkeley Shenzhen Institute and Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, China;

²Institute of Functional Porous Materials, School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China;

³International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba 305-0044, Japan;

⁴Faculty of Materials Science and Engineering/Institute of Technology for Carbon Neutrality, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China;

⁵Shenyang National Laboratory for Materials Sciences, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China;

⁶Advanced Technology Institute, University of Surrey, Guildford, Surrey GU2 7XH, UK

#Contributed equally to this work.

*Corresponding author (email: bilu.liu@sz.tsinghua.edu.cn)

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Abstract: Two-dimensional (2D) semiconductors have attracted great attention to extend Moore's law, which motivates the quest for fast growth of high-quality materials. However, taking MoS₂ as an example, current methods yield 2D MoS₂ with a low growth rate and poor quality with vacancy concentrations three to five orders of magnitude higher than silicon and other commercial semiconductors. Here, we develop a strategy of using an intermediate product of iodine as a transport agent to carry metal precursors efficiently for ultrafast growth of high-quality MoS₂. The grown MoS₂ has the lowest density of sulfur vacancies ($\sim 1.41 \times 10^{12} \text{ cm}^{-2}$) reported so far and excellent electrical properties with high on/off current ratios of 10^8 and carrier mobility of $175 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Theoretical calculations show that by incorporating iodine, the nucleation barrier of MoS₂ growth with sulfur-terminated edges reduces dramatically. The sufficient supply of precursor and low nucleation energy together boost the ultrafast growth of sub-millimeter MoS₂ domains within seconds. This work provides an effective method for the ultrafast growth of 2D semiconductors with high quality, which will promote their applications.

Keywords: 2D semiconductors, molybdenum disulfides, ultrafast growth, defect density, sulfur vacancy, iodine-assisted, sulfur-terminated edge

INTRODUCTION

Two-dimensional (2D) semiconductors have drawn significant attention for next generation electronics owing to their ultrathin body, dangling-bond-free nature, high mobility, and flexibility. Monolayer transition

metal dichalcogenides (TMDCs), including MoS₂ and WS₂, are the most extensively studied 2D semiconductors [1–4]. However, the ultrafast growth of high-quality 2D TMDCs is still challenging, which restricts their practical applications in electronics and optoelectronics. Among the reported synthesis methods [5–11], chemical vapor deposition (CVD) is one of the most promising methods to grow 2D semiconductors with large area and high quality [12–18]. In general, the fast growth of large single crystals of TMDCs by the CVD method requires sufficient precursor supply and low nucleation energy of products [19,20]. Until now, some CVD methods have been used to grow TMDCs at fast speeds. For example, some research groups [5,21,22] used alkali metal halides to grow TMDCs, which achieved 1000 μm within 3 min. In another work, Zhang *et al.* [20] proposed that high growth temperature promotes the growth rate of WS₂ and MoS₂ with the reverse flow method, in which single crystals with the size of 450 μm were grown within 10 s.

Besides the growth rate, another key concern about monolayer semiconductors is the material quality. In fact, imperfections especially vacancies are inevitable in these monolayer TMDCs. These vacancies affect the electronic properties of TMDCs at different levels, which is currently under intense investigation [23–26]. Until now, most CVD-grown TMDCs have a high density of sulfur vacancies of $\sim 10^{14} \text{ cm}^{-2}$, which deteriorates the electronic properties of TMDCs and limits their further applications [23,26]. Many methods have been applied to decrease the density of sulfur vacancies. For example, an early report has shown that CVD-grown monolayer MoS₂ has a high density of sulfur vacancy [27], which is $\sim 7.8 \times 10^{13} \text{ cm}^{-2}$. Recently, Feng *et al.* [28] have used thiol as a liquid precursor for CVD growth of high-quality MoS₂ with a low density of sulfur defects ($\sim 1.6 \times 10^{13} \text{ cm}^{-2}$). In another work, Zuo *et al.* [29] have reported a strategy of using active chalcogen monomer supply to grow high-quality TMDCs with a much lower density of sulfur defects ($\sim 2 \times 10^{12} \text{ cm}^{-2}$). However, the density of defects in these TMDCs is still three to five orders of magnitude higher than that of silicon [30], which is $\sim 10^9 \text{ cm}^{-2}$ (corresponding to $\sim 10^{12}$ – 10^{13} cm^{-3} in bulk materials). It is therefore urgent to grow high crystalline MoS₂ with a high growth rate and low density of defects.

Here, we develop a strategy for ultrafast growth of high-quality MoS₂ with sulfur-terminated edges by iodine-assisted CVD. When MoO₃ and KI are mixed as the metal precursor, the iodine is released during the growth process. The newly formed iodine acts as a transport agent which helps deliver sufficient metal precursors onto the substrate surface to grow MoS₂. Density functional theory (DFT) calculations show that the iodine reduces the nucleation energy by 1.68 eV for MoS₂ growth with sulfur-terminated edges, compared with growth without salt. Combining the supply of sufficient precursors and low nucleation energy of MoS₂ together, the iodine drastically boosts the growth speed of MoS₂ and MoS₂ domains with a size of $\sim 780 \text{ μm}$ are grown in just five seconds. Furthermore, the MoS₂ has ultrahigh crystalline quality with the lowest density of sulfur vacancies of $\sim 1.41 \times 10^{12} \text{ cm}^{-2}$. The field-effect transistor (FET) based on MoS₂ exhibits carrier mobility of $175 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and with an on/off current ratio of $\sim 10^8$, supporting their high quality with potential for electronic applications.

RESULTS AND DISCUSSION

Ultrafast growth of monolayer MoS₂ with the iodine-assisted CVD method

The idea of the iodine-assisted growth method is schemed in Figure 1A and Figure S1. Briefly, the sulfur

powder is put into a quartz boat upstream of the furnace, whose temperature can be controlled by the distance from the furnace center. The aged mixture of KI and MoO_3 is used as the metal precursors, which is loaded into another quartz boat and put at the center of the CVD furnace (see growth details in the EXPERIMENTAL SECTION). First, we noticed that the color of the mixed precursors changed from gray to dark purple after 100 days in Ar, indicating the iodine is released (Figure S2). Then, when the temperature is over $\sim 505^\circ\text{C}$, the mixed precursors react with each other and form K_2MoO_7 and I_2 , which is confirmed by the thermogravimetric analysis/mass spectrometry (TGA-MS, Figure S3) and X-ray photoelectron spectroscopy (XPS, Figure S4) characterizations. Figures S3A and S3B show the mass-loss step of the mixture of MoO_3 and KI at $\sim 505^\circ\text{C}$. The differential results of the mass-loss curve (see the blue line) also indicate the step. Figure S3C is the spectra of the thermos mass photo at $\sim 530^\circ\text{C}$, indicating that iodine is released from the reaction between MoO_3 and KI. Figure S4D is the XPS spectra of I 3d before and after heating the mixture at $\sim 550^\circ\text{C}$, which confirms the iodine element disappeared after heating. All the results confirm that the iodine is released. There are two unique roles of KI. First, similar to NaCl, the KI also reacts with metal precursors (MoO_3) and form active intermediate products with a low melting point. Second, similar to the chemical vapor transport method, the by-product of iodine acts as the transport agent to deliver the metal precursors onto the surface of the substrate for MoS_2 growth [31–33]. Both two factors largely improve the growth rate of MoS_2 .

Figure 1B is a typical optical microscopy (OM) image of MoS_2 grown with an iodine-assisted CVD method with a growth time of 5 s, where the domain size can be $\sim 780\ \mu\text{m}$, suggesting its ultrafast growth rate (also see Figure S5A). When the growth time reaches 10 s, we obtain continuous MoS_2 monolayer film (Figure S5B). In comparison, the traditional method (without KI) only grows MoS_2 with a domain size of $\sim 15\ \mu\text{m}$ after 20 min (Figure 1C and Figure S5C). We then compare the ten largest MoS_2 domains grown by two kinds of methods and find that the iodine-assisted method grown MoS_2 has two orders of magnitude larger domain sizes than that without KI. Figure 1D compares the domain size and the growth time of the MoS_2 grown by different methods [5,34–39], showing the great advantages of this iodine-assisted CVD method. Figure 1E shows the aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the MoS_2 , suggesting its high crystallinity. We also collected more STEM images of the MoS_2 with large scale ($\sim 380\ \text{nm}^2$) to show the low density of the sulfur vacancies (Figure S6). Figure 1G compares the density of sulfur vacancies with other reported work [14,28,29,40–44], showing that our work has the lowest value of sulfur vacancies ($1.41 \times 10^{12}\ \text{cm}^{-2}$) reported so far in CVD-grown monolayer MoS_2 . Overall, the characterizations above confirm that the as-grown MoS_2 has high crystalline quality with a very low density of sulfur vacancies.

To better understand the effect of KI on the growth of MoS_2 , a series of experiments are conducted with different weight ratios of KI/ MoO_3 (Figure S7). When this ratio increases, the domain size of MoS_2 also increases, presumably because more iodine is formed as the transport agent (Figures S2 and S3). In addition, we carried out a series of experiments to analyze the effect of temperature on the growth of MoS_2 while the weight ratio of KI/ MoO_3 is fixed at the optimized ratio of 1:3 (Figure S8). Interestingly, the MoS_2 is grown at a low temperature of 540°C , due to the low formation temperature of iodine is $\sim 505^\circ\text{C}$. When the growth temperature increases, the as-grown MoS_2 domains get larger, and the largest domain with a size of $\sim 780\ \mu\text{m}$ is achieved in 5 s at 790°C (Figure S5A). When the growth temperature is over 830°C , we grow bilayer MoS_2 domains (Figure S8E), probably due to the oversupply of precursors. Moreover, the iodine-assisted CVD

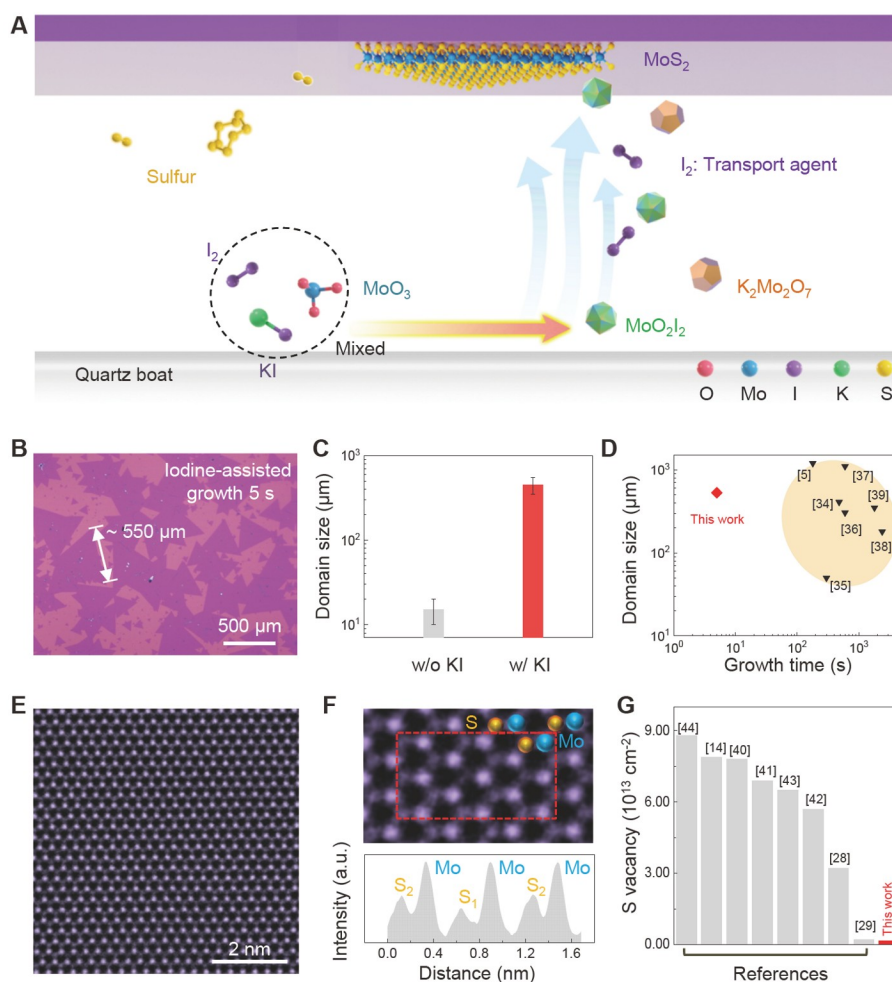


Figure 1 Iodine-assisted ultrafast CVD growth of high-quality monolayer MoS₂. (A) Scheme of the ultrafast growth approach. (B) OM image of MoS₂ grown with iodine-assisted CVD method in 5 s. (C) Domain sizes of MoS₂ grown with and without iodine-assisting during growth. (D) Comparison of the growth time and domain size of as-grown MoS₂ with other work. (E) HAADF-STEM image of the MoS₂. (F) Zoomed in image of the MoS₂ with mono-sulfur vacancy. The bottom panel is the corresponding intensity line profile along the red square. (G) Comparison of the sulfur vacancies of iodine-assisted grown MoS₂ with other work.

method shows good universality for the growth of other monolayer TMDCs like 2D WS₂ (Figure S9). Overall, our results indicate iodine-assisted CVD method provides an effective way to grow MoS₂ with a large domain size at a fast speed.

High quality and uniformity of the MoS₂

To study the quality and uniformity of the as-grown MoS₂, we performed the Raman and photoluminescence (PL) spectroscopic characterizations. Figure 2A is the typical Raman spectrum of the monolayer MoS₂, which exhibits the characteristic peaks of in-plane E_{2g} phonon mode at 384.1 cm⁻¹ and out-of-plane A_{1g} mode at 404.8 cm⁻¹. The representative PL spectrum exhibits a sharp and narrow peak with the full width at half maximum (FWHM) of ~19.3 nm at room temperature (Figure 2B). Figure 2C is the PL of the MoS₂ with

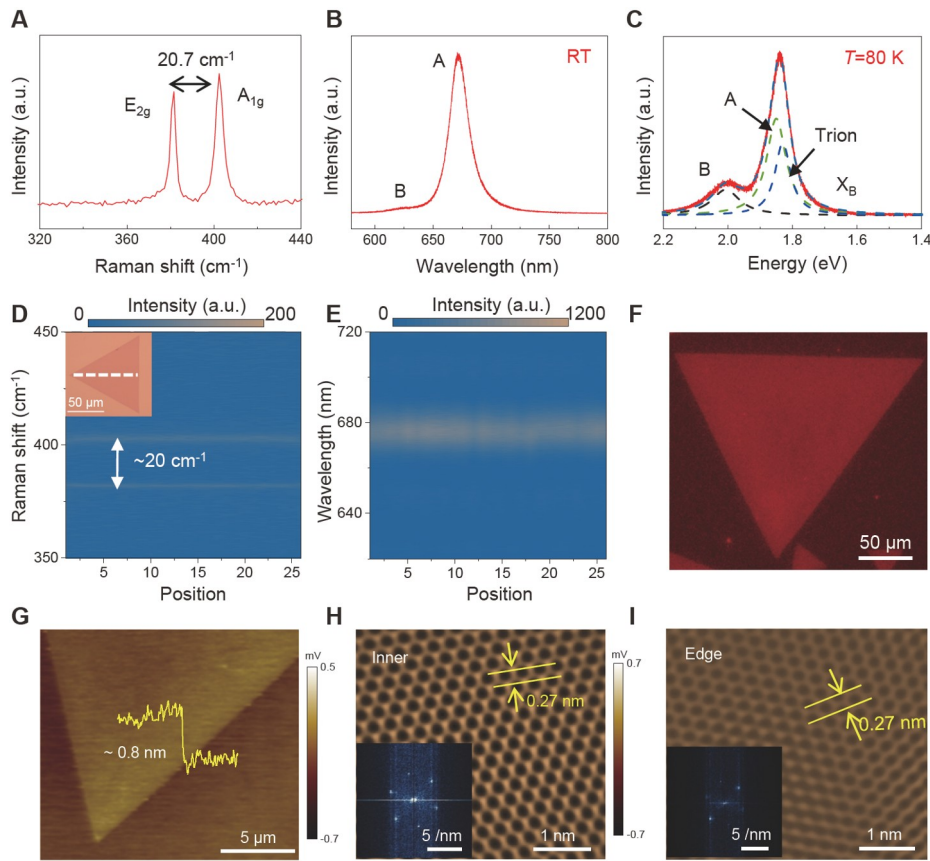


Figure 2 Iodine-assisted CVD grown MoS₂ with high quality and uniformity. (A), (B) The typical Raman and PL of the MoS₂, respectively. (C) Low temperature PL of the MoS₂ at 80 K. (D), (E) Line-scan Raman spectra and PL spectra of the MoS₂, and the inset in (D) is the OM image of the corresponding MoS₂ domain. (F) Typical fluorescence image of the as-grown MoS₂ with large size. (G) AFM image at the corner of a MoS₂ domain. (H), (I) IFFT HRAFM image at the inner and edge parts of the MoS₂ domain in (G).

FWHM of ~ 76.4 meV (or 16.2 nm) measured at low temperature of 80 K, which is fitted into three peaks. The most dominant feature contains two peaks, labeled as neutral A excitons and negatively charged trions. The B excitons of the third peak are observed at ~ 2.01 eV. In addition to these three peaks, the lower energy peak resulting from the radiative recombination of deep level defect-bounded excitons (X_B) is not observed [45], which is a clear and strong evidence of high-quality MoS₂ with a low defect density and in agreement with our HAADF-STEM observations (Figure 1G and Figure S6).

Then, we focus on the uniformity of the MoS₂ by measuring the line-scanning Raman and PL along the dashed white line in the inset of OM image in Figure 2D, showing uniform and monolayer features of MoS₂ domains (Figures 2D and 2E). Besides, the fluorescence microscopy image shows high uniformity of the MoS₂ domains with large domain size (~ 200 μm) (Figure 2F). The height is around 0.8 nm of as-grown MoS₂ measured by atomic force microscopy (AFM) (Figure 2G), indicating it is monolayer [7]. Figures 2H and 2I are the inverse fast Fourier transform (IFFT) pattern, taken by high-resolution lateral force microscopy (LFM) mode at the inner and edge part of the flake in Figure 2G, the insets are the corresponding FFT patterns, indicating that the MoS₂ has high uniformity and quality. All the characterizations prove that the iodine-assisted CVD grown MoS₂ has high uniformity and crystallinity quality over the whole domain.

Electrical performance

Based on the achieved high-quality monolayer MoS₂ domains, we fabricated FETs to characterize their electrical properties. The structure of the back-gated MoS₂ FETs is illustrated in the inset of Figure 3A and Figure S10. Figure 3A shows the transfer characteristics of FET based on as-grown MoS₂ as channel material. The device exhibits both high on/off current ratio of 10⁸ and decent mobility of 175 cm² V⁻¹ s⁻¹. The device shows a linear relationship in the output curves, indicating the Ohmic contact (Figure 3B). Besides, transfer curves of six more typical MoS₂ FETs with different channel lengths and widths are shown in Figure 3C. These data exhibit small device-to-device variation, reflecting the uniformity of the as-grown MoS₂ domains. In Figure 3D and Table S1, we compared the on/off ratio and mobility of our devices with the previous CVD-grown monolayer MoS₂ [5,29,34–39,46–48], suggesting the good electrical performance of the iodine-assisted CVD grown MoS₂.

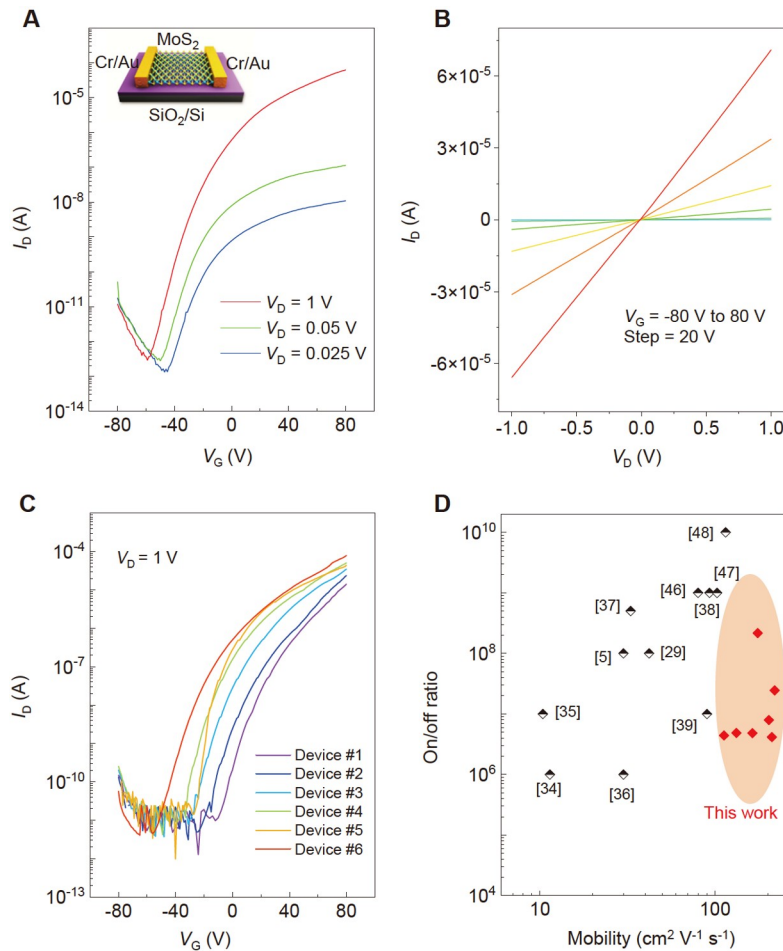


Figure 3 Electrical performance of the iodine-assisted CVD grown MoS₂. (A), (B) Typical transfer and output curves of the devices. The inset in (A) is a schematic of the back gate MoS₂ FET. (C) Transfer curves of six more MoS₂ FETs. (D) Comparisons of the mobility and on/off ratios of MoS₂.

Mechanism for the iodine-assisted growth of MoS₂ with sulfur-terminated edges

To shed light on the growth mechanism of ultrafast growth of MoS₂ with the iodine-assisted CVD method, we carried out DFT calculations to simulate the nucleation process with and without iodine. The energy diagrams for MoS₂ growth along the S-terminated edges were calculated with and without halogen element adsorption as shown in Figures 4A and 4B. With the incorporation of iodine, the highest nucleation barrier reduces from 3.41 to 1.73 eV for MoS₂ growth under near equilibrium S-rich conditions. The nucleation process can even become barrierless under non-equilibrium growth conditions (Figure S11). Meanwhile, the adsorption of iodine is proven to be the most favorable for the growth of MoS₂ above the halogen elements, since its nucleation energy drops off the most (Figure 4B and Figure S12). Moreover, to confirm the edge structure of terminated atoms, TEM and selective area electron diffraction (SAED) pattern are used. Figures 4C and 4D are the TEM images of the corner of the triangle domain and the corresponding SAED pattern. As is known that the lattice of monolayer MoS₂ has two types of molybdenum and sulfur sublattices, which

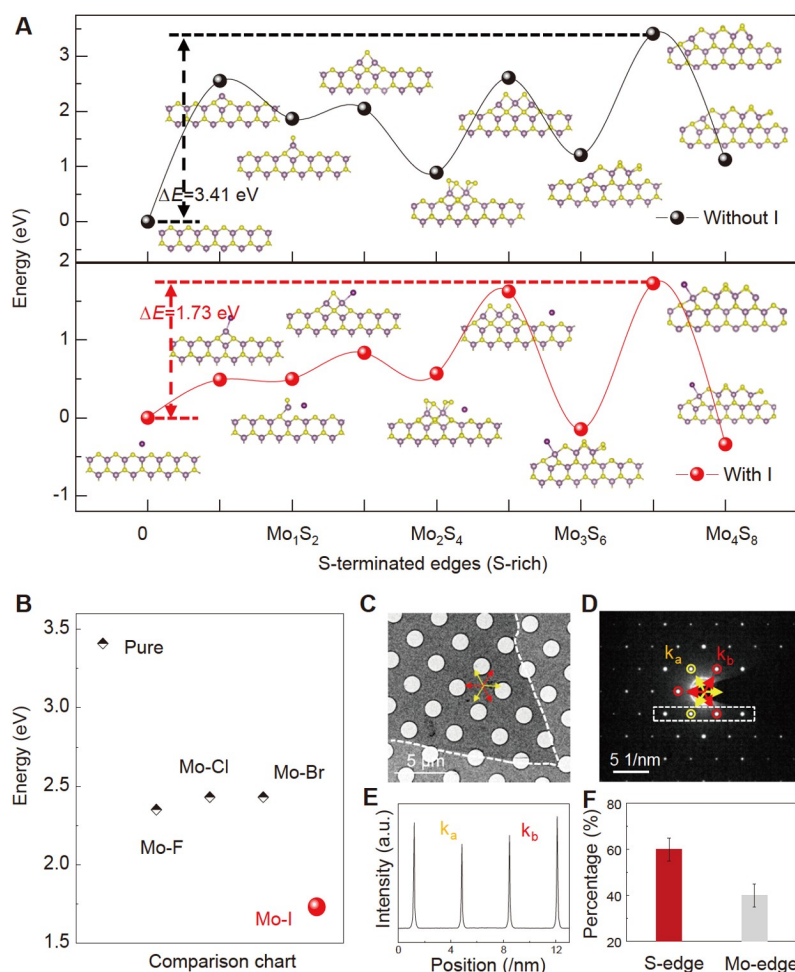


Figure 4 Edge-structure dependent growth mechanism. (A) DFT calculations of the free energy for MoS₂ growth with and without iodine assisting under near equilibrium S-rich condition. (B) DFT calculation of the nucleation energy for different halogen elements under near equilibrium S-rich condition. (C) TEM image of the as-grown MoS₂. (D) The corresponding SAED pattern of (C). (E) A line profile through the measured diffraction spots in (D). The higher intensity k_b spots towards the Mo sublattice, as indicated by the arrows in (C) and (D). (F) Diagram of large MoS₂ domains with S-terminated edges vs. Mo-terminated edges.

reduces the hexagonal lattice from six-fold to three-fold symmetry [27]. As a result, the six $[-1100]$ diffraction spots are broken into two families: $\mathbf{k}_a = \{(-1100), (10-10), (0-110)\}$ and $\mathbf{k}_b = -\mathbf{k}_a$ (Figure 4D). Moreover, the intensity of diffraction spots pointed toward $\mathbf{k}_a$ is lower than that of the spots toward $\mathbf{k}_b$. Figure 4E shows that the $\mathbf{k}_a$ spots are higher in intensity ($\sim 10\%$ for 80 kV electron beam) and spots represent the molybdenum sublattice, which matches well with the previous work [27]. Combining all the results, we confirm that the edge structure of the iodine-assisted MoS₂ domain in Figure 4C is S-terminated. We also analyze other MoS₂ domains (Figure S13) and draw the diagram in Figure 4F, showing that over 60% of the triangle domains have edges with an S-terminated structure. Besides, the edge type of CVD-grown MoS₂ is highly dependent on the S/Mo ratio of precursors [49]. In this regard, we can tune S/Mo ratio by using the iodine-assisted CVD method to realize fast growth of MoS₂ with Mo- or S-terminated edge structures. Such MoS₂ with specific types of edges may be a good platform to study edge structure-dependent properties and for applications in electronics, optoelectronics, and catalysis [50–52]. Taking all the results together, the iodine boosts the ultrafast growth of MoS₂ domains with an S-terminated structure, matching well with TEM results.

CONCLUSION

In conclusion, we have developed an iodine-assisted CVD method for the ultrafast growth of high-quality monolayer MoS₂ with the lowest density of defects. Monolayer MoS₂ with large domain sizes is obtained in just seconds of growth time. These domains possess ultrahigh crystalline quality with the lowest density of sulfur vacancies ($\sim 1.41 \times 10^{12} \text{ cm}^{-2}$) reported so far. FET based on iodine-assisted grown MoS₂ shows a high on/off ratio of 10^8 and mobility of $175 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. DFT calculations indicate that iodine benefits from fast nucleation and growth of MoS₂ and decreases the nucleation energy barrier by 1.68 eV, which is responsible for the ultrafast growth behavior. Our results add fresh knowledge for the growth of high-quality 2D semiconductors in short time scales, showing promise for electronic and optoelectronic applications.

EXPERIMENTAL SECTION

Iodine-assisted CVD growth of MoS₂

First, sulfur powder (100 mg, 99.5%, Sigma-Aldrich, USA) and the mixed precursors of KI (99.9%, Sigma-Aldrich, USA)/MoO₃ (99.9%, Sigma-Aldrich, USA) with different weight ratios (between 0.1 and 1 of KI/MoO₃) were loaded into the CVD furnace. Then the temperature increased to 790°C within 20 min. During the heating process, the sulfur powder was introduced into the growth chamber at 680°C from room temperature. By this way, when the sulfur reaches its melting point, the temperature of the furnace gets 790°C for the growth of MoS₂. When the growth time is 5 s, we moved away from the quartz tube from the heating zone immediately. Meanwhile, a fan was used to cool down the furnace. In this way, the temperature of the growth substrate is decreased from 790°C to below 400°C within 1 min. For the MoS₂ growth without KI, sulfur powder and pure MoO₃ were loaded into the CVD furnace under the same growth conditions with iodine-assisted MoS₂ growth.

Transferring process of MoS₂

To transfer MoS₂ from SiO₂/Si substrate to the target substrate (like TEM grid). We used the following steps. First, PMMA was spin-coated on the SiO₂/Si substrate with MoS₂ grown at 4500 r min⁻¹ for 4 min. The sample was heated on a hot plate at 90°C for 5 min. The sample was then submerged in an HF solution (5%) for a few seconds to etch the substrate. The PMMA/MoS₂ sample was then rinsed with deionized water and transferred to the target substrate. Finally, the PMMA was removed using acetone.

Characterization

The morphology of the samples was examined by optical microscope (Carl Zeiss Microscopy, Germany). AFM (Cypher ES, Asylum Research, USA) was used to measure the thickness and surface of the samples. SAED patterns were collected in FEI Tecnai F30 (USA) with an acceleration voltage of 80 kV. The HAADF-STEM imaging was carried out in a cold-field-emission double Cs-corrected STEM (FEI Spectra 300 with an acceleration voltage of 80 kV). Reflectance contrast spectra of the as-grown MoS₂ were conducted in a home-built optical measurement system. Raman and PL spectra and mappings were collected using a 532-nm laser excitation with a beam size of ~1 μm (Horiba LabRAB HR Evolution, Japan).

DFT calculations

All calculations were performed using the density functional theory as implemented in the Vienna *Ab-initio* Simulation Package [53]. The core-electron interactions were described by projected augmented wave methods [54]. Perdew-Burke-Ernzerhof generalized gradient approximation was adopted for the exchange-correlation effect [55]. The perfect MoS₂ nanoribbon was modeled by a 9×4×1 supercell. Mo and S₂ were introduced stepwise to the Mo- or S-terminated growth front of MoS₂ following the kink-flow scheme using a nanoreactor model [56]. The situation for growth on Mo-terminated front is shown in Figure S14, from which we can see negligible effect of iodine on the growth of MoS₂. The energy for every considered configuration is calculated as $E_{\text{form}}(\text{Mo}_m\text{S}_n) = E(\text{Mo}_m\text{S}_n + \text{NR}) - E(\text{NR}) - m\mu_{\text{Mo}} - n\mu_{\text{S}}$, where $E(\text{Mo}_m\text{S}_n + \text{NR})$ is the energy of MoS₂ nanoribbon with Mo_mS_n grown on it, and $E(\text{NR})$ is the energy of the initial MoS₂ nanoribbon. μ_{Mo} and μ_{S} are the corresponding chemical potential of Mo and S. Here, two scenarios, i.e., near equilibrium S-rich and non-equilibrium conditions were used to obtain the energies. For equilibrium S-rich condition, μ_{S} is the chemical potential of an S atom in bulk S. Based on that, μ_{Mo} is calculated by $\mu_{\text{Mo}} + 2\mu_{\text{S}} = \mu_{\text{MoS}_2}$, where μ_{MoS_2} is the chemical potential gained from MoS₂ monolayer. For non-equilibrium conditions, μ_{Mo} and μ_{S} were taken from the chemical potentials of bulk Mo and bulk S, respectively.

Device fabrication and measurements

The source and drain electrodes (5/50 nm Cr/Au) were fabricated on the MoS₂ using a direct laser writing system (miDALIX, DaLI, Germany) followed by e-beam evaporation and lift-off processes. The FET was measured using the semiconductor parameter analyzer (Keithley 4200A-SCS, USA) and probe station (LakeShore, USA) with a vacuum at a pressure of 10⁻⁵ mbar at room temperature. Then, we calculated carrier mobility (μ) using the following formula

$$\mu = \frac{L}{WV_d C_{\text{ox}}} \frac{dI_d}{dV_g},$$

where L and W are the length and width of the channel, respectively, I_d is the drain-source current at the gate voltage (V_g), C_{ox} is the gate oxide capacitance evaluated as 11.5 nF cm^{-2} for 300 nm SiO_2 , and V_d is the source-drain voltage.

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Author contributions

Q.W., L.T., and B.L. conceived the idea. Q.W. conducted the CVD growth of MoS_2 . Q.W. performed most of OM, Raman, PL, XPS, and TEM characterization. U.K. performed the device fabrication and measurements. R.Z. performed the high resolution AFM characterization. J.Z. and X.Z. performed the theoretical calculations. H.N., S.Z., Y.S., R.Z., J.W., J.T., Q.Y., L.H., and S.L. took part in part of the experiments and discussions. B.L. supervised the project and directed the research. Q.W., L.T., X. Z., H.-M.C., and B.L. interpreted the results and wrote the manuscript with feedbacks from the other authors.

Conflict of interest

The authors declare no conflict of interest.

Supplementary information

The supporting information is available online at <https://doi.org/10.1360/nso/20230009>. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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