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Zhu, Dancheng, Shu, Haibo, Jiang, Feng et al. (6 more authors) (2017) Capture the growth kinetics of CVD growth of two-dimensional MoS 2. *2D Materials and Applications*. 8. pp. 1-8. ISSN 2397-7132

<https://doi.org/10.1038/s41699-017-0010-x>

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ARTICLE OPEN

Capture the growth kinetics of CVD growth of two-dimensional MoS₂Dancheng Zhu¹, Haibo Shu², Feng Jiang¹, Danhui Lv¹ , Vijayshankar Asokan¹, Omar Omar³, Jun Yuan^{1,3}, Ze Zhang¹ and Chuanhong Jin¹

Understanding the microscopic mechanism is fundamental for function-oriented controlled chemical vapor deposition growth of two-dimensional (2D) materials. In this work, we reveal the growth kinetics of 2D MoS₂ by capturing the nucleation seeds, evolving morphology, edge structure, and edge terminations at the atomic scale during chemical vapor deposition growth using the transmission electron microscopy and scanning transmission electron microscopy. The direct growth of few-layer and mono-layer MoS₂ onto graphene-based transmission electron microscopy grids helped us to perform the subsequent transmission electron microscopy characterization without any solution-based transfer. Two seeding centers are observed: (i) Mo-oxysulfide (MoO_xS_{2-y}) nanoparticles either in multi-shelled fullerene-like structures or as compact nanocrystals for the growth of fewer-layer MoS₂; (ii) Mo-S atomic clusters. In the early stage growth, irregular polygons with two primary edge terminations, S-Mo Klein edges and Mo zigzag edges, appear approximately in equal numbers. The morphology evolves into a near-triangle shape in which Mo zigzag edges predominate. Results from density-functional theory calculations are consistent with the inferred growth kinetics, and thus support the growth mechanism we proposed. In general, the growth mechanisms found here should also be applicable in other 2D materials, such as MoSe₂, WS₂ and WSe₂.

npj 2D Materials and Applications (2017)1:8; doi:10.1038/s41699-017-0010-x

INTRODUCTION

Two-dimensional molybdenum disulfide (2D MoS₂), a representative member of the rediscovered transition metal dichalcogenide (TMDC) family, holds promising interest owing to their excellent performance in electronic, optoelectronic, catalytic and bio applications.^{1–10} However, many challenges remain to be overcome in realizing the potential applications, for instance, the carrier type and concentration, i.e., equivalent good performance for both n-type and p-type in electronic devices, the structure/morphology, wafer-size sample and in high quality. Out of these, the controlled growth seems to be a key issue. So far, chemical vapor deposition (CVD), as one of the most successful routes, has been widely adopted to grow 2D material from graphene,^{11, 12} hexagonal boron nitride¹³ to 2D TMDC materials,^{14–17} while the growth mechanisms, particularly in the CVD growth of 2D TMDC materials, is still poorly understood.

Previous studies have successfully revealed the roles of a number of important parameters determining the CVD growth behaviors of 2D MoS₂, i.e., hydrogen carrier gas, precursors/promoters, and screw dislocations etc.^{18–26} Recently Rajan et al.²² have proposed a generalized mechanistic model to quantitatively explain the shape evolution of MoS₂ monolayers observed experimentally. In spite of these successes, our knowledge on the microscopic process during the growth including nucleation and growth kinetics seems to be still limited, partly due to the few practical difficulties, i.e., the challenge in transferring ultra-fine clusters formed at an early stage of growth and possible loss of intermediate/by-products (some of them are aqueous soluble). As

such, comprehensive studies to reveal the microscopic growth mechanism of 2D MoS₂ are needed.

In this work, we carried out transmission electron microscopy (TEM) study to capture the nucleation and growth kinetics of 2D MoS₂. Here few-layer and mono-layer MoS₂ were grown directly on graphene-supported TEM grids,^{27–30} and then loaded into the microscope chamber for further microscopic characterizations. No solution was involved in the film transfer process, thus allowing us to visualize the seeding centers, shape morphology, edge structures, and the associated morphology evolved during the growth. We firstly confirmed there exists two forms of seeding centers: (1) Mo-oxysulfide (MoO_xS_{2-y}, $y \geq x$) nanoparticles either in nested multi-shelled fullerene-like structures or compact nanocrystals, for few-layer MoS₂; and (2) atomic scale MoS₂ monolayer cluster. For the growth of mono-layer MoS₂, the irregular polygon-shaped morphology comprised the following configurations: S-Mo Klein edges and Mo zigzag edges. As the growth proceeded, nearly-triangular shapes were found predominantly, terminated with Mo zigzag edges. Microscopic nucleation mechanism and the growth kinetics can be deduced based on our experimental finding, which were further supported by density-function theory (DFT) calculations.

RESULTS AND DISCUSSION

Figure 1a shows the schematic of our CVD system in which (home-made) graphene-supported TEM grids were placed facing-down towards a MoO₂-containing boat. Figure 1b, c show two low-magnification annular dark field-scanning transmission electron

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Received: 7 November 2016 Revised: 17 January 2017 Accepted: 30 January 2017

Published online: 08 May 2017

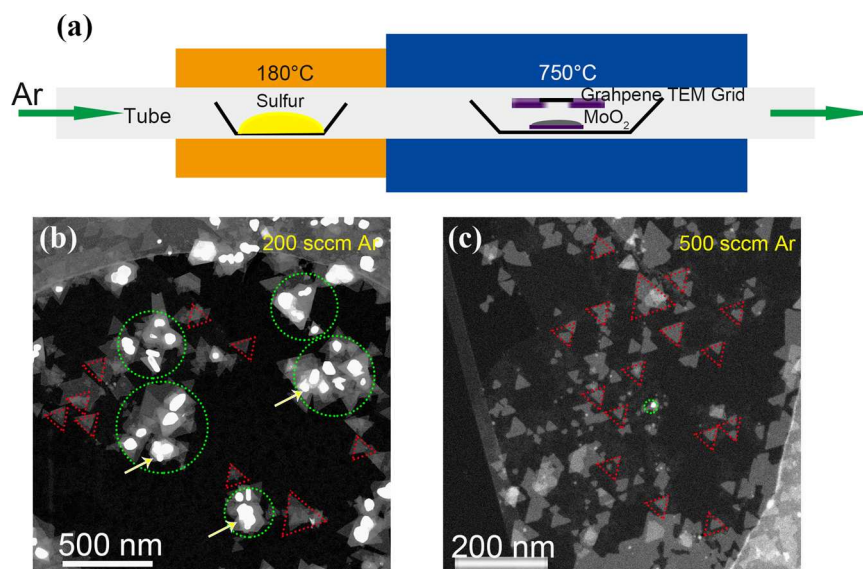


Fig. 1 **a** Schematic illustration of our CVD system in which graphene-supported TEM grids were placed face down to the MoO₂-containing boat. **b** A typical low-magnification ADF-STEM image representing as-grown products on graphene supports at 200 sccm Ar. The *green dotted circles* indicate few-layer MoS₂ bound with thick/heavy nanoparticle and nanorods (*arrowed*), while the *red dotted circles* show monolayer MoS₂. **c** A typical low-magnification ADF-STEM images representing as-grown products at 500 sccm Ar, where monolayer MoS₂ predominates (in *red dotted circles*)

microscopy (ADF-STEM) images of the as-grown MoS₂ samples on graphene under two typical growth conditions where the argon (Ar) flow rates (carrier gas) are different: 200 sccm (Fig. 1b) and 500 sccm (Fig. 1c), respectively. In the former case (i.e., the low argon flow rate region), we observed two primary forms of products (Fig. 1b): few-layer regions bound with thicker/heavier nanoparticles (*arrowed*) or nanorods (marked with *dotted circles* in *green*) and monolayer MoS₂ with a nearly-triangular shape (see *dotted triangles* in *red*). In contrast, in the latter case (the high argon flow rate region), as-grown samples contained predominat monolayer MoS₂, as shown in Fig. 1c.

Further ADF-STEM imaging and X-ray energy dispersive spectroscopy (XEDS) analysis were carried out to probe the atomic structure and the chemical compositions of those nanoparticles-like or nanorods-like cores on few-layer MoS₂ as shown in Fig. 2 and Fig. S1a, b. Two primary forms were observed: multi-shell fullerene structure (Fig. 2a) or multi-shelled tube (Fig. 2b), with either empty or partially (even completely) filled cores, similar to that of MoS₂ inorganic fullerenes;^{18, 19} compact nanocrystals (Fig. 2c) with few-layer samples. Chemical analysis via STEM-XEDS mapping confirm that it was mostly composed of molybdenum (Mo), sulfur, and oxygen in the shells, while a higher concentration of oxygen was found in the compact core. As such, we can conclude that those nanoparticles or nanorods bound with few-layer flakes are MoS₂ multi-shelled fullerenes (nanotubes)¹⁹ filled with Mo-oxysulfide (MoO_xS_{2-y}, $y \geq x$) nanoparticles. During the preparation of this manuscript, we became aware of another work reporting similar fullerene as the seeding materials monolayer MoS₂Se_(2-x).³¹ Importantly, we additionally observe another form of nanoparticles, which further XEDS analysis has proved to be MoO_xS_{2-y} nanocrystals similar to those cores filled in the multi-shelled fullerene/tubular structure in Fig. 2a. More microscopic studies were carried out to understand the link between these particles and the few-layer MoS₂ as shown in Fig. 3 and Fig. S1c in [Supplementary Information](#). Fast fourier-transform (FFT) show the single crystalline nature of most of few-layer MoS₂ with different crystallography orientations (see Fig. S1d). The MoS₂ fullerene is filled with two MoO_xS_{2-y} nanocrystals. No obvious linking was found in crystallography orientation relationship between MoO_xS_{2-y} nanoparticles, MoS₂ fullerene, and planar

few-layer MoS₂. The MoO_xS_{2-y} compact nanoparticle (*red dotted circle*) and the few layer MoS₂ appear to share a certain crystal orientation relationship with $(1\bar{1}0)_{\text{MoO}_x\text{S}_{2-y}} // (1\bar{1}0)_{\text{MoS}_2}$, and there are identical spacing in $\{1\bar{1}0\}$ planes of few-layer MoS₂ (*yellow dotted circle*) that of the MoO_xS_{2-y} compact nanoparticles, as shown in Fig. 3d and the corresponding FFT patterns. Based on these results, a microscopic process from MoO₂ to MoS₂ during the CVD growth may be speculated as follows: MoO₂ belongs to tetragonal crystal system with the $\{1\bar{1}0\}$ spacing of 0.34 nm. During the sulfurization, the intermediate products prefer to retain their tetragonal structure while undergoing a reduction of $(1\bar{1}0)$ spacing from 0.34 nm (MoO₂) to 0.27 nm (MoO_xS_{2-y}, MoS₂). As the sulfurization proceeds, the MoO_xS_{2-y} was further transformed into hexagonal few-layer MoS₂.

Given the results shown above, we could assign these nanoparticles (either fullerene/tubular like structure or compact MoO_xS_{2-y} nanocrystals) as the centers for the nucleation and feeding source for the growth of MoS₂. Under this condition, the sublimated molecular clusters of MoO₂ exit mostly in large sizes, and thus may not be completely sulfurized due to the limited reaction time before their deposition onto the graphene substrate. As such, MoO_xS_{2-y} nanoparticles are formed on the substrate, and serve as the heterogeneous nucleation sites for the growth of MoS₂ in few-layer forms. Such nuclei should also facilitate the nucleation and growth of few-layer MoS₂, rather than the monolayer form, either from a few-layer nuclei or through a layer-on-layer growth process. As reaction proceeds, the nanoparticles have two different routes, as the nucleation sites: (1) The chemical conversion occurs much faster than the diffusion of the sulfur gas into the MoO_xS_{2-y} nanoparticles, which will be further sulfurized to form the nested multiple-fullerene nanostructures as shown earlier.³² As the sulfurization proceeds, eventually these as-deposited MoO_xS_{2-y} nanoparticles may also serve as the feeding source for the growing MoS₂. The fully or partially empty cores observed on those multiple fullerenes may be formed as a result of self-sacrifice as the seeding source. Other mechanisms such as Kirkendall effect³³ during the sulfurization may also lead to the observed empty-core structures. In some cases, the outer shells in high qualities may block the mass transport and thus the sulfurization, leading the central core having a higher

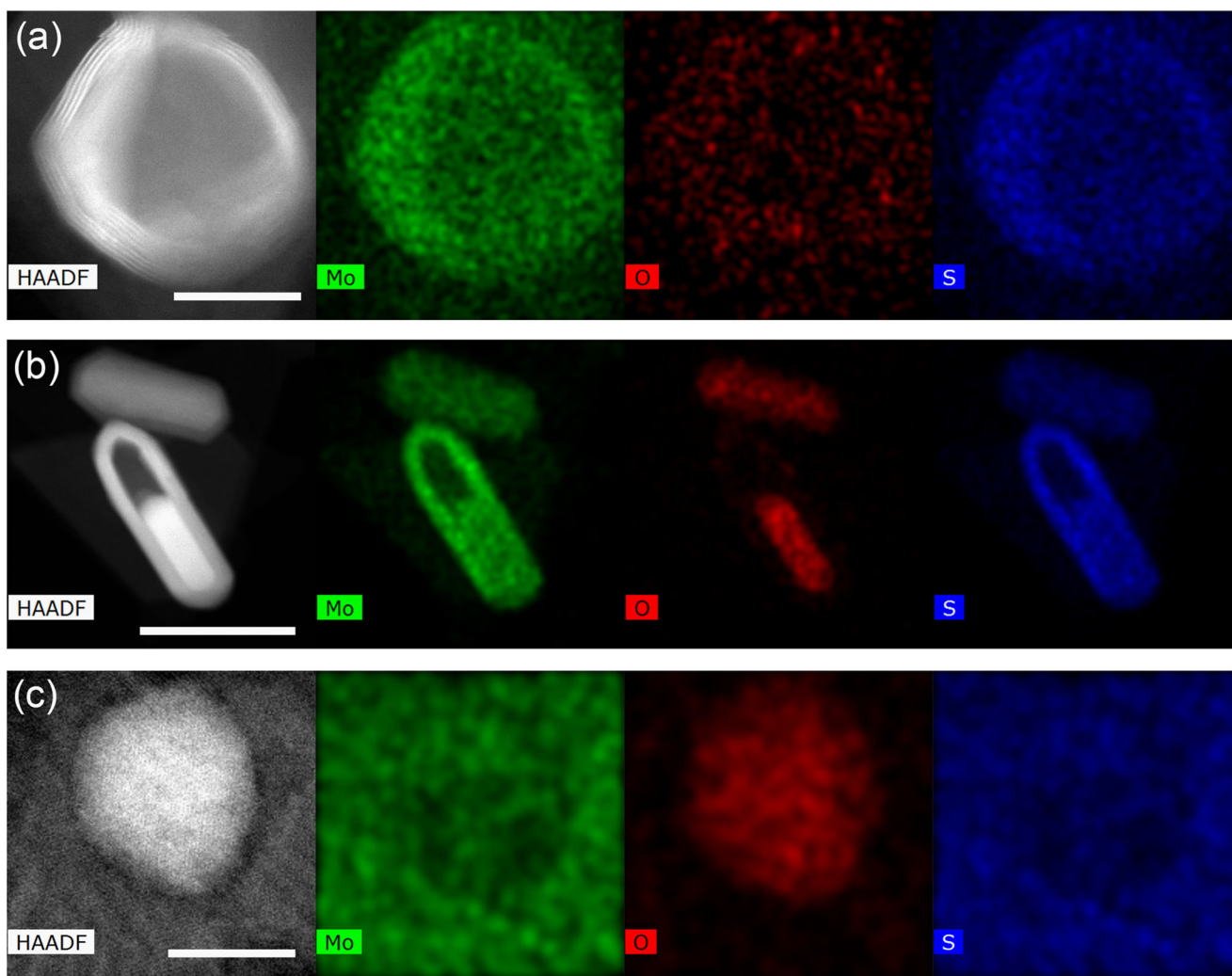


Fig. 2 STEM-XEDS mapping showing the atomic structural and chemical composition of thick structures on few-layer MoS₂: **a** a multi-shelled fullerene with nearly empty core, **b** a tubular like structure with partly sacrificed core, **c** a core without fullerene structure (scale bar: 20 nm)

concentration of oxygen, as shown in Fig. 1b. (2) When the *c*-axis of these as-deposited MoO_xS_{2-y} nanoparticles is perpendicular to the graphene plane, the particles will serve as the center of epitaxial growth, so the multiple-fullerene nanostructures will not form.

We now turn our attention to detail the case of monolayer MoS₂ growth. Figure 4a–l presents the ADF-STEM images of the graphene-supported as-grown monolayer MoS₂ with different sizes and morphology. Note here the MoS₂ monolayers were grown on different regions of the graphene support under the same CVD condition, and then grouped in size. The varying size and morphology of these MoS₂ monolayers on different regions of the same graphene substrate may result from the local fluctuations responsible for nucleation and growth. Of more than 100 samples we checked, it is clearly seen that there are no thick/heavy nanoparticles bound with the MoS₂ monolayers, a situation distinctly different with that in few-layer MoS₂. On the other hand due to the unavoidable oxygen-containing PMMA residue (frequently found in Fig. 4a–l) on graphene membranes used during the graphene transferring; therefore it becomes impossible for us to identify residual oxygen within the lattice of MoS₂, if any, particularly at the atomic level.

We studied the evolution of shape morphology and edge structure of MoS₂ monolayers, another key issue for the growth mechanism study. We treated size-dependent monolayer images,

as seen in Fig. 4, as an approximated reflection of the structure evolution that would be followed by the same MoS₂ monolayer at the different growth stages. The smallest one found in our experiments has a diameter of close to 3.0 nm (Fig. 4a), and an irregular polygon shape. As the size increases, MoS₂ atomic clusters evolve into irregular hexagon shape (Fig. 4f–h); and then into near-triangle shape with truncated corners (Fig. 4i), before they finally form well-known triangular shape, which are decorated mainly with Mo-terminated zigzag edges^{14–16, 34} (written as Mo-zz edge hereafter, see Fig. 4k). Terraces and kinks (arrowed) can be frequently found along the edge of all MoS₂ monolayers, serving as chemically active sites for the epitaxy addition of Mo–S molecules or atomic clusters from the supply, either by direct deposition in gas phase or in solids phase after a surface diffusion process. From the results shown above, we can infer that the morphology of MoS₂ monolayers changes from irregular polygonal shape to triangular one with an increasing size (Fig. 4a–j).

Accompanying the evolution of structure and morphology during the growth, the edge structure and termination also changed as shown in Fig. 5. Here three MoS₂ monolayer samples with different characteristic morphology (irregular polygon, near-hexagon and near-triangle) were chosen as an example for ease of display (Fig. 5a–c) and associated structural models (Fig. 5d–f). Over two primary types of edge structure were found: Mo-zz edge

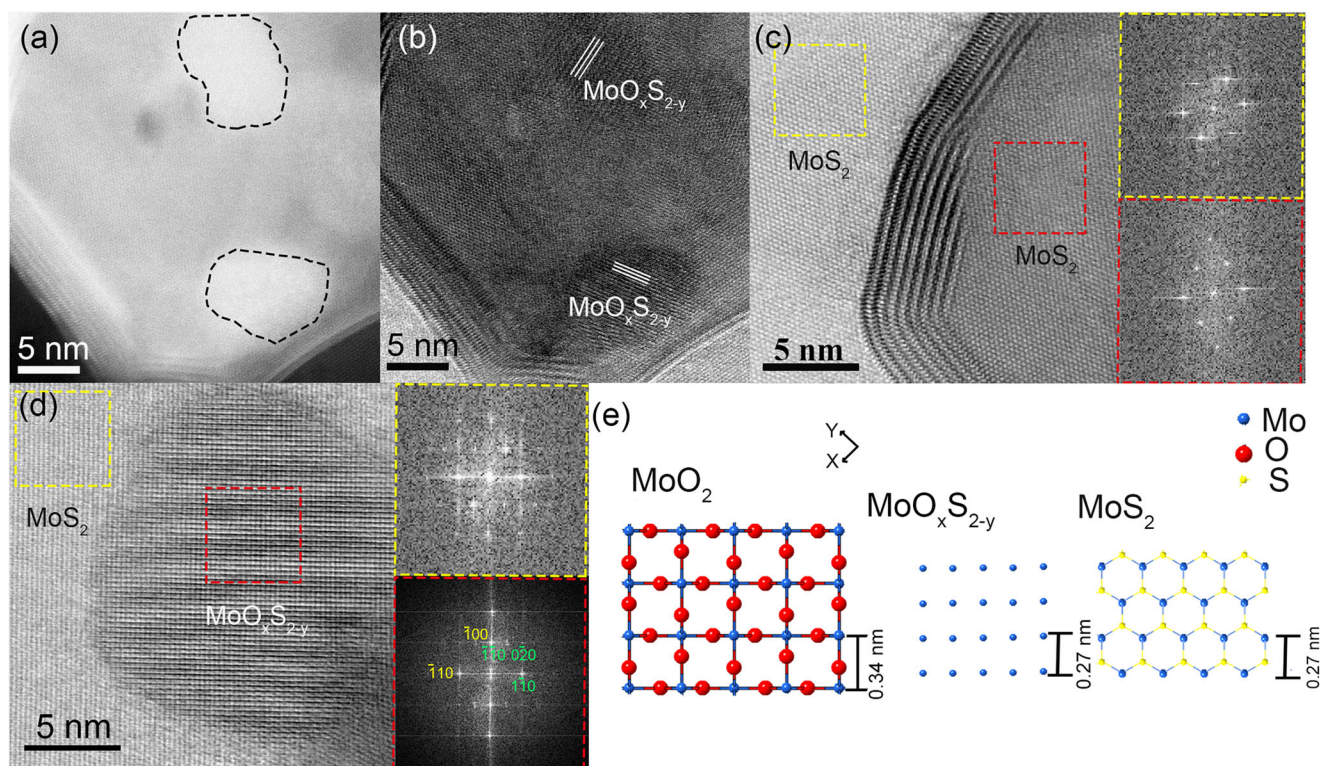


Fig. 3 **a** ADF-STEM image of typical nanoparticles with the core-shell fullerene structure. **b** The corresponding bright field-scanning transmission electron microscopy (BF-STEM) image of typical nanoparticles with the core-shell fullerene structure. **c** BF-STEM image of structure of empty area of the core. **d** BF-STEM image of nanoparticles without the core-shell fullerene structure and the corresponding FFT patterns collected from selected regions on few-layer MoS₂ (yellow dotted circle) and MoO_xS_{2-y} nanoparticle (red dotted circle). **e** Schematic represents the formation of MoS₂ from MoO₂ in a CVD process (blue sites are Mo atoms, red sites are S atoms, yellow sites are O atoms)

(highlighted with blue lines) and a bare Mo atom bound with zigzag terminated sulfur atoms, similar to the so-called Klein edge in graphite³⁵, written as S-Mo (marked by red lines in Fig. 5a–c) with the corresponding structural models shown as inset in Fig. 5a (blue sites are Mo atoms and red sites are S atoms). For the smallest MoS₂ cluster (Fig. 5a, 4b), these two types of edge structure are found approximately in equal number of quantities, and then the Mo-zz edge increases relative to the size of MoS₂ and finally becomes predominant. Such an evolution can be more clearly read out from the quantitative analysis (Fig. 5g). In order to explain these experimentally observed edge structures and their evolution, we further performed DFT simulations to calculate the formation energies of four zigzag edge structures (S-Mo, Mo-zz, S-zz (S-terminated zigzag edges) and Mo-S (Mo-terminated zigzag edges attached with two bare S atoms)) as a function of the chemical potential difference $\Delta\mu_{\text{Mo}}$, $\Delta\mu_{\text{Mo}} = \mu_{\text{Mo}} - \mu_{\text{Mo}}(\text{bulk})$, where μ_{Mo} and $\mu_{\text{Mo}}(\text{bulk})$ represent the chemical potential of Mo atoms in the source precursor and in MoS₂ monolayer, respectively. Please refer to the computation details section in Supplementary Information for details of modeling used in this study. The calculated results are shown in Fig. 5h, from which one can read: (i) Mo-terminated edges (S-Mo and Mo-zz) have lower formation energies than those of S-terminated edges (S-S and Mo-S) under the Mo-rich condition (taken to be $\Delta\mu_{\text{Mo}} > -0.3$ eV); (ii) the formation energies of Mo-zz and S-Mo are quite close (i.e., differ only 0.01 eV at $\Delta\mu_{\text{Mo}} = 0.1$ eV).

The case of microscopic MoS₂ monolayers seems to be different from that of the few-layer case. Since no residual MoO_xS_{2-y} nanostructures were observed on as-prepared MoS₂ monolayers as shown in Fig. 1c and Fig. 4, we can infer that the sublimated MoO₂ precursor should mostly form molecular clusters ((MoO₂)_n, (MoO₃)_n, etc.),³⁶ and sulfurized completely before its deposition on graphene substrate either as nucleation centers, or addition onto

already formed nucleation center either directly from vapor ambient or via surface diffusion on graphene substrate. Relative ratios of these clusters can change as the carrier gas flow changes; the presence of MoO_xS_{2-y} reduces the sulfur concentration in the reaction zone. As such, it can also well explain the difference in the as-formed products where few-layer MoS₂ or monolayer MoS₂ dominates, as shown in Fig. 1b, c. According to the DFT calculations, S-Mo and Mo-zz edges are dominant and with comparable ratio at the initial stage during the growth, as shown in Fig. 4. Comparing to the Mo-zz edge, the S-Mo edge should possess relatively higher chemical reactivity due to the bare Mo atoms that will facilitate the incorporation of sourcing clusters, thus leading to a faster growth rate. According to the classic crystal growth theory,³⁷ fast growing edges/facets gradually disappear, while slow-growing edges/facets remain. In this case, it will eventually lead to the formation of triangle-shaped MoS₂ monolayer decorated with Mo-zz edges, as most frequently observed. The slightly truncated shape observed on MoS₂ monolayers shown in Fig. 4j, k may be formed due to insufficient growth time, which again provides clear evidence for the proposed kinetics in edge structures, as discussed previously.

Figure 6a–c presents a summarized schematic diagram showing the microscopic process during the growth of few-layer MoS₂ under low gas flow (200 sccm) and Fig. 6d–f is the schematic of route for the nucleation and growth kinetics of MoS₂ monolayers. We note that Li et al.³⁸ proposed a three-step reaction pathway via examining the distribution of intermediate products in different forms.

From the results and discussions mentioned above, we could put forward some perspectives that may help us get high-quality MoS₂. (1) A steady stream-containing partial pressure of Mo and sulfur-containing vapor can help one get a large area MoS₂, and is essential towards the precisely controlled growth of MoS₂ atomic

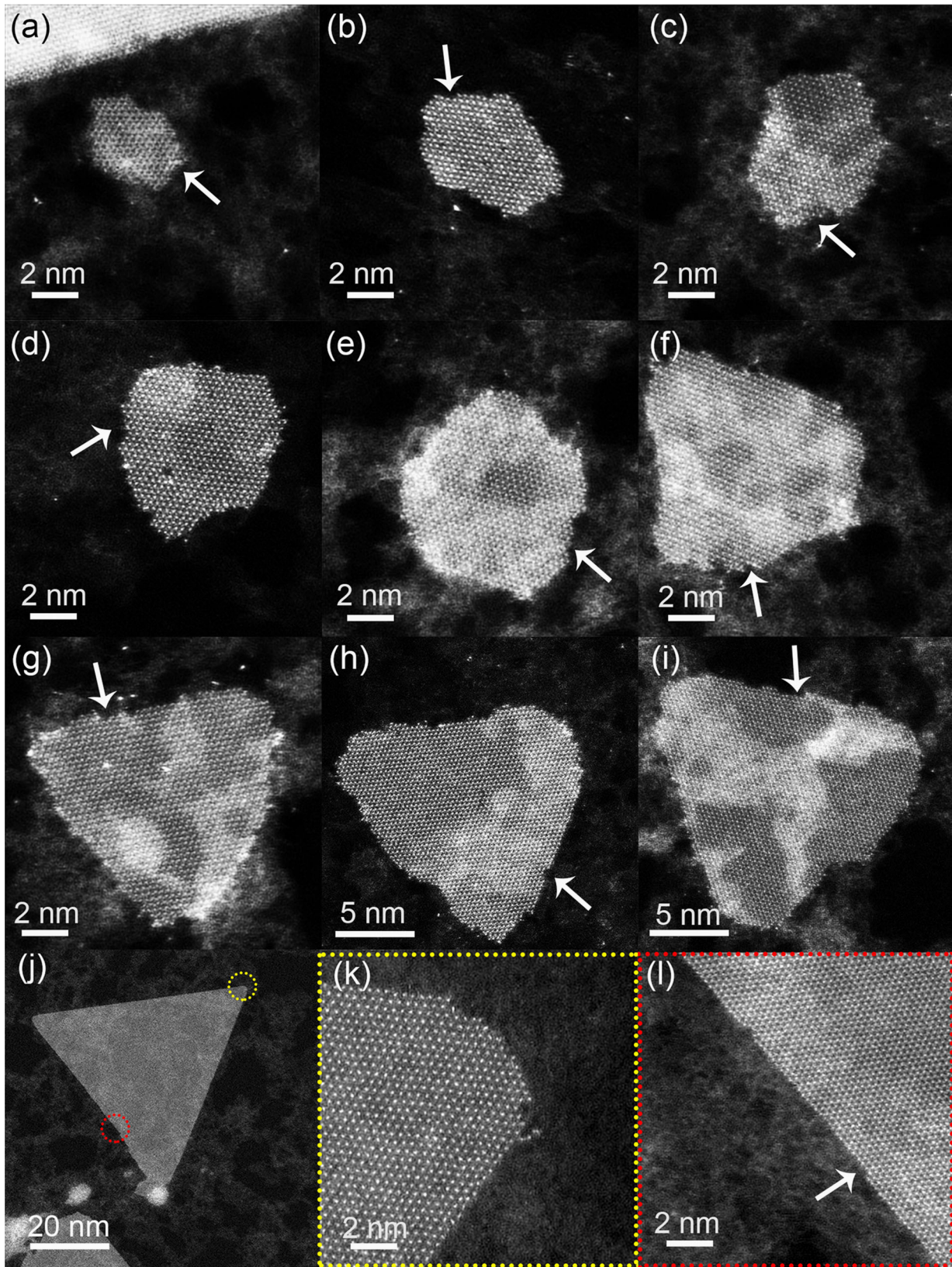


Fig. 4 **a–i** ADF-STEM images of monolayer MoS₂ with different sizes found on graphene, illustrating the shape evolution during CVD growth. A number of terraces with atomic steps can be found on the edge (arrowed, not all arrowed). **j** Low-mag ADF-STEM image of a triangle-shaped MoS₂ monolayer, **k** atomic structure of the region highlighted in yellow dotted circle, **l** atomic structure of the local region highlighted in red dotted circle

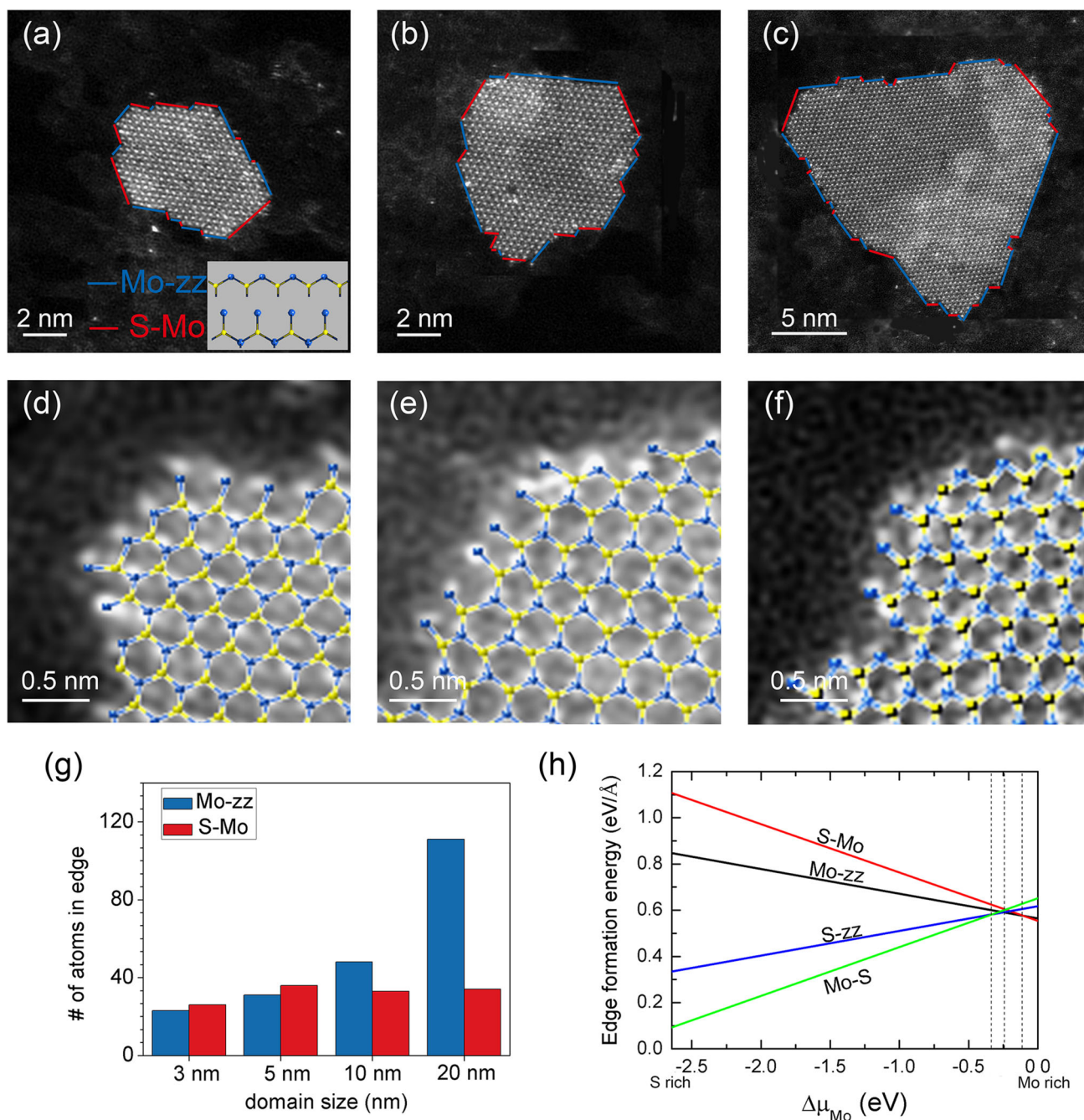


Fig. 5 **a** ADF-STEM image of irregular shaped monolayer MoS₂ cluster with two primary types of edge structure: Mo-zz edge (denoted by blue lines) and S-Mo edge (denoted by red lines) with the corresponding structural models (blue sites are Mo atoms and red sites are S atoms). **b** ADF-STEM image of hexagonal-shaped MoS₂. **c** ADF-STEM image of triangle MoS₂. **d** The edge structural model of the irregular MoS₂. **e** The edge structural model of the near-hexagonal MoS₂. **f** The edge structural model of the near-triangular MoS₂. **g** Histogram of the amount of the edge atoms with different size. **h** Results from DFT calculations for the formation energies of different edges as a function of $\Delta\mu_{\text{Mo}}$.

layers with desired edge structures and shape morphology. (2) For the precisely controlled layer thickness, extra care should be taken to control the sublimation of Mo precursor, and restrain the formation of larger MoO_xS_{2-y} nanoparticles on the substrate for growth. (3) Given these considerations, the widely used strategy of the sulfurization of Mo-O precursor in a CVD furnace seems to be too simplistic to fulfill this requirement. Further improvements, including the use of metal-organic CVD^{39, 40} or molecular beam epitaxy,⁴¹ may be a better option. In summary, we directly probe the nucleation seeds, evolution of edge structures and shape of evolution of pristinely-prepared MoS₂ materials. Two different

types of nucleation centers were resolved: Mo-oxysulfide (MoO_xS_{2-y}) nanoparticles on few-layer samples, and pure molybdenum sulfide clusters for monolayer samples. Nevertheless, it was proposed for a growing MoS₂ monolayer that it originates from an irregular polygonal-shaped cluster decorated with S-Mo and Mo-zz edges in a comparable ratio under the Mo-rich condition; then triangle-like shapes with dominant Mo-zz edges are formed as its size increases. A deep understanding of the growth mechanisms of atomically thin MoS₂ material via CVD, and other related two-dimensional TMD materials, will pave the way for specific function and property-oriented growth under precise control.

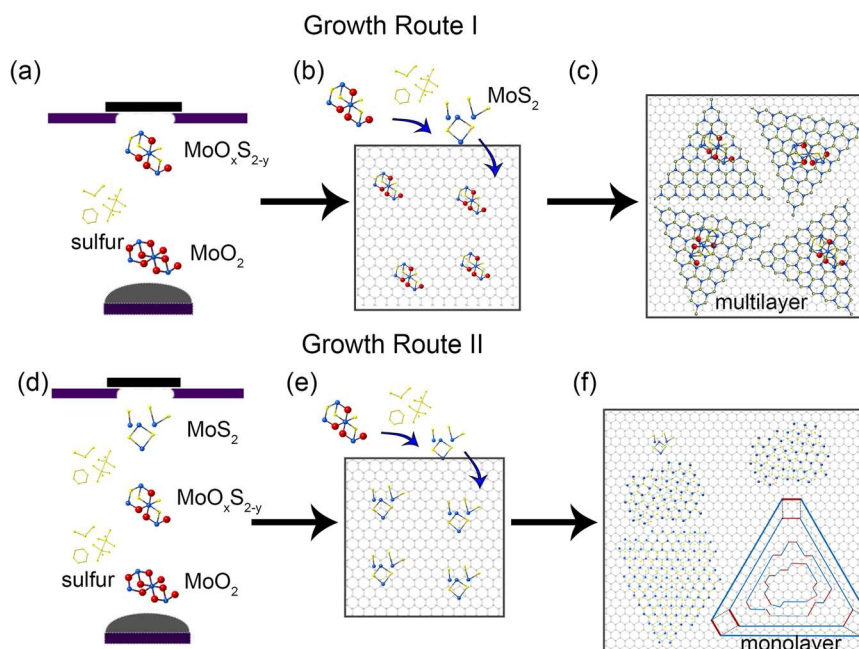


Fig. 6 a–c Schematic sketches explaining the possible route for the nucleation and growth kinetics of few-layer MoS₂ bound with thick core, and that d–f for the nucleation and growth kinetics of MoS₂ monolayers

METHODS

Graphene films used here were grown on polycrystalline copper foils, and then transferred onto molybdenum-based TEM grids via a PMMA-assisted wet chemistry process.⁸ Graphene-supported TEM grids were mounted onto a home-built ceramic carrier and loaded into a CVD system, facing down above a boat containing 1 mg of MoO₂ precursors (Sigma-Aldrich, 99%). Here we choose MoO₂, rather than MoO₃ as the precursor for two considerations because of the single-step chemical reaction $\text{MoO}_2 + 3\text{S} \rightarrow \text{MoS}_2 + \text{SO}_2$: (1) to reduce the reaction complexity, as a multi-step reduction reaction occurs for the sulfurization of MoO₃, (2) to grow high quality MoS₂ monolayer.¹³ The whole CVD setup is shown in Fig. 1a. Within a typical CVD process, the furnace was firstly heated to 300 °C for 10 min and held for additional 10 min, and then heated to 750 °C in 40 min and kept for next 25 min. At about 15 min after the furnace temperature reached 750 °C, heating of 300 mg of sulfur source (Aladdin, 99.999%) was started, with its temperature reaching 180 °C in 2 min, and then held for the next 10 min. During the whole process, argon (99.999%) was used as the carrier gas, with an optimized flow rate of 200 standard-state cubic centimeter per minute (sccm) for growing few-layer samples and of 500 sccm for monolayer samples. The total growth time lasts for about 10 min, and the furnace cooled down naturally. ADF-STEM was conducted with a FEI Chemi-STEM Titan G² 80–200, which was equipped with a probe-side spherical aberration-corrector and operated at an acceleration voltage of 200 kV. The convergent angle for illumination was set to 24 mrad with a probe current of 50–70 pA, and the collection angle was 50–100 mrad. XEDS was carried out on a Bruker super-X detection system.

ACKNOWLEDGEMENTS

We thank Prof. Feng Ding for his critical comments, Zhepeng Zhang and Prof. Yanfeng Zhang for providing us highquality graphene samples and the Center of Electron Microscopy of Zhejiang University for the access to the microscope facilities. J.Y. acknowledges supports from Pao Yu-Kong International Foundation for a Chair Professorship in ZJU. H.B.S. acknowledged computational resources from the Shanghai Supercomputer Center. This work was financially supported by the National Basic Research Program of China (Grant No. 2014CB932500 and No. 2015CB921004), the National Science Foundation of China (Grant No. 51472215, No. 51222202, and No. 11404309) and the 111 project (No. B16402). J.Y. acknowledges the EPSRC (UK) funding EP/G070326.

AUTHOR CONTRIBUTIONS

C.J. conceived the project; D.Z. carried out most of the experiments (CVD, Raman and TEM), and analyzed the data with the assistance of F.J. V.A. and D.L., under the

supervision of C.J.; H.S. carried out the DFT calculations; O.O. J. Y. and Z.Z. contributed to the discussions; D.Z. and C.J. wrote the paper together with the inputs and suggestions from others.

COMPETING INTERESTS

The authors declare no competing financial interests.

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Supplementary Information accompanies the paper on the *npj 2D Materials and Applications* website (doi:10.1038/s41699-017-0010-x).