Hindawi
Journal of Nanomaterials
Volume 2017, Article ID 6865282, 6 pages
https://doi.org/10.1155/2017/6865282

Research Article

Growth and Mechanism of MoS_2 Nanoflowers with Ultrathin Nanosheets

Yifei Guo,[1,2] Xiuli Fu,[1] and Zhijian Peng[2]

[1]*State Key Laboratory of Information Photonics and Optical Communications and School of Science, Beijing University of Posts and Telecommunications, Beijing 100876, China*
[2]*School of Engineering and Technology, China University of Geosciences, Beijing 100083, China*

Correspondence should be addressed to Xiuli Fu; xiulifu@bupt.edu.cn and Zhijian Peng; pengzhijian@cugb.edu.cn

Received 26 October 2016; Accepted 14 February 2017; Published 19 March 2017

Academic Editor: Jean M. Greneche

Two-dimensional molybdenum disulfide (MoS_2) with few layers, due to their excellent optical and electrical properties, has great potential for applications in electronic and optoelectronic devices. In this work, flower-like MoS_2 nanostructures with ultrathin nanosheets (petals) were successfully deposited onto silicon substrates by a facile process based on chemical vapor deposition via using MoO_3 and S powders as starting materials. Their composition and structure were explored by field emission scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, and photoluminescence. The reported nanoflowers vertically and separately stood on the substrates, consisting of several bonded MoS_2 nanosheets with a thickness of 10–30 nm and high crystallinity. On the basis of these results, a growth mechanism for the MoS_2 nanoflowers was proposed.

1. Introduction

Over the past decades, two-dimensional semiconducting transition metal dichalcogenides (TMDs) have received extensive attention because of their unique structure as well as excellent optical and electrical properties [1–4]. Recently, some authors have reported the exciting applications of TMDs (such as MoS_2, WS_2, $MoSe_2$, and WSe_2) in photovoltaics [5], energy storage [6], photocatalysts [7], and optoelectronic devices [8, 9]. Among them, MoS_2 exhibits novel properties because of its unique atomic structure. MoS_2 is composed of three atomic layers: the molybdenum atoms layer sandwiched between two layers of sulfur atoms. There are strong covalent bonds within the layers and weak van der Waals force between the lattice layers. So far, various morphologies of MoS_2 have been reported, including nanoplates [10, 11], nanorods [12], nanowires [13], nanotubes [14], and nanoflowers [15]. In addition, more recent studies have revealed that three-dimensional MoS_2 structures are much more desirable in many specific applications because of their remarkable advantages, such as more actively exposed edges and high aspect ratio [16, 17]. For instance, the exposed edges may play a crucial role in electrochemical and catalytic reactions due to the active dangling bonds.

With regard to the synthesis of MoS_2, several groups have prepared MoS_2 by a variety of methods, including mechanical exfoliation [18], lithium-based intercalation [19, 20], hydrothermal synthesis [21, 22], chemical vapor transport [23], and chemical vapor deposition (CVD) [24, 25]. To date, three-dimensional MoS_2 nanostructures, such as nanoflowers and nanospheres, are obtained mainly by hydrothermal synthesis [26, 27]. Compared to hydrothermal synthesis, CVD, a typical bottom-up growth method, has several advantages, such as being more facile, having a lower cost, and causing less pollution, presenting great potential as an efficient technique towards scalable synthesis of high-quality MoS_2. However, there are very few studies on the growth of MoS_2 nanoflowers by CVD methods [28, 29]. So, in this work, we designed a facile process based on CVD, which can obtain a kind of flower-like MoS_2 nanostructures with ultrathin nanosheets (petals). And the growth mechanism of the reported MoS_2 nanoflowers was proposed.

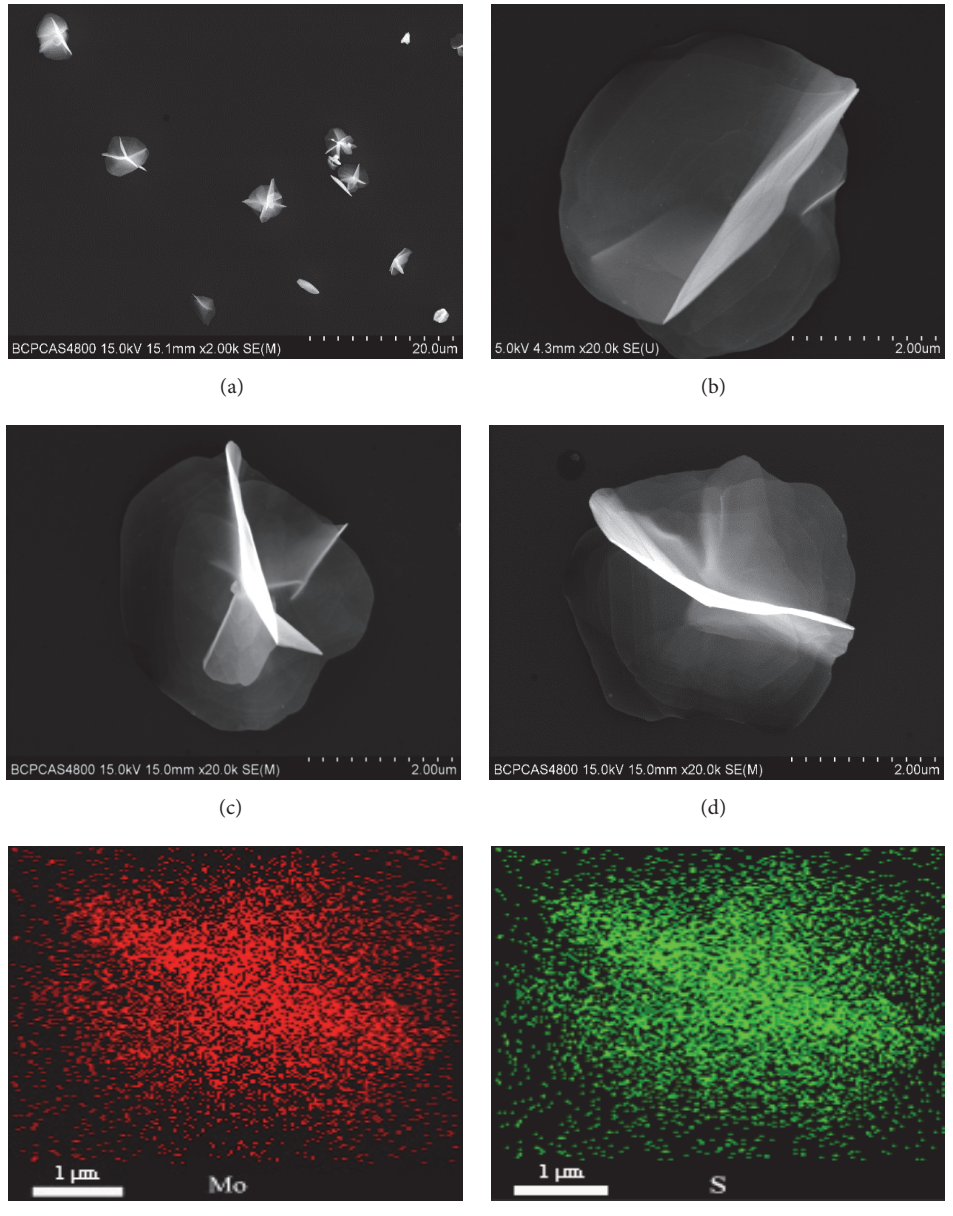

Figure 1: Typical SEM images of the obtained samples in low magnification (a) and high magnification (b, c, d). (e, f) EDX mapping results on one sheet of the sample.

2. Experimental

The as-proposed vertically grown MoS_2 nanoflowers with ultrathin nanosheets were prepared by CVD in a horizontal quartz tube furnace with two temperature zones working with different heating resistors [30]. By making use of this equipment, we can effectively and accurately control the temperature gradient of the furnace along the quartz tube. In a typical process, pure MoO_3 and S powders as starting materials were loaded in two different alumina boats. The boat with MoO_3 powder was placed at the center of the high-temperature zone, and that with S powder was located at 12 cm away from the MoO_3 powder on the upstream of the carrier gas in the furnace. Meanwhile, by placing on a quartz plate, a Si wafer was set on the carrier gas downstream of the furnace at the center of the low-temperature zone, which was about 60 cm apart from the evaporation source MoO_3 powder. Before heating, the tube furnace was first evacuated and flushed repeatedly with Ar gas several times to deplete the remnant oxygen in the whole system. Subsequently, the high-temperature zone was ramped up to 850°C in 40 min and then held at 850°C for 1 h, while the low-temperature zone was heated up to 500°C in 30 min and held at 500°C for 70 min. After heating, the furnace was

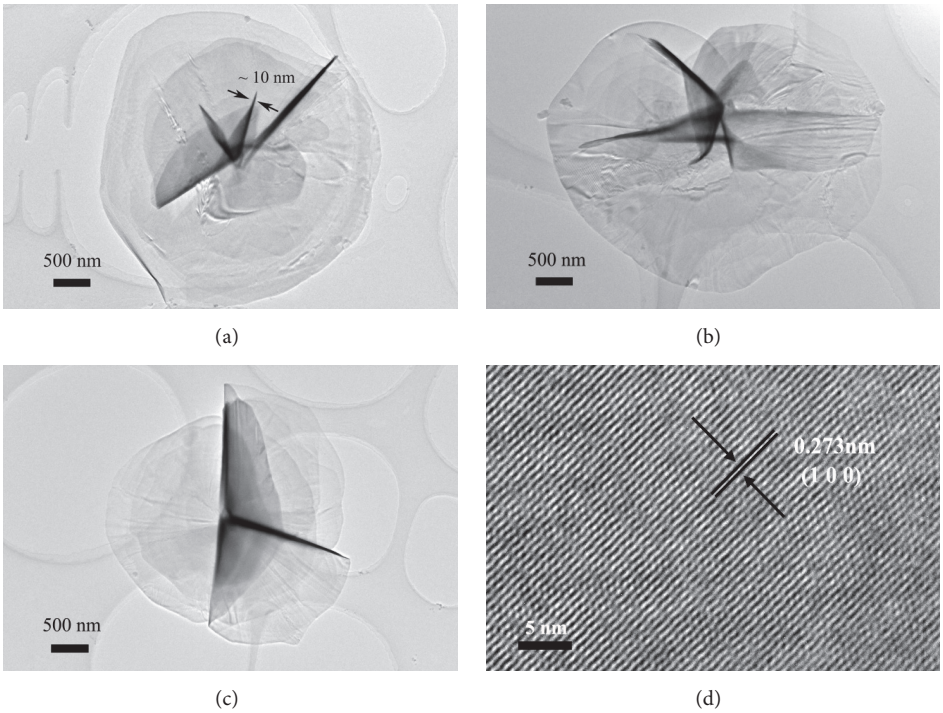

Figure 2: (a, b, c) TEM images of the obtained flower-like MoS_2 nanostructures. (d) HRTEM image of typical MoS_2 nanosheet.

cooled naturally to room temperature. Throughout the whole reaction process, an Ar gas flow of 200 sccm was kept inside the quartz tube. Finally, the samples were collected on the Si wafer.

The morphology and structure of the as-synthesized samples were characterized by optical microscopy (OM, Olympus BX53), field emission scanning electron microscopy (SEM, S4800), transmission electron microscopy (TEM, Tecnai G2 F20 U-TWIN), and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 U-TWIN). An energy-dispersive X-ray (EDX) spectroscope attached to the SEM was used to measure the composition of the samples. The optical properties and quality of the as-grown samples were examined by Raman spectroscopy and photoluminescence (PL), which were carried out on a Jobin Yvon HR800 Raman system with a laser excited at 532 nm. A laser power of 0.1 mW was used to avoid heating the sample and PL saturation.

3. Results and Discussion

The morphology of the as-prepared samples was first examined by SEM. Typical results are presented in Figure 1. The low magnification image as shown in Figure 1(a) displays a number of flower-like nanostructures, all of which stood on the substrate (Si wafer). For individual nanostructure, the high magnification images as shown in Figures 1(b)–1(d) indicate that although the morphology of the flowers might vary somewhat, all of them consist of several bonded ultrathin nanosheets (petals), which are of largely exposed surfaces (including side edges) and grow relatively independently of each other. Notably, the petals of nanostructures display different curving angles and are of a diameter of roughly 4–6 μm. Furthermore, the EDX mapping images of the sample (as shown in Figures 1(e) and 1(f)) reveal that the as-grown samples were molybdenum sulfide nanostructures, and the calculated atomic ratio of the samples is approximately Mo : S = 1 : 2.08, which is very much approaching the stoichiometric ratio of MoS_2.

In order to elucidate the crystalline structure of the samples, TEM examinations were carried out. The characteristics of the present nanostructures with some thin petals could be also observed from the TEM images as illustrated in Figures 2(a)–2(c). Although the TEM samples were prepared by ultrasonic dispersion and transferred onto the supporting grid, the intact morphology of MoS_2 nanoflowers as shown in Figures 2(a)–2(c) indicates good structural stability and high crystallinity of the samples, confirming the flower-like nanostructure of the samples. Moreover, under the irradiation of electron beam, the nanosheets of the flower-like nanostructures were found to be very much transparent, revealing that they are ultrathin pieces. The size of the flower-like nanostructures was also evaluated by TEM (see Figure 2(a)). It was calculated that their diameter was in the range of roughly 4–6 μm, which is consistent with the SEM observation, and the thickness of the nanosheets (petals) was in the range of approximately 10–30 nm. Moreover, a typical HRTEM image on a nanosheet of the obtained nanostructures was presented in Figure 2(d), showing that the lattice distance is 0.273 nm, corresponding to the (100) plane of the MoS_2 phase, which is consistent with the EDX results from SEM.

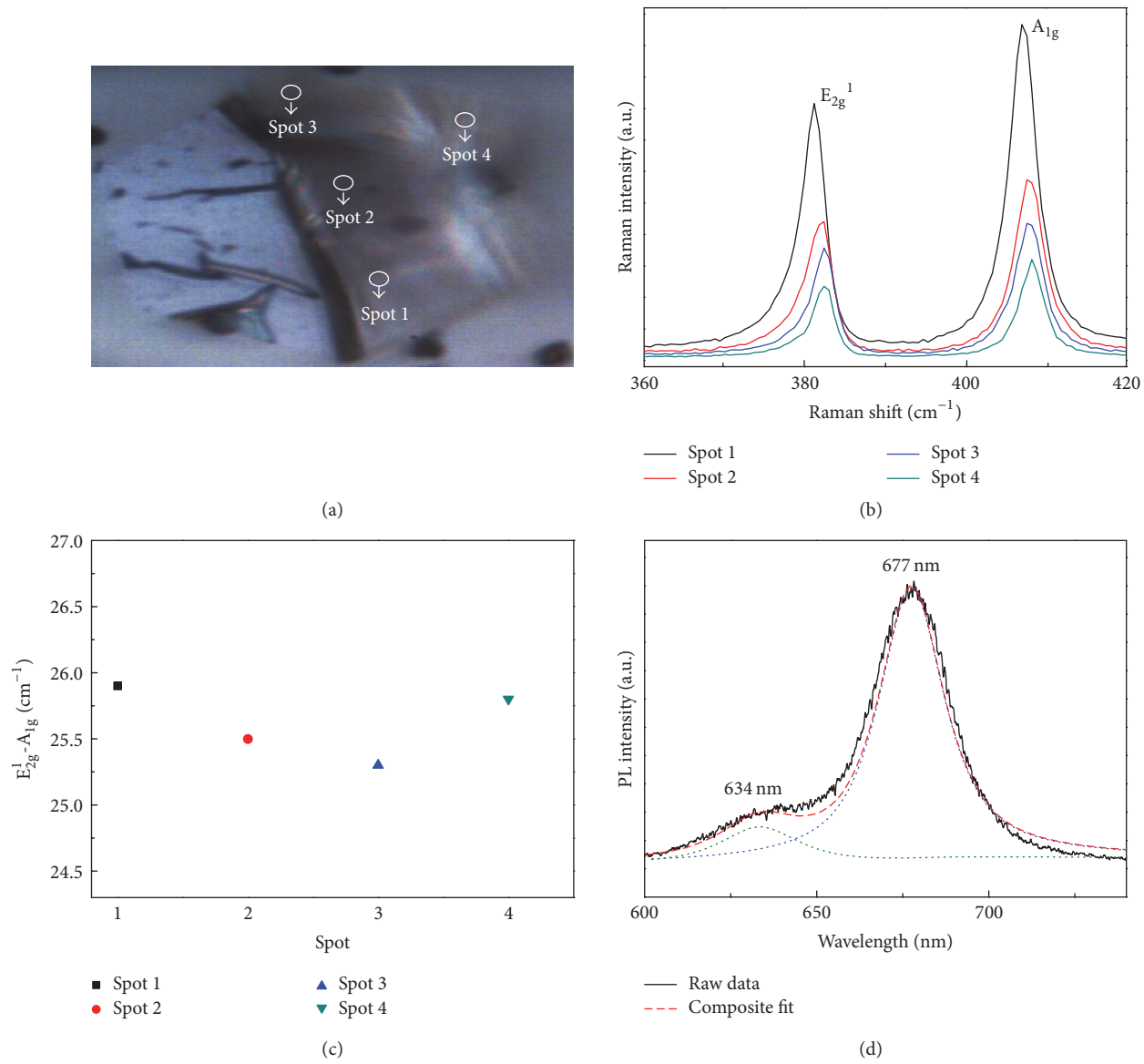

Figure 3: (a) OM image of a typical MoS_2 nanosheet, where the Raman spectra were recorded at different places, marked as Spots 1–4. (b) The recorded Raman patterns from the different spots on the MoS_2 nanosheet and (c) their corresponding differences between E_{2g}^1 and A_{1g} modes. (d) Typical PL spectrum of a MoS_2 nanosheet.

To further investigate the optical properties and quality of the as-grown nanostructures with ultrathin MoS_2 nanosheets, Raman and PL measurements were performed. Figure 3(a) displays the OM image of a typical MoS_2 nanosheet, where the Raman spectra were recorded at different places marked as Spots 1–4 in the figure. The results are presented in Figure 3(b). As shown in Figure 3(b), two typical Raman active peaks of MoS_2, in-plane vibration E_{2g}^1 and out-of-plane vibration A_{1g}, are exhibited, which are located at about 381 and 407 cm^{-1}, respectively. As is well known, the difference (Δ) between E_{2g}^1 and A_{1g} modes can be used to estimate the thickness difference and layer number of MoS_2 nanosheets; and the Δ value is about 20 cm^{-1} for monolayer and approximately 25 cm^{-1} for multilayer MoS_2 [31]. From Figure 3(c), it can be seen that the calculated Δ values from the different spots on a typical MoS_2 nanosheet fluctuate in a very narrow range of 25.3–25.9 cm^{-1}, indicating that the nanosheets were multilayer MoS_2 and the thicknesses of the MoS_2 nanosheet are quite homogeneous. Moreover, the PL spectrum as shown in Figure 3(d) can be fitted into two prominent emission peaks at about 634 and 677 nm, which are, respectively, assigned to the A_1 excitation with a peak energy of about 1.96 eV and the resonance of B_1 excitation with a peak energy of approximately 1.83 eV. Additionally, due to the A_1 and B_1 direct excitonic transitions, the emissions could not found from their direct band-gap bulk materials. Therefore, the above Raman and PL

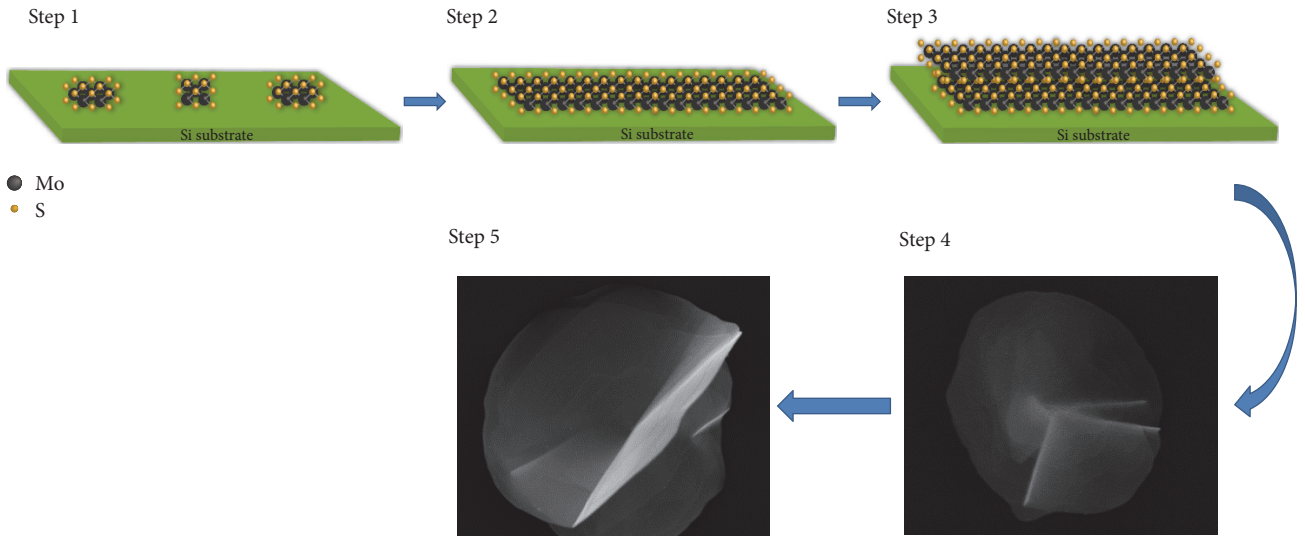

Figure 4: Schematic diagram for the growth mechanism of the flower-like MoS_2 nanostructures.

results qualitatively indicate that the obtained MoS_2 nanosheets are of few layers and could exhibit a very strong PL emission.

Finally, we try to propose a growth mechanism for the flower-like MoS_2 nanostructures. In the early stage of reactions, S vapor transported by the Ar carrier gas reacts with the MoO_3 powder, and the MoO_3 would be reduced gradually, forming gaseous MoS_2, which will spread to the silicon substrate. The nucleation sites (crystal seeds) of MoS_2 thin films are subsequently formed (see Step 1 in Figure 4) [32]. As the growth proceeded, MoS_2 thin films were formed owing to the growth and merging of the crystal seeds (Step 2). With the growth continued, MoS_2 thin films firstly grew into a layer-by-layer pattern until a critical thickness reached, and then merged and extended constantly (Step 3). During the growth, due to possible dynamics cause and local heating, slight edge dislocation and little curve would be formed. Then, the curve direction gradually became energetically favorable, which led to the vertically grown MoS_2 nanosheets (Step 4). At last, MoS_2 films slipped and grew in a vertical pattern, forming the as-proposed MoS_2 nanoflowers (Step 5). And at the temperature holding stage, some amorphous and defect structures grew further, leading to the nanoflowers with high crystallinity. From our result, it can be inferred that the formation of the edge dislocations and curve may result in distinct morphologies of flower-like structures in several areas. Obviously, some petals grew gradually along the preferred curly growth direction, forming a number of single MoS_2 nanoflowers.

In addition, because many two-dimensional semiconducting TMDs have similar layered structure and physical property with MoS_2, the above-observed edge dislocation and curve during their formation would usually occur [33, 34]. Therefore, under an appropriate condition on dynamics and local heating, the present CVD approach might be also used to grow flower-like or more complex structures of other two-dimensional layered materials, such as oxides, sulphides, and selenides, by using their oxides and/or S/Se powders as the starting materials.

4. Conclusions

Flower-like MoS_2 nanostructures with ultrathin nanosheets (petals) were successfully synthesized by a facile CVD technique onto silicon substrates via using MoO_3 and S powders as starting materials. The vertically and separately standing nanoflowers consist of few layers of MoS_2 nanosheets with a thickness of 10–30 nm and have high crystallinity, which would be promising in the applications in nanoscaled electronic and optical devices. And the growth of MoS_2 nanoflowers is caused by the formation of edge dislocations and curve, which may be used in growing flower-like or more complex structures of other two-dimensional layered materials.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors would like to acknowledge the financial support for this work from the National Natural Science Foundation of China (Grants nos. 11674035, 61274015, and 11274052) and Fund of State Key Laboratory of Information Photonics and Optical Communications (Beijing University of Posts and Telecommunications).

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