Synthesis and characterization of vertically standing MoS$_2$ nanosheets

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Molybdenum disulfide (MoS$_2$) has been attracting much attentions due to its excellent electrical and optical properties. We report here the synthesis of large-scale and uniform MoS$_2$ nanosheets with vertically standing morphology using chemical vapor deposition method. TEM observations clearly reveal the growth mechanism of these vertical structures. It is suggested that the vertical structures are caused by the compression and extrusion between MoS$_2$ islands. More importantly, the vertical morphology of two dimensional (2D) materials hold many promising potential applications. We demonstrate here the as-synthesized vertically standing MoS$_2$ nanosheets could be used for hydrogen evolution reaction, where the exchange current density is about 70 times of bulk MoS$_2$. The field emission performance of vertically standing MoS$_2$ were also improved due to the abundantly exposed edges.

Graphene has attracted extensive interests in various research fields since it was obtained through mechanical exfoliation by Novoselov et al. in 2004$^1$. Due to the distinctive physical properties of one-layer thin 2D materials compared with their bulk counterparts$^{2,3}$, layered materials have attracted much attentions, such as transition metal dichalcogenides (TMDCs)$^4$, transition metal oxides$^5$, boron nitride (BN)$^6$, etc. Lots of efforts have been made by using 2D materials in the fields of microelectronics$^7,8$, optoelectronics$^9$, sensors$^{10}$ and energy storage$^{11,12}$. However, these works have been devoted to utilize 2D materials lying flat on the substrates. Less of attention has been paid on their alternative configuration$^{13–15}$. Amongst these nanometric architectures, vertically standing 2D materials hold great potential in many applications due to their high aspect ratio and extensively exposed edges$^{16}$.

For example, the minimized dimension and vertically aligned morphology of 2D materials consequently enable the fabrication of mini-sized energy storage devices with high capacity and high packing density, such as hydrogen storage devices, batteries and supercapacitors. The exposed edges with dangling bonds are chemical active and may play an important role in many catalytic reactions, such as hydrodesulfurization, hydrogen evolution reaction (HER) etc$^{17–20}$. J. Shi et al.$^{20}$ demonstrate that the HER activity relates closely to the edge sites of MoS$_2$ flakes and the basal surfaces are catalytically inert, revealing the importance of exposed edges in catalytic reactions$^{21}$. Furthermore, It has been demonstrated that vertically growth 1D nanotubes/nanowires and 2D nanosheets with atomically thin edges can significantly improve the field emission properties$^{22,23}$, making vertically standing 2D materials promising candidates in field emission applications$^{24–26}$.

There have already been lots of works based on the one dimensional (1D) nanowires and nanotubes. And the growth mechanism for vertical 1D nanowires and nanotubes are widely discussed. Normally, nanowires and nanotubes are assumed to be grown at the interface between catalytic and nanowires (nanotubes) via vapor-liquid-solid (VLS) or vapor-solid-solid (VSS) process in 1D growth$^{27,28}$. In contrast, the growth mechanism for vertically standing 2D materials are still vague. L. Jiang et al.$^{24}$ demonstrated that a transition from 2D complete films to 3D clusters beyond a critical layer thickness may be caused by the sufficient accumulation of strain energy and the defects of the as-deposited film during vertical graphene growth process. J. Zhao et al.$^{29}$ demonstrated that vertically standing graphene could be nucleated from the buffer layer or from the surface of carbon onions. However, there are no clear evidences demonstrating that how these transitions from 2D films to 3D clusters happened. We believe that a clear understanding of the growth mechanism would facilitate the

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development of vertically standing materials based applications. In addition, the growth mechanism could also promote the process in designing more complex nanometric structures.

In this work, we propose a method to synthesize vertically standing MoS₂ nanosheets using a conventional chemical vapor deposition (CVD) method. Various characterizations techniques were used to give a deep analysis of those vertically standing MoS₂ nanosheets. In addition, a possible mechanism is proposed based on the experimental results. Furthermore, the field emission properties and the HER performance of vertically standing MoS₂ nanosheets were reported.

**Results**

**Synthesis and characterization of vertically standing MoS₂.** A typical SEM image of the vertically standing MoS₂ nanosheets grown on SiO₂/Si substrate is shown in Fig. 1a. It clearly shows that MoS₂ nanosheets were uniformly grown on the substrate. The 52.5° tilt SEM image (Fig. 1b) demonstrates that the as-grown MoS₂ nanosheets are nearly perpendicular to the substrate. AFM height profile is shown in Fig. 1c, where the corresponding AFM image is shown in the inset. The nanometric edges of different MoS₂ layers could be clearly observed in the high magnification SEM image (see Supplementary Fig. S1 online). It is believed that these
MoS2 islands were formed on top of MoS2 films at the same time (Fig. 2b). More triangle-shaped MoS2 islands were formed above MoS2 films after 5 minutes growth (Fig. 2c), after that, a transformation from 2D growth to 3D growth started (Fig. 2d). Raman spectroscopy analysis have been applied on those samples with different growth time. As shown in Supplementary Fig. S4, the intensity ratios between A1g and E1g modes of CVD grown MoS2 nanosheets samples are higher than that of bulk MoS2 samples, revealing a higher density of exposed edges in those CVD grown MoS2 nanosheets samples. With growth time increased from 5 minutes to 10 minutes, the ratio between A1g and E1g mode intensity was also increased, suggesting a transformation from 2D to 3D growth.

More SEM observations were performed on the intermediate state of MoS2 nanosheets to find out how these MoS2 nanosheets are originated from the buffer layers and formed by the extension and the curl of the plane of MoS2 islands. Based on above results, it could be inferred that vertical standing MoS2 nanosheets are originated from a thick MoS2 film at the bottom. High resolution TEM image (Fig. 2h) shows the thick MoS2 film has clear layered structure. From TEM observations, it could be observed that the vertical MoS2 nanosheet are originated from the MoS2 island layers. Based on above results, it could be inferred that vertical standing MoS2 nanosheets may originate from the curling force induced by the increasing defects and strain energy. Figure 2i display the nanobeam electron diffraction (NBD) pattern from Fig. 2h (selected area marked by the circle), which shows only regularly arranged diffraction spots, corresponding to the hexagonal crystal structure of MoS2.

TEM analyses were performed on the collision or distortion area where the vertically standing MoS2 nanosheets nucleated from. Basically, two kinds of vertical morphology and their corresponding base structure were observed (Fig. 3). It can be clearly observed in the TEM images that the vertical MoS2 nanosheets were grown from the buffer layer underneath on both cases. The first kind of vertical morphology is shown in Fig. 3a,b. The MoS2 nanosheets are originated from the buffer layers and formed by the extension and the curl of the plane MoS2 buffer layers. Alternatively, the vertical structure could be originated from the merge of two separated MoS2 films (Fig. 3e,f). The formation of vertical morphology may be caused by the collision between two MoS2 islands. The same triangular structure could be clearly observed at the intermediate state as shown in Supplementary Fig. S5. In addition, the stable triangle could be observed on the bottom structure on other TEM observations. Energy-dispersive X-ray spectroscopy (EDX) (see Supplementary Fig. S6 online) certify that nearly no chemical elements are existed in the triangle area, suggesting that the empty triangle was formed due to the curl of MoS2 films instead of other chemical reaction. We believe that the self-formative triangular area could enhance the stability of the whole vertical structure.

Based on the above observations, a vertical growth mechanism is proposed to explain the formation of vertically standing MoS2 nanosheets. It is believed that the intensive compression between different MoS2 islands cause the collision and slide of MoS2 plates, which induce the vertical structure growth. As shown in Fig. 3c,d, when a high barrier of MoS2 islands or plates block the extension of MoS2 islands, the MoS2 islands may slip and change to vertical growth. Alternatively, when two MoS2 island push and collide against each other, the compression force may produce obvious distortion that an arch structure could be formed to release the pressure (Fig. 3g,h), which
would subsequently act as the growth template for the vertical growth of MoS₂ nanosheets. Because vertical MoS₂ are associated with MoS₂ islands, it could be inferred that the alignment of vertically standing MoS₂ nanosheets would be improved by synthesizing uniform MoS₂ islands with constant growth direction. MoS₂ growth orientation has been reported to be facet-dependent. Thus, the alignment might be improved by choosing a specific substrate.

To better understand the growth model, schematic graphs are shown in Fig. 4a–e. During the growth period, firstly, MoO₃ powder was partially reduced by sulfur vapor to form volatile MoO₃−ₓ or gaseous MoS₂ and these sub-oxide compounds or gaseous MoS₂ were adsorbed and diffused to the substrate, and subsequently formed nucleation sites of MoS₂ films (Fig. 4a). With growth time increased, separated 2D MoS₂ films were generally formed due to the growth and merging of the seeds as illustrated in Fig. 4b. It has been shown that the concentration of the gaseous MoS₂ or sub-oxide compounds is an important thermodynamics and kinetics factor for the MoS₂ growth. Due to the high concentration of the reactants introduced by the fast evaporation of sulfur powder in our experiment (see Methods), the growth of MoS₂ films would be facilitated by the supersaturated MoS₂ vapor and sub-oxide compounds vapor. And multi-layer MoS₂ films were consequently formed with increasing growth time. After that, MoS₂ films are grown in a layer-by-layer fashion until a certain critical thickness (Fig. 4c). And then MoS₂ islands were formed (Fig. 4d) to get an energetic favorable morphology according to the Stranski-Krastanov (SK) growth model. With growth continued, MoS₂ islands quickly extended and merged. A high strain energy would be introduced due to the fast chemical reaction. Thus, MoS₂ seedlings could originate from the collision or distortion area of different MoS₂ islands as shown in Fig. 4e. It is worth to note that though vertically standing MoS₂ could originate from different based structures, the growth direction and the dominated surface facets remain the same: with ±(002) planes defining the two dominant surfaces (see Fig. 4f). The observed

Figure 2. SEM and TEM observation on the formation of vertically standing MoS₂ nanosheets. (a–d) SEM images of the MoS₂ films grown at the same condition but with different growth time: (a) 2 minutes, (b) 3 minutes, (c) 5 minutes and (d) 7 minutes. (e–f) SEM observations on the initial stage of the vertical MoS₂ formation. (g) Cross-sectional TEM image of vertically standing MoS₂. (h) HR-TEM image of plane MoS₂ nanosheets. (i) NBD pattern from h (selected area marked by the circle).
morphologies of the MoS₂ are driven by the requirement for reducing surface energy. Such a (002)-dominant surface structure is caused by the lowest surface-energy of (002) surface, which is consistent with previous report⁴⁰.

**HER and field emission performance.** To evaluate the catalytic activity of vertically standing MoS₂ nanosheets, a typical three-electrode setup was used for HER test. Vertically standing MoS₂ nanosheets were deposited on gold films using the same CVD method as described previously (see Supplementary Fig. S7 online). Typical cathodic polarization curves and corresponding Tafel plots are shown in Fig. 5a,b. The polarization curve of bare gold electrodes is also given in Fig. 5a. As it is known, Tafel slope is determined by the rate-limiting step of HER⁴¹. The Tafel slope in our sample was measured to be about 92 mV/decade (Fig. 5b). Previous studies have shown a large range of Tafel slope from 40 mV to 140 mV/dec and the reaction mechanism on MoS₂ still remains inconclusive⁴⁸⁻⁴⁰,⁴²⁻⁴³.

The charge-transfer resistance could be estimated by using electrochemical impedance spectroscopy (EIS) method, revealing a lower charge-transfer resistance than gold films (see Supplementary Fig. S8 online). The
exchange current density, $j_0$, is determined by fitting the linear portion of Tafel plot at low cathodic current to the Tafel equation (see Supplementary Fig. S9 online). Based on the results, it is found the exchange current density $j_0$ is about 22.3 μA/cm², which is 70 times of bulk MoS₂. The large value of $j_0$ is due to the high density of exposed edges²⁰,²¹. However, the interlayer hopping of electrons between different MoS₂ layers may limit the HER performance of vertically aligned MoS₂ nanosheets⁴²,⁴⁵. Thus we believe the overall performance of our samples could be further improved by introducing doping during CVD process, which will be explored in the future. Another important criterion for a good electrocatalyst is its high durability. To evaluate this, continuous cyclic voltammetry were performed. The polarization curves before and after 1000 cycle are shown in Fig. 5c, where negligible loss of cathodic current could be observed.

In order to characterize the field-emission properties of vertically standing MoS₂ nanosheets, a series of field emission measurement experiments were performed (Fig. 6). The anode was an indium tin oxide (ITO)-coated glass, and the vertically standing MoS₂ nanosheets grown on SiO₂/Si substrate was used as the cathode. Figure 6a shows the field-emission current versus electric field of the as-prepared MoS₂ nanosheets. The turn-on electric field ($J = 10 \mu$A/cm²) is around 2.46 V/μm, which is smaller than previous reported MoS₂ nanosheets (~2.8–5.5 V/μm)²⁵,⁴⁶,⁴⁷. Fowler-Nordheim (FN) theory is the most commonly used model for understanding the electron-emission behaviour of various nanostructures. A modified F-N equation is used here to analyze the field emission property of MoS₂, which could be expressed as:

$$J = \lambda_M \phi \beta e^{b \phi / \beta E} \exp \left( -\frac{v_F b \phi^{3/2}}{\beta E} \right)$$  \hspace{1cm} (1)

Where $a = 1.54 \times 10^{-6}$ A eV V⁻¹ is a constant which depends on the surface structure and $b = 6.83 \times 10^7$ V cm⁻¹ eV⁻¹/². $J$ is the emission current density, $E$ is the applied average field, $\phi$ is the work function of emitter, $\lambda_M$ is the macroscopic pre-exponential correction factor and $v_F$ (correction factor) is a particular value of the principal Schottky-Nordheim barrier function $v$. The ratio of the actual local electric field and the applied average electric field is known as the field enhancement factor $\beta$. Fig. 6b shows the ln($J/E^2$) versus 1/E curve which has good agreement with the FN equation. The field-enhancement factor $\beta$ of the vertical standing MoS₂ sheets was calculated to be 6240 by taking the work function $\phi$ of bulk MoS₂ to be 4.3 eV⁴⁶. The large enhancement factor is due to the nanometric protrusions and sharp edges as we observed in Fig. 1.
The stability of emission current from the vertically standing MoS$_2$ nanosheets was also measured (Fig. 6c). A stable emission current density of about 22 $\mu$A/cm$^2$ over 170 min was recorded without any indication of degradation. Some spike-like fluctuations were observed. The main reason of these fluctuations are believed to be caused by the adsorption/desorption and ion bombardment of residual molecules during the high field. This test shows fairly stable emission current from vertically standing MoS$_2$ nanosheets. The SEM observations on MoS$_2$ nanosheets after field emission were carried out and shown in Supplementary Fig. S10. No severe deterioration of emitter surface was observed, demonstrating the stability of MoS$_2$ nanosheets during field emission process.

Discussion

We have developed a CVD process for synthesizing vertically standing MoS$_2$ nanosheets. High density MoS$_2$ nanosheets with sharp edges could be synthesized. TEM observations on the nucleation sites reveal the growth mechanism for the based structure of vertically standing MoS$_2$. The based structures act as the growth templet and promote the subsequently vertical growth of MoS$_2$ nanosheets. It is suggested that the high strain energy caused by the compression between MoS$_2$ islands are the main reason for vertically standing MoS$_2$ nanosheets growth. These MoS$_2$ nanosheets exhibit enhanced field-emission properties with low turn-on electric field and good emission stability, suggesting promising in field emission based devices applications. In addition, we further confirmed the catalytic activity in HER. A high exchange current density of $\sim$28 $\mu$A/cm$^2$ is achieved, which is caused by high density of the exposed edge sites. More generally, the ultrathin material, that is, the three-atoms-thick MoS$_2$, together with its vertical morphology, would hold great promising potential in catalytic, sensor, field emission applications.

Methods

Growth method. The MoS$_2$ growth was performed in a conventional quartz tube. Silicon substrates with 285 nm SiO$_2$ layer were cleaned in Piranha solution, followed by acetone, isopropanol and deionized bath for 5 minutes, and then finally dried using nitrogen gas. After that, samples were mounted on top of a quartz boat and faced down above high purity MoO$_3$ powder (14 mg, 99.998%, Alfa Aesar). Also, 120 mg sulfur powder (99.5%, Alfa Aesar) was placed in a separate quartz boat located in the upstream of the quartz tube. The distance between sulfur powder and MoO$_3$ powder was kept at 13 cm. After that, the tube was pumped down to base pressure ($<0.1$ Pa) and flushed with high purity nitrogen repeatedly. The tube was then filled with 1000 sccm nitrogen until one-atmosphere. During the synthesis process, the MoO$_3$ was heated up to 750 $^\circ$C at a rate of 15 $^\circ$C/min in an argon environment at atmospheric pressure for 10 min. 5 sccm N$_2$ was used as a carrying gas. Meanwhile, the sulfur was sublimated rapidly at approximately temperature of 700$^\circ$C. After growth procedure, the substrate was cooled down rapidly. Supplementary Fig. S11 shows the schematic diagram of the CVD equipment used in this study.
Characterization. The surface morphology which reveals the coverage and uniformity of the grown MoS₂ nanosheets was observed directly by SEM (Quanta FEG 450). Raman spectroscopy (Horiba, LabRAM HR-800), atomic force microscopy (AFM, Veeco Nanoscope IIIa) and transmission electron microscopy (TEM, FEI Tecnai G² F20) were used to further characterize structure and quality of the as-grown MoS₂ nanosheets.

A diode setup in a vacuum chamber was adopted for field emission tests. The prepared samples were placed as the cathode and an indium tin oxide (ITO)-coated glass was used as the anode. Five 150-µm-thick and electrically insulating alumina films were used as spacers, making the distance between the cathode and anode at 250 µm (see Supplementary Fig. S12 online). The base pressure of the vacuum chamber was kept at 10⁻⁶ Pa. The overpotential (η) of 0.12V with an AC voltage of 5 mV was measured. Voltammetry was conducted with a scan rate of 5 mV/s. And AC impedance measurement was carried out at an appropriate frequency using a computer controlled data acquisition system.

In order to evaluate the catalytic effects of those vertically standing MoS₂ nanosheets, the HER tests were carried out. All of the electrochemical measurements were performed in 0.5 M H₂SO₄ solution using a three-electrode setup on an electrochemical workstation, with a saturated calomel electrode as the reference electrode (SCE), MoS₂ nanosheets grown on Au films the working electrode and a Pt foil the counter electrode. It was calibrated with respect to reversible hydrogen electrode (RHE). The calibration was performed in the high purity H₂ saturated electrolyte with two Pt foils as the working electrode and counter electrode. In 0.5 M H₂SO₄, E (RHE) = E (SCE) + 0.252 V. All the potentials reported in our manuscript are against RHE. Linear sweep voltammetry was conducted with a scan rate of 5 mV/s. And AC impedance measurement was carried out at an overpotential (η) of 0.12V with an AC voltage of 5 mV.

References
1. Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. Science 306, 666–669 (2004).
2. Kuc, A., Zibouche, N. & Heine, T. Influence of quantum confinement on the electronic structure of the transition metal sulfideTiS₂. Phys. Rev. B 83 (2011).
3. Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically ThinMoS₂: A New Direct-Gap Semiconductor. Phys. Rev. Lett. 105 (2010).
4. Ramakrishna Matte, H. S. S. et al. MoS₂ and W₃S Nanosheets of Graphene. Angew. Chem. 122, 4153–4156 (2010).
5. Osada, M. & Sasaki, T. Two-dimensional dielectric nanosheets: novel nanoelectronics from nanocrystal building blocks. Adv. Mater. 24, 210–228 (2012).
6. Dean, C. R. et al. Boron nitride substrates for high-quality graphene electronics. Nat. Nanotechnol. 5, 722–726 (2010).
7. Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V. & Kis, A. Single-layer MoS₂ transistors. Nat. Nanotechnol. 6, 147–150 (2011).
8. Cui, X. et al. Multi-terminal transport measurements of MoS₂ using a van der Waals heterostructure device platform. Nat. Nanotechnol. 10, 534–540 (2015).
9. Splendiani, A. et al. Emerging photoluminescence in monolayer MoS₂. Nano Lett. 10, 1271–1275 (2010).
10. Liu, B. et al. High-Performance Chemical Sensing Using Schottky-Contacted Chemical Vapor Deposition Grown Monolayer MoS₂ Transistors. ACS nano 8, 5304–5314 (2014).
11. Puthungan, D. B., Lin, S. H., Wei, C. M. & Kuo, J. L. Li adsorption, hydrogen storage and dissociation using monolayer MoS₂: an ab initio random structure searching approach. Phys. Chem. Chem. Phys. 17, 11367–11374 (2015).
12. Aceree, M., Voiry, D. & Chhowalla, M. Metallic 1T phase MoS₂ nanosheets as supercapacitor electrode materials. Nat. Nanotechnol. 10, 313–318 (2015).
13. Romo-Herrera, J. M., Terrones, M., Terrones, H., Dag, S. & Meunier, V. Covalent 2D and 3D networks from 1D nanostructures: designing new materials. Nano Lett. 7, 570–576 (2007).
14. Wang, P. P., Sun, H., Ji, Y., Li, W. & Wang, X. Three-dimensional assembly of single-layer MoS₂. Adv. Mater. 26, 964–969 (2014).
15. Yu, J. H. et al. Vertical heterostructure of two-dimensional MoS₂(2) and WS₂(2) with vertically aligned layers. Nano Lett. 15, 1031–1035 (2015).
16. Jiang, S. et al. Vertical ultrathin MoS₂ nanosheets on a flexible substrate as an efficient counter electrode for dye-sensitized solar cells. Nanoscale 7, 10459–10464 (2015).
17. Xu, X., Faglioni, F. & Goddard, W. A. Methane activation by transition-metal oxides, MoOₓ (M = Cr, Mo, W; x = 1, 2, 3). J. Phys. Chem. A 106, 7171–7176 (2002).
18. Jaramillo, T. F. et al. Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts. Science 317, 100–102 (2007).
19. Li, Y. et al. MoS₂ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction. J. Am. Chem. Soc. 133, 7296–7299 (2011).
20. Shi, J. et al. Controllable growth and transfer of monolayer MoS₂ on Au foils and its potential application in hydrogen evolution reaction. ACS Nano 8, 10196–10204 (2014).
21. Kong, D. et al. Synthesis of MoS₂ and MoSe₂ films with vertically aligned layers. Nano Lett. 13, 1341–1347 (2013).
22. Huang, C. K., Ou, Y. X., Bie, Y. Q., Zhao, Q. & Yu, D. P. Well-aligned graphene arrays for field emission displays. Appl. Phys. Lett. 98 (2011).
23. Huang, H. et al. Field emission property of layered Bi₂Se₃ nanosheets with atom-thick sharp edges. Nanoscale 6, 8306–8310 (2014).
24. Jiang, L. et al. Controlled synthesis of large-scale, uniform, vertically standing graphene for high-performance field emitters. Adv. Mater. 25, 250–255 (2013).
25. Kashid, R. V. et al. Enhanced field-emission behavior of layered MoS₂ sheets. Small 9, 2730–2734 (2013).
26. Hallam, T., Cole, M. T., Milne, W. I. & Duesberg, G. S. Field emission characteristics of contact printed graphene fins. Small 10, 95–99 (2014).
27. Kodambaka, S., Tessof, J., Reuter, M. C. & Ross, F. M. Germanium nanowire growth below the eutectic temperature. Science 316, 729–732 (2007).
28. Wang, N., Cai, Y. Y. & Zhang, R. Q. Growth of nanowires materials Science and Engineering R. Reports 60, 1–51 (2008).
29. Zhao, J., Shaygan, M., Eckert, J., Meyyappan, M. & Rummeli, M. H. A growth mechanism for free-standing vertical graphene. Nano Lett. 14, 3064–3071 (2014).
30. Li, H. et al. From Bulk to Monolayer MoS₂: Evolution of Raman Scattering. Adv. Funct. Mater. 22, 1385–1390 (2012).
31. Lai, D. S., Liu, J., Liu, B., Matte, H. S. S. R., Rao, C. N. R. & Dravid, V. P. Rapid Characterization of Ultrathin Layers of Chalcogenides on SiO₂/Si Substrates. Adv. Funct. Mater. 22, 1894–1905 (2012).
32. Thirupurathuka, M., Kashid, R. V., Sekhar Rout, C. & Late, D. J. Temperature-dependent Raman spectroscopy of chemically derived few-layer MoS₂ and WS₂ nanosheets. Appl. Phys. Lett. 104, 081911 (2014).
33. Verble, L. L. & Wieting, T. J. Lattice Mode Degeneracy in MoS₂ and Other Layer Compounds. Phys. Rev. Lett. 25, 362 (1970).
34. Zhu, M. Y. et al. A mechanism for carbon nanosheet formation. *Carbon* **45**, 2229–2234 (2007).
35. Shi, J. et al. Substrate Facet Effect on the Growth of Monolayer MoS2 on Au Foils. *ACS nano* **9**, 4017–4025 (2015).
36. Yu, Y. et al. Controlled scalable synthesis of uniform, high-quality monolayer and few-layer MoS2 films. *Scientific reports* **3**, 1866 (2013).
37. Lin, Z. et al. Controllable Growth of Large-Size Crystalline MoS2 and Resist-Free Transfer Assisted with a Cu Thin Film. *Scientific reports* **5**, 18596 (2015).
38. V, Y. et al. Boucaud, D. & Bouchier, D. Kinetics of the heteroepitaxial growth of Ge on Si(001). *J. Vac. Sci. Technol. B* **20**, 1251–1258 (2002).
39. Baskaran, A. & Smereka, P. Mechanisms of Stranski-Krastanov growth. *J. Appl. Phys.* **111**, 044321 (2012).
40. Weiss, K. & Phillips, J. M. Calculated Specific Surface-Energy of Molybdenite (MoS2). *Phys. Rev. B* **14**, 5392–5395 (1976).
41. Conway, B. E. & Tilak, B. V. Interfacial processes involving electrocatalytic evolution and oxidation of H2, and the role of chemisorbed H. *Electrochim. Acta* **47**, 3571–3594 (2002).
42. Yu, Y. et al. Layer-dependent electrocatalysis of MoS2 for hydrogen evolution. *Nano Lett.* **14**, 553–558 (2014).
43. Tao, L., Duan, X., Wang, C., Duan, X. & Wang, S. Plasma-engineered MoS2 thin-film as an efficient electrocatalyst for hydrogen evolution reaction. *Chem Commun (Camb)* **51**, 7470–7473 (2015).
44. Seo, B. et al. Monolayer-Precision Synthesis of Molybdenum Sulfide Nanoparticles and Their Nanoscale Size Effects in the Hydrogen Evolution Reaction. *ACS nano* **9**, 3728–3739 (2015).
45. Xie, J. et al. Controllable disorder engineering in oxygen-incorporated MoS2 ultrathin nanosheets for efficient hydrogen evolution. *J. Am. Chem. Soc.* **135**, 17881–17888 (2013).
46. Li, Y. B., Bando, Y. & Golberg, D. MoS2 nanoflowers and their field-emission properties. *Appl. Phys. Lett.* **82**, 1962 (2003).
47. Late, D. J. et al. Pulsed laser-deposited MoS2 thin films on W and Si: field emission and photoresponse studies. *ACS Appl. Mater. Interfaces* **6**, 13881–13888 (2014).
48. Forbes, R. G. Extraction of emission parameters for large-area field emitters, using a technically complete Fowler-Nordheim-type equation. *Nanotechnology* **23**, 095706 (2012).
49. Kim, S. et al. High-mobility and low-power thin-film transistors based on multilayer MoS2 crystals. *Nat. Commun.* **3**, 1011 (2012).
50. Xiao, Z. et al. Field electron emission characteristics and physical mechanism of individual single-layer graphene. *ACS Nano* **4**, 6332–6336 (2010).

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Author Contributions
H.L. and S.Y. synthesized and characterized the materials. H.L. conducted the electrochemical characterization and field emission experiments. H.L. and H.W. conducted the TEM measurements and analysis. H.L. and H.W. wrote and edited the manuscript. The project was supervised by H.W. and H.Q.

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