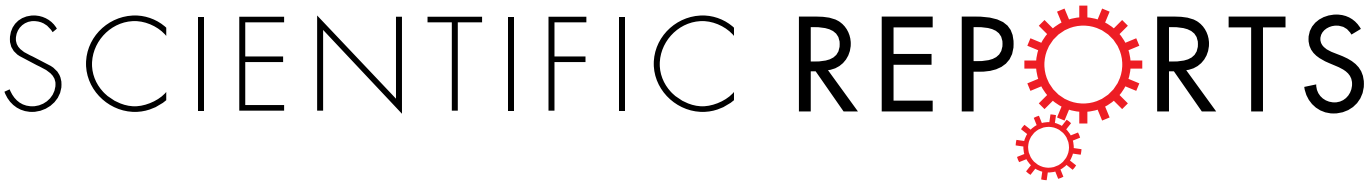

OPEN

Synthesis of Vertically Standing MoS_2 Triangles on SiC

Feifei Lan, Zhanping Lai, Yongkuan Xu, Hongjuan Cheng, Zaien Wang, Chengjun Qi, Jianli Chen & Song Zhang

Received: 03 June 2016
Accepted: 25 July 2016
Published: 23 August 2016

Layered material MoS_2 has been attracting much attention due to its excellent electronical properties and catalytic property. Here we report the synthesis of vertically standing MoS_2 triangles on silicon carbon(SiC), through a rapid sulfidation process. Such edge-terminated films are metastable structures of MoS_2, which may find applications in FinFETs and catalytic reactions. We have confirmed the catalytic property in a hydrogen evolution reaction(HER). The Tafel slope is about 54mV/decade.

In the past few years, transition metal dichalcogenides(TMD) have attracted great attention for their considerable potential applications in the fields of catalysis, microeletronics, optoelectronic devices on both conventional and flexible substrates[1–9]. Lots of efforts have been made to realize the applications of TMD. But almost all of these works that have been done are based on the platelet-like morphology on the surface of different substrates. In contrast, a few works have been done to use the edges of these layered materials. In fact, vertically standing TMD materials hold high aspect ratio and dangling bonds[10]. For MoS_2, the exposed edges means the S dangling bonds. It is the active sites for catalytic reactions. As a layered material, MoS_2 usually expose the basal planes (it means the flat triangles with the Mo atom terminating surface) as the terminating surface with minimal roughness and dangling bonds. But in the condition of vertically standing MoS_2, the edges sites were exposed maximally. The exposed edges with high chemical active and may play an important role in many catalytic reactions, such as hydrogen production[11–15], photocatalysis[16], hydrogen evolution reaction(HER), hydrodesulfurization catalyst used for removing sulfur compounds from oil[17–23]. In addition, these vertical structures of TMD are ideal channel materials for FinFET[24]. However, edges are usually the rare surface sites of layered materials due to their inherently high surface energy. Increasing the edge dimension is therefore challenging.

Methods

In this work, we develop a rapid sulfidation process through a large carrier gas flow rate on SiC using a CVD method. The MoS_2 triangles are aligned vertically to the surface of the substrate. Various characterizations techniques were used to have a good understand to the mechanism of the vertically standing triangles. Furthermore, HER performance of vertically standing MoS_2 triangles was researched.

The synthesis process of vertically standing MoS_2 triangles is schematically illustrated in Fig. 1. At the beginning, MoO_3 powder was placed in the centre of the furnace, 6H SiC was placed next to the MoO_3 powder. Sulphur powder was placed inside of a steel cylinder out side of the furnace, with a heating tape around it. High pure argon was chosen as carrier gas to convey sulphur and MoO_3 vapor to downstream. The temperature of MoO_3 powder was 1000 °C, sulphur powder was heated to 260 °C, the growth pressure was atmospheric.

A typical optical image of the MoS_2 triangles grown on SiC substrate is shown in Fig. 2a. It clearly shows that most of the triangles on the surface were vertically standing, there are a few flat triangles on the surface. The SEM image demonstrates that the as grown triangles are nearly perpendicular to the substrate. There is a small angles of inclination of some triangles. The edges of different MoS_2 triangles could be clearly observed in SEM images. The lateral dimensions of the triangles are tens micrometer, the heights are from 30 nm to 2 μm. Figure 2c is the Raman spectrum of the vertically standing triangles on SiC and monolayer MoS_2 on sapphire. Two Raman characteristic bands of vertically standing triangles at 410 cm^{-1} and 383 cm^{-1} corresponding to A^1_g and E^1_{2g} respectively[25–27]. Comparing to the flat monolayer MoS_2 on sapphire, the intensity ratio between A^1_g and E^1_{2g} of the vertically standing triangles is higher, revealing a higher density of exposed edges in those vertically standing triangles. Figure 2d,e are the XPS spectra of Mo 3d and S 2p peak. The Mo 3d shows two peaks at 232.5 eV and 229.2 eV. The peaks, corresponding to the S 2p1/2 and S 2p3/2 orbital of divalent sulfide ions (S^{2-}), are observed at 163.3 and 162 eV. These results agree well with the reported values for MoS2 crystal[23,28,29].

Electronic Material Research Institute of Tianjin, Tianjin 300220, P. R. China. Correspondence and requests for materials should be addressed to F.L. (email: lanfeifei0601@126.com)

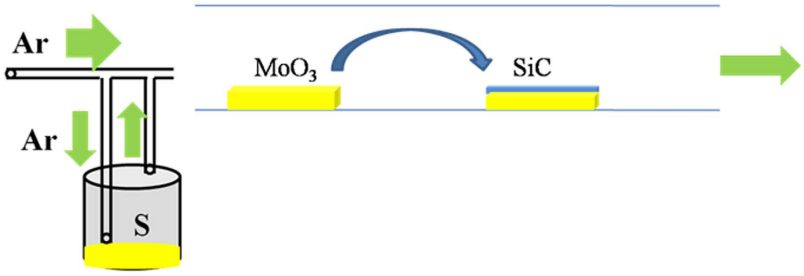

Figure 1. Schematic illustration of the synthesis of vertically standing triangles on SiC.

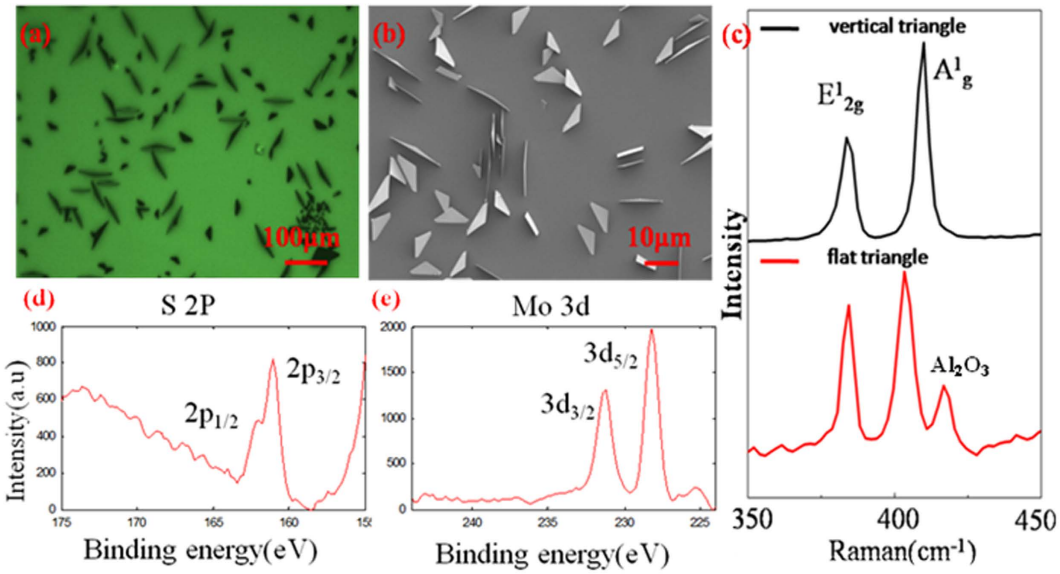

Figure 2. Characterization of synthesized vertically standing MoS_2 triangles. (**a**) optical image of vertically standing triangles. (**b**) SEM image to clearly shows the vertically standing triangles. (**c**) Raman spectrum of the triangles on SiC and single-layer MoS_2 obtained by CVD on sapphire. (**d**) XPS spectra of Mo 3d. (**e**) XPS spectra of S2p peak.

Due to the anisotropic bonding and the general tendency to minimize the surface energy, nanoparticles of layer materials usually exhibit platelet-like morphology[30,31]. Alternatively, vertically standing triangles can also be obtained by a fast growth process[32], the synthesis rate is mainly affected by the diffusion of product gas on the surface of the substrate. By controlling the reactant concentration, we can obtain the MoS_2 films with different morphologies. Through regulating the carrier gas flow rate, the sulfidation rate of MoO_3 can be controlled well. In addition, by changing the carrier gas flow rate, we can have a good understand of the growth process of MoS_2 film.

As shown in Fig. 3a, when the carrier gas flow rate is 100sccm, the concentration of sulfidation vapor is too low to meet the needs. Meanwhile, with a slow carrier gas flow rate, the forming of MoO_{3-x} is limited, and the transport rate of MoO_{3-x} to the surface of substrate is also affected. In this condition, there are only some nanoparticles and some small rectangles on the surface of SiC, because of the lacking of S. So we increasing the carrier gas flow rate to 180sccm, the size of the rectangles increased, but we still do not obtained the vertically standing triangles. When the carrier gas flow increased to 260sccm, the synthesis rate is faster with the increasing of sulfidation concentration. Under this condition, we obtained the vertically standing triangles on the surface of SiC, the result is shown in Fig. 3c. Some of flat triangles were observed on the surface of SiC, only a few vertically standing triangles were obtained. So we increased the carrier gas flow to 340sccm, almost all of the triangles are perpendicular to the substrate, as shown in Fig. 3d. Figure 3e,f were the SEM images of flat rectangles and triangles. Figure 3f–h show the SEM images of vertically standing triangles. From the results, we can see that, only under a fast growth rate, can we get the vertically standing triangles of MoS_2.

To have a better understand, the growth model is shown in Fig. 4. At the beginning of the growth, there was neither buffer layer nor seed on the surface of the substrate, so nucleation process was a 3D. The triangles are all coming from the islands of Fig. 4a. When the carrier gas flow rate is small, the atoms and molecules have enough time to mobility and diffusion on the surface of the substrate, so the synthesis process of MoS_2 will be a 2D growth. With the supply of the sulfur vapor, the small islands grew into larger domain size, at last, the flat triangles of MoS_2 were obtained, as shown in Fig. 4b. When the carrier gas flow rate is high enough, the chemical

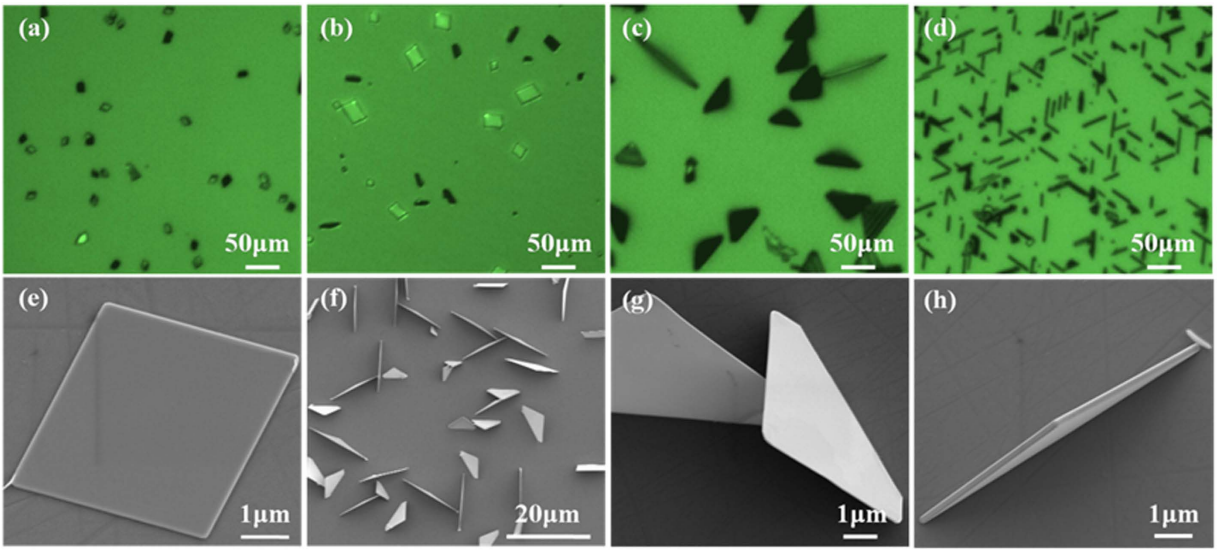

Figure 3. Optical and SEM images of MoS_2 triangles. (**a–d**) optical images of the MoS_2 triangles with different carrier gas flow rates. (**e**) SEM image of MoS_2 rectangles with a low condition of sulfur. (**f–h**) SEM images of vertically standing MoS_2 triangles.

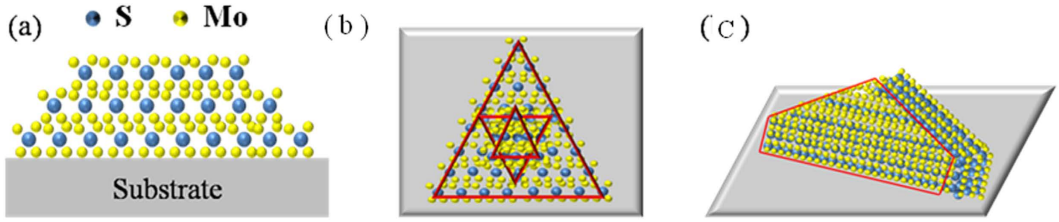

Figure 4. Growth model of vertically standing and flat MoS_2 triangles.

conversion occurs much faster than the diffusion of sulfur gas into the film. Under this condition, the sulfidation process will be rate-limiting. Meanwhile, with the anisotropic structure, the diffusion along the layers through van der Waals gaps is much faster than diffusion across the layers. Accordingly, the layers naturally orient perpendicular to the film, exposing van der Waals gaps for fast reaction. In this condition, the vertically structure formed, as shown in Fig. 4c.

As we know, the wettability has a great effect to the nucleation process at the begining of the growth. If the wettability of the subbstrate is good, the film will be a two dimmendional growth, along the surface of the subbstrate, then flat film will be obtained. If the wettability of the subbstrate is poor, the film will maintain a 3D growth along the layers. In order to prove our conclusion, and have a contrast, we also synthesis the MoS_2 film on sapphire with the same condition: the temperature of MoO_3 powder is 1000 °C, carrier gas flow rate were 100sccm, 180sccm, 260sccm, 340sccm respectively. The results were shown in Fig. 5. we can see that, the film on the sapphire are all flat triangles. There is no vertically standing triangles obtained on the sapphire. This is because the perfect wettability of MoS_2 on the sapphire, the growth process will be 2D. Under this condition, there will not be vertically standing triangles formed. In contrast, with a poor wettability between MoS_2 and SiC, the nucleation of the film on the surface of SiC is more difficult, and the growth process will be 3D, which is useful to synthesis the vertically standing triangles. Through the results, we can see that the wettability is also a important factor during the growth of the vertically standing MoS_2.

HER catalytic activity of vertically standing MoS_2 triangles on SiC was tested. Typical cathodic polarization curves and corresponding Tafel plots are shown in Fig. 6a,b. The Tafel slope in our vertically standing triangles was about 54 mV/decade. The related reports about vertically standing structures of MoS_2 is about 94 mV/dec[10] and 105–120 mV/dec[23]. Tafel plots are commonly used to evaluate the efficiency of the catalytic reaction. which indicated that the surface coverage of absorbed hydrogen was relatively low. The small Tafel plots means the high efficiency of the reaction. This indicating a good catalytic property of vertically standing triangles on SiC.

Conclusions

We have developed a rapid sulfidation process for the synthesis of vertically standing MoS_2 triangles. SEM images reveal the synthesis mechanism of the triangles. It is suggested that under a high concentration of sulfur, the growth process will by a 3D growth, all these vertically standing triangles come from the small islands on the surface of SiC. In addition, by a comparision between the films grown on sapphire and SiC, we find the wettability

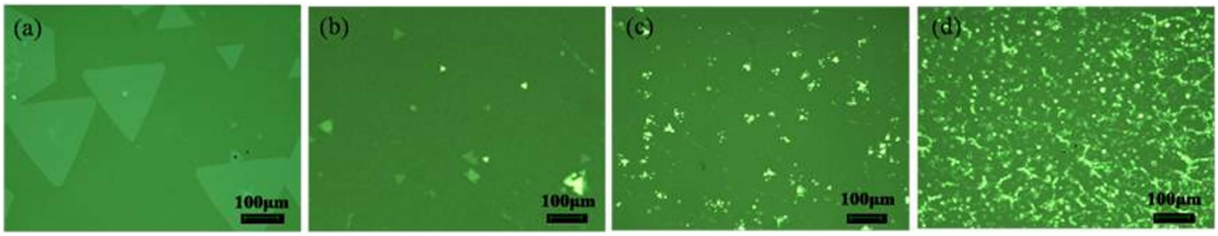

Figure 5. Optical microscope images of the synthesis MoS_2 on Al_2O_3 with the carrier gas flow rate of 100sccm, 180sccm, 260sccm, 340sccm.

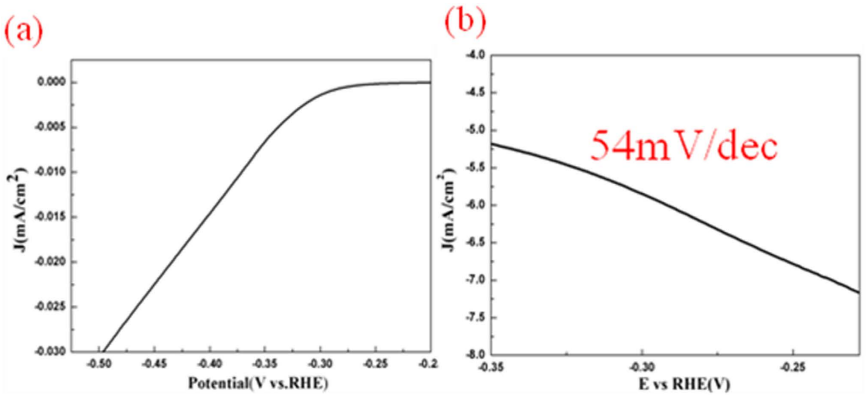

Figure 6. Cathodic polarization curves of vertically standing triangles, Tafel plots of vertically standing triangles.

is another factor for the forming of vertically standing triangles. At last, the HER properties of the triangles was tested. The Tafel slope is about 54 mV/decade, which is much smaller than the related reports about vertically standing MoS_2 nanosheets.

References

1. R. Tenne, L. Margulis, M. Genut & G. Hodes. Polyhedral & cylindrical structures of tungsten disulphide. *Nature* **360,** 444–446 (1992).
2. Y. Feldman, E. Wasserman, D. J. Srolovitz & R. Tenne. High-Rate, Gas-Phase Growth of MoS_2 Nested Inorganic Fullerenes & Nanotubes. *Science* **267,** 222–225 (1995).
3. Y. Golan *et al.* Microtribology & Direct Force Measurement of WS_2 Nested Fullerene-Like Nanostructures. *Adv. Mater* **11,** 934–937 (1999).
4. J. Huang, S. Somu & A. Busnaina. A molybdenum disulfide/carbon nanotube heterogeneous complementary inverter. *Nanotechnology* **23,** 5203–5208 (2012).
5. Y. Zhang, J. Ye, Y. Matsuhashi & Y. Iwasa. Ambipolar MoS_2 thin flake transistors. *Nano Lett* **12,** 1136–1140 (2012).
6. H. Liu, A. T. Neal & Peide D. Ye. Channel length scaling of MoS_2 MOSFETs. *ACS* NANO **6,** 8563–8569 (2012).
7. Edney, G. S. Firmiano *et al.* Graphene oxide as a highly selective substrate to synthesize a layered MoS_2 hybrid electrocatalyst. *Chem. Commun* **48,** 7687–7689 (2012).
8. B. Hinnemmann *et al.* Biomimetic hydrogen evolution: MoS_2 nanoparticles as catalyst for hydrogen evolution. *J. Am. Chem. Soc* **127,** 5308–5309 (2005).
9. T. F. Jaramillo *et al.* Identification of active edge sites for electrochemical H_2 evolution from MoS_2 nanocatalysts. *Science* **317,** 100–102 (2007).
10. D. Kong *et al.* Synthesis of MoS_2 and $MoSe_2$ films with vertically aligned layers. *Nano Lett* **13,** 1341–1347 (2013).
11. T. F. J. *et al.* Identification of active edge sites for electrochemical H_2 evolution from MoS_2 nanocatalysts. *Science* **317,** 100–102 (2007).
12. B. H. *et al.* Biomimetic hydrogen evolution: MoS_2 nanoparticles as catalyst for hydrogen evolution. *J. Am. Chem. Soc.* **127,** 5308–5309 (2005).
13. D. Kong *et al.* Synthesis of MoS_2 and $MoSe_2$ films with vertically aligned layers. *Nano Lett.* **13,** 1341–1347 (2013).
14. H. I. Karunadasa *et al.* A molecular MoS_2 edge site mimic for catalytic hydrogen generation. *Science* **335,** 698–702 (2012).
15. D. Merki, S. Fierro & X. Hu. Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution. *Chem. Sci.* **3,** 2515–2525 (2012).
16. J. Wilcoxon, T. Thurston & J. Martin. Applications of metal and semiconductor nanoclusters as thermal and photo-catalysts. *Nanostruct Mater* **12,** 993–997 (1999).
17. J. Lauritsen *et al.* Atomic-scale structure of Co–Mo–S nanoclusters in hydrotreating catalysts. *J. Catal* **197,** 1–5 (2001).
18. T. Todorova, R. Prins & T. Weber. A density functional theory study of the hydrogenolysis and elimination reactions of C_2H_5SH on the catalytically active (100) edge of 2H-MoS_2. *J. Catal* **246,** 109–117 (2007).
19. P. G. Moses, B. Hinnemann, H. Topsoe & J. K. Norskov. The hydrogenation and direct desulfurization reaction pathway in thiophene hydrodesulfurization over MoS_2 catalysts at realistic conditions: a density functional study. *J. Catal* **248,** 188–203 (2007).

20. J. V. Lauritsen *et al.* Location and coordination of promoter atoms in Co-and Ni-promoted MoS_2-based hydrotreating catalysts. *J. Catal* **249,** 220–233 (2007).
21. P. Raybaud *et al.* Ab initio study of the H_2–H_2S/MoS_2 gas–solid interface: The nature of the catalytically active sites. *J. Catal* **189,** 129–146 (2000).
22. J. Lauritsen *et al.* Atomic-scale insight into structure and morphology changes of MoS_2 nanoclusters in hydrotreating catalysts. *J. Catal* **221,** 510–522 (2004).
23. H. Li, H. Wu, Sh Yuan & He Qian. Synthesis and characterization of vertically standing MoS_2 nanosheets. *Sci. Rep.* **6,** 2117–2124 (2016).
24. M. Chen *et al.* TMD FinFET with 4 nm thin body and back gate control for future low power technology. *IEEE*. **978,** 4673–9894 (2015).
25. Bret, C. Windom, W. G. Sawyer & David, W. Hahn. A Raman spectroscopic study of MoS_2 and MoO_3: applications to tribological systems. *Tribol Lett*. **42,** 301–310 (2011).
26. H. Li *et al.* From bulk to monolayer MoS_2: evolution of Raman scattering. *Adv. Funct. Mater* **22,** 1385–1390 (2012).
27. B. Chakraborty, H. S. S. R. Matte, A. K. Sood & C. N. R. Rao. Layer-dependent resonant Raman scattering of a few layer MoS_2. *Raman Spectrosc.* **44,** 92–96 (2013).
28. K. Lee *et al.* Electrical Characteristics of Molybdenum Disulfide Flakes Produced by Liquid Exfoliation. *Adv. Mater.* **23,** 4178–4182 (2011).
29. Zh Lu *et al. In situ* fabrication of porous MoS_2 thin-films as high-performance catalysts for electrochemical hydrogen evolution. *Chemical Communication*. **10,** 1039–1042 (2013).
30. D. Kong *et al.* Few-layer nanoplates of Bi_2Se_3 and Bi_2Te_3 with highly tunable chemical potential. *Nano Lett.* **10,** 2245–2250 (2010).
31. Y. Li *et al.* MoS_2 nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction. *Am. Chem. Soc.* **133,** 7296–7299 (2011).
32. Y. Cheng *et al.* Van der Waals epitaxial growth of MoS_2 on SiO_2/Si by chemical vapor deposition. *RSC Adv.* **3,** 17287–17293 (2013).

Author Contributions

Z.L., Y.X. and H.C. H.J. conceived the experiments. F.L., Z.W. and C.Q. synthesized the MoS_2 flakes. J.C. and S.Z. perofomed the characterizations of Raman, SEM, optical microscope and HER catalytic activity. F.L. and Y.X. wrote the manuscript. All authors reviewed the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Lan, F. *et al.* Synthesis of Vertically Standing MoS_2 Triangles on SiC. *Sci. Rep.* **6**, 31980; doi: 10.1038/srep31980 (2016).