MoS$_2$ Surface Structure Tailoring via Carbonaceous Promoter

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Atomically thin semiconducting transition-metal dichalcogenides have been attracting lots of attentions, particularly, molybdenum disulfide (MoS$_2$) monolayers show promising applications in field effect transistors, optoelectronics and valleytronics. However, the controlled synthesis of highly crystalline MoS$_2$ remain a challenge especially the systematic approach to manipulate its structure and morphology. Herein, we report a method for controlled synthesis of highly crystalline MoS$_2$ by using chemical vapor deposition method with carbonaceous materials as growth promoter. A uniform and highly crystalline MoS$_2$ monolayer with the grain size close to 40 μm was achieved. Furthermore, we extend the method to the manipulation of MoS$_2$ morphology, flower-shape vertical grown MoS$_2$ layers were obtained on growth promoting substrates. This simple approach allows an easy access of highly crystalline MoS$_2$ layers with morphology tuned in a controllable manner. Moreover, the flower-shape MoS$_2$ grown on graphene oxide film used as an anode material for lithium-ion batteries showed excellent electrochemical performance.

Direct bandgap semiconducting transition metal dichalcogenide (TMD) monolayers are attractive for optoelectronics and energy harvesting$^{1,2}$. Their high carrier mobility$^3$, excellent on-off ratio$^4$ and good bendability$^5$ are promising for future flexible and low-power consumer electronics$^6,7$. The fundamental studies on their electronic structures and valley-spin relations are also emerging$^8,9$. Being a member of the TMDs family, molybdenum disulfide (MoS$_2$) has already attracted considerable attention for its great potential in the fields of hydrogen evolution reaction (HER)$^{10,11}$, bio-sensing$^{11,12}$ and energy storage$^{13,14}$. Recently, it has been demonstrated that ultra-thin MoS$_2$ crystals with a typical thickness of ~0.65 nm holds even more significant promise in electronics$^{15,16,17}$ and optoelectronics$^{7,18,19}$. Given the great promises hold, it is highly desirable to develop a scalable method to obtain large-area and high quality TMD monolayers. On the other hand, controlling the surface structure of MoS$_2$ layers at the atomic scale is also critical for their successful implementation in each applications. For example, large specific surface areas are preferred for the energy storage application$^{20,21}$. For the application of HER, only the edge sites of MoS$_2$ are catalytically active, which require the controllable synthesis of MoS$_2$ layers with abundant exposed edge sites$^{22,23}$. Recently, chemical vapor deposition (CVD) method has led towards high-quality TMD layers with scalable size, controllable thickness and excellent electronic properties. Several groups have made remarkable progress in MoS$_2$ synthesis$^{8,24,25}$. Among the various approaches for MoS$_2$ synthesis, those using MoO$_3$ and sulfur powder as solid state precursors become dominant$^{26,27}$, which is due to the simplified process and high yield of monolayers.

However, it is more challenging to grow single crystalline monolayer MoS$_2$ thin film by CVD method comparing to other 2D materials synthesis such as graphene$^{31,32}$ and boron nitride$^{33,34}$, where catalyst were used to control the geometry, thickness and crystallinity. In contrast, the growth of MoS$_2$ by CVD does not involve any catalysts$^{35,36}$ and the growth of MoS$_2$ is very sensitive to the substrate treatment prior to the growth$^{18,22}$. Previous reports demonstrate nucleation of MoS$_2$ can be facilitated by seeding...
the substrate with graphene-like species\textsuperscript{29,30,37}. Meanwhile Najmaei et al. have shown that the MoS\textsubscript{2} crystals commonly nucleate on the step edges during growth without the present of seeding molecules\textsuperscript{28}. Recently, Van der Zande et al. proved that large MoS\textsubscript{2} crystalline islands can be obtained by using ultraclean substrates and fresh precursors and neither seeding molecules nor step-edge were used to promote the nucleation of MoS\textsubscript{2}\textsuperscript{27}. It was suggested that the MoS\textsubscript{2} growth normally follows an analogous layer-plus-island (or Stranski-Krastanov) growth mode\textsuperscript{6}. The Stranski-Krastanov mode is a two-step process: initially, monolayer MoS\textsubscript{2} domains gather and interconnect with each other till the full coverage of monolayer is nearly completed. Beyond the critical layer number (1 for MoS\textsubscript{2}), the growth of MoS\textsubscript{2} continues through the nucleation and coalescence of MoS\textsubscript{2} nanoparticles or few layers islands\textsuperscript{5}. In other words, the thermodynamics favors the basal plane growth, which limits the usability of surface structure.

Nevertheless, the widely used method for MoS\textsubscript{2} synthesis is based on the direct chemical vapor phase reaction of MoO\textsubscript{3} by S gas in which the MoO\textsubscript{3} vapor generated from MoO\textsubscript{3} powder reacts with sulfur vapor at elevated temperatures to form monolayer MoS\textsubscript{2} on the collecting substrates\textsuperscript{26,28}. Thus, it is common to obtain molybdenum oxide microcrystals byproducts since the reduction of MoO\textsubscript{3} also produce MoO\textsubscript{2} crystals under similar growth condition\textsuperscript{38}. MoO\textsubscript{2} was selected by Li et al. as an precursor for MoS\textsubscript{2} growth on the basis that it has an evaporation temperature of \sim 700 °C\textsuperscript{26}. However, the growth dynamics of MoO\textsubscript{3-x} and S are still not fully understood. It has been suggested in literatures\textsuperscript{39,40} that there are two channels for MoO\textsubscript{3-x}, to react with S, one is it adsorb and diffuse on the substrate, reacting with S to form MoS\textsubscript{2}; the other is forming MoS\textsubscript{2} clusters in vapour phase and crystallize on substrate. Both these two channels require the forming of vapour phase MoO\textsubscript{3-x}; and the growth temperature ranging from 530 °C to 850 °C. Thus far, it is demanding to have a better understanding of the growth mechanism and further develop a method which is capable of producing large monolayer MoS\textsubscript{2} crystals, preventing the forma-
tion of MoO\textsubscript{2} byproducts, meanwhile controlling the surface structure of MoS\textsubscript{2} layers at the atomic scale.

Herein, we engineer the reduction process of MoO\textsubscript{3} precursor by carbon based materials. In a typical synthesis, the solid state precursor of MoO\textsubscript{3} powder is covered by a piece of carbon cloth. The carbon cloth is chosen simply due to its thermal stability, good mechanical property and micro porous structure. MoO\textsubscript{3} powder can be thermally evaporated and only the gas phase MoO\textsubscript{3} can pass through the opening of woven micro carbon fibers and it is then reduced by sulfur vapor at 650 to 700 °C. It was found that carbon can help reducing MoO\textsubscript{3} and large MoO\textsubscript{2} crystals can be trapped by the carbon cloth which effectively prevents the co-deposition of MoO\textsubscript{3} and MoS\textsubscript{2} on the collecting substrates. Finally, continuous large-area MoS\textsubscript{2} thin films was successfully grown on substrate. The synthesized MoS\textsubscript{2} layers are in a well-defined triangular shape with a typical lateral size \sim 40 μm. We further investigated the effects of carbonaceous promoter in the growth of MoS\textsubscript{2} on various substrates. By simply replacing the SiO\textsubscript{2}/Si substrates with GO film or GO flakes, few-layer MoS\textsubscript{2} preferentially form on the surface of GO under the same growth condition. The results suggest, the growth of MoS\textsubscript{2} is very sensitive to the substrate treatment and carbon based materials can significantly promote the growth rate and yield of MoS\textsubscript{2}, which is due to the assisted reduction of MoO\textsubscript{3} by carbon.

This work elucidates how morphological control of MoS\textsubscript{2}, at the nanoscale can be achieved by carbo-
naceous promoter. The surface morphology engineering of MoS\textsubscript{2} layers enables new opportunities for enhancing surface properties for catalysis, energy storage and other important technological applications. As a proof-of-concept, the MoS\textsubscript{2}/GO composites were used as electrode materials to demonstrate its application in lithium ion batteries (LIBs). The surface structure engineering of MoS\textsubscript{2}/GO provides highly efficient pathways for both electronic and Li ion exchange during the charge/discharge cycles of the battery, which allows the composite to be directly used as working electrode and assembled into a coin cell without adding any conductive or binder materials. A remarkably high specific capacity (i.e., \textgreater 1000 mAh g\textsuperscript{-1}) was achieved at the current density of 100 mAg\textsuperscript{-1}, which is much higher than theoretical value for either GO or MoS\textsubscript{2} alone (\sim 566 and \sim 670 mAh g\textsuperscript{-1}, respectively). The MoS\textsubscript{2}/GO com-
pies also show an outstanding high-rate charge/discharge performance. Even at a very high current density of 1000 mAg\textsuperscript{-1}, the composite electrode can still deliver a capacity of 776 mAh g\textsuperscript{-1} after 500 cycles. The reversible capacity only slightly decreases to 727 mAh g\textsuperscript{-1} after an additional 440 cycles under 2000 mAg\textsuperscript{-1}. The high rate capability can be attributed to the unique nano-architecture engineering of MoS\textsubscript{2}, which provides structural stability and transport advantages for both electrons and lithium ions.

**Materials and Methods**

**Monolayer CVD-MoS\textsubscript{2} growth.** CVD-MoS\textsubscript{2} was prepared using chemical vapor deposition method with carbon based materials as a growth promoter. High-crystal-quality MoS\textsubscript{2} can be grown on a silicon substrate with 300 nm SiO\textsubscript{2} layer on top inside a hot-wall horizontal tube furnace. To be brief, the MoS\textsubscript{2} films were synthesized using high purity MoO\textsubscript{3} (99%, Aldrich) and S powder (99.5, Sigma-Aldrich) as precursors. The precursors were placed in two separated Al\textsubscript{2}O\textsubscript{3} crucibles and the substrates were placed on the downstream side of the Ar carrying gas. A piece of carbon cloth was put on top of MoO\textsubscript{3} powder for better growth control. The growth chamber was firstly heated to 105 °C with Ar flow rate of 1000 sccm, this step helps to remove the oxygen and moistures in the chamber. After that, the temperature was further increase to 700 °C with a heating rate of 15 °C/min. MoS\textsubscript{2} monolayer in a triangle shape were obtained by annealing at 700 °C for 10 min followed by a naturally cooling process to room temperature Ar flow rate was kept at 10 sccm during MoS\textsubscript{2} growth.
Flower shape MoS$_2$ growth. Before the CVD synthesis, 1 mg/ml Graphene oxide (GO) dispersion in water was obtained after 30 min probe sonication of GO flakes (Graphene Supermarket, USA) in deionized water (DI Water). The 300 W probe sonicator was set at 30% amplitude with alternating pulse. GO coated Si substrate was prepared by drop casting GO dispersion on a piece of cleaned SiO$_2$/Si substrates and gently blow dried using N$_2$ gas. Self-supporting GO thin film was obtained by vacuum filtration of GO dispersion with a polymer filter membranes (pore size 0.02 mm, GE Whatman, USA). The filtration membrane was further removed by dissolving it in hot Acetone solution (at ~80°C). The GO substrates were carried into the growth chamber after baking on hot plate at 90°C for 1 hour to remove organic solvent and water. The growth condition was kept the same as monolayer MoS$_2$ synthesis.

Chemicals and precursors. Graphene oxide powder was purchased from Graphene Supermarket, Calverton, NY, USA. MoO$_3$ (purity 99%) and S powder (purity 99.5%) powder purchased from Sigma-Aldrich Co. (Singapore) were directly used for MoS$_2$ synthesis without further purification. Carbon cloth was purchased from Hesen Shanghai Co., Ltd, China.

MoS$_2$/GO transfer for TEM characterization. The CVD synthesized MoS$_2$/GO composite was transferred by coating the film with a thin layer (~100 nm) of Poly[methylmethacrylate] (PMMA). After etching the underlying SiO$_2$/Si substrates with NaOH aquariums (with a concentration of 3 M) at 80°C, the PMMA/ MoS$_2$/GO film was transferred to DI water and was suspended on the surface of water to remove the etchant residue for several hours. Subsequently, the film can be transferred to any substrate or TEM grids for analysis and characterization. Finally, the top layer of PMMA can be removed by acetone or by directly annealing the samples in an Ar and H$_2$ atmosphere at 450°C for 2 hours.

Raman measurements. The Raman measurements were carried out using a WITec alpha 300 confocal Raman microscope. The Raman spectra presented in this paper were collected using a 532 nm solid-state laser for excitation with the beam focused by a 100X objective lens. The laser beam diameter on sample is around 500 nm. Scanning electron microscopy (SEM) was performed on a field emission SEM (FESEM) instrument (JSM-7600F, Japan). A field-emission transmission electron microscope (JEOL JEM-2100F, operated at 200 keV), equipped with an energy dispersive spectrometer (EDS) was used to obtain the information of the microstructures and the chemical compositions.

Electrochemical measurement. The electrochemical performance of MoS$_2$/GO nanocomposites electrode was measured with a half-cell lithium ion battery (LIBs) configuration. The 2032 coin-type cells were assembled in an argon-filled glove-box with both the moisture and oxygen level less than 0.5 ppm. MoS$_2$/GO composites were directly used as cathodes. For control samples, the working electrode materials of GO and MoS$_2$ were prepared by mix GO and MoS$_2$ powders with a certain weight percentage in solution phase and then freeze-dried to form a self-supporting membrane. Lithium sheet was used as anodes and 1 M LiPF6 in a 1/1 (volume ratio) mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) as electrolyte. Celgard® 2400 was used as the separator of the battery. The cells were tested on a NEWARE multi-channel battery test system with galvanostatic charge and discharge in the voltage range between 0.01 and 3.0 V vs. Li/Li$^+$ at various current density at room temperature. The cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested on an electrochemical workstation (VMP3, Bio-Logic).

Results and Discussion

Effect of carbon based materials on monolayer MoS$_2$ growth. A schematically illustration of the experimental set-up used for MoS$_2$ synthesis is presented in Fig. 1 (a). MoS$_2$ monolayers were grown by CVD with solid MoO$_3$ and S precursors. In contrast to previous reports, the MoO$_3$ powder with a weight of ~15 mg was directly placed on a silicon wafer which is next to the collecting substrates for MoS$_2$ growth. A piece of carbon cloth (thickness: 0.34 ± 0.02 mm, surface area ~50 mm$^2$) was put on the top of MoO$_3$ powder. Prior to the growth, argon gas was used to flush the quartz tube thoroughly in order to remove the oxygen and moisture. 10 sccm of argon was supplied during the synthesis of MoS$_2$ monolayers, while the growth chamber was heated from room temperature to 700°C with a temperature profile as shown in Fig. 1 (a).

Detailed growth procedure can be found in the method section. At such temperature, MoO$_3$ powder evaporated and reacted with sulfur vapor to form a continuous MoS$_2$ films and isolated triangular MoS$_2$ domains can also be found at the edges along the film which are shown in the optical microscopy images (with different magnifications) of Fig. 1 (b), (c) and (d) where the MoS$_2$ sheets were grown on the SiO$_2$/Si substrate. The triangular shape of the crystallites reflects the 3-fold symmetry of MoS$_2$ that suggests they are single-crystalline$^{30,41}$. Similar to previous work, the monolayer MoS$_2$ can be merged to form a large MoS$_2$ sheet$^{29}$, and among different growths the average size of MoS$_2$ islands varies between 10 to 40 μm. The intensity of photoluminescence (PL) peak and the energy separation between the Raman A$_{1g}$ and E$_{2g}$ peaks have been found related to the number of MoS$_2$ Layers$^{42-44}$. Therefore, Raman and PL measurement were carried out to confirm the quality of the individual crystallites. Fig. 1 (e) and (f) show the PL intensity mapping and the corresponding intensity mapping of Raman peak of an isolated triangular MoS$_2$ crystallite. Figure 1 (g) displays the typical spectra taken from the MoS$_2$ crystallite that consisting...
both the Raman and PL peaks. The strong PL peak and high PL to Raman intensity ratio suggest the direct band gap photoluminescence. The inset figure in Fig. 1 (g) presents the Raman peak of monolayer MoS$_2$, the E$_{2g}$ and A$_{1g}$ peaks locate at 385.8 and 403.8 cm$^{-1}$, respectively with a peak distance of 18 cm$^{-1}$. The small E$_{2g}$ and A$_{1g}$ peak distance suggests the monolayer nature of these MoS$_2$ crystallites$^{45,46}$.

We note that without the carbon cloth, triangular shape MoS$_2$ can also be obtained but there will be few-layer MoS$_2$ and/or MoO$_2$ crystallites distributed among them, as shown in Supporting Data (Fig. S1). As a consequence, under our growth condition, carbon based materials play an important role in facilitating the monolayer MoS$_2$ growth. It is worthy to mention that, recently reports demonstrated aromatic molecules are helpful for the nucleation of the MoS$_2$ layers$^{29,30}$. However, it is still controversial that a larger single layer MoS$_2$ can be obtained by using carefully cleaned substrates$^{27,28}$. In this study, the carbon cloth is separated from the collecting substrates, and pre-annealed at 700°C to exclude the influence of any impurities from the carbon cloth. It is generally believed that at elevated temperatures the MoO$_x$ vapor generated from MoO$_3$ powder reacts with sulfur vapor and being sulfurized to form monolayer MoS$_2$ on the collecting substrates, therefore the reduction of MoO$_x$ is a critical step for the MoS$_2$ formation$^{38}$.

Accordingly we further investigated the surface reaction of carbon cloth with MoO$_x$ during MoS$_2$ synthesis. Figure 1 (h) and (i) show the Scanning Electron Microscope (SEM) images of the carbon cloth surface before and after the CVD process; (j) and (k) SEM images show large crystals can be found on carbon cloth surface; (l) Raman spectrum taken from the pristine carbon cloth and the one after CVD synthesis.
at around 1300 and 1600 cm⁻¹ become comparatively weaker. According to the literature, the additional Raman peaks obtained after CVD process belongs to MoO₃. However, there are no detectable MoS₂ Raman peaks from carbon cloth.

The forming of MoO₂ crystals on the surface of carbon cloth suggests carbon is more reductive under elevated temperature to react with vapor phase MoO₃. In our experiments, the carbon cloth directly contacted with MoO₃ powder, thus no sufficient sulfur vapor can penetrate through the carbon layer to react with the precursor underneath. In other words, the additional carbon layer helped to create an abrupt MoO₃ concentration change between the top and bottom layer of the carbon cloth. It is well know that the reduction of MoO₃ by sulfur can produce MoO₂ and further sulfurization gives MoS₂ layers. Therefore, it is likely that during the growing process where the carbon layer provides a more steady and sustainable flow of MoO₃ (x>1) and results a more constant ratio of Mo and S to form stoichiometry MoS₂ crystallites. The reduction capability of carbon cloth was also compared with other form of carbon such as well crystallized highly ordered pyrolytic graphite (HOPG). Our results suggest well crystallized carbon, such as HOPG is more inert in the reaction with MoO₃ during the growth (See the Supporting Data). The Raman spectra in Fig. 1 (l) show a strong D band at around 1300 cm⁻¹, which indicates the defective nature of carbon cloths. The defective nature of carbon cloth makes it more reactive and attractive for molybdenum source with a large interacting surface with MoO₃-x. Thus these carbon fibers assist the reduction of MoO₃-x for MoS₂ growth with improved reactivity and efficiency.

Recently, Kong et al. reported vertically aligned MoS₂ and molybdenum diselenide (MoSe₂) layers can be produced by a rapid sulfurization/selenization process at 550 °C. It is suggested that the formation of vertically aligned TMD layers is driven by a kinetic process. When the growth is limited by the diffusion of sulfur/selenium, due to the anisotropic structure of TMD layers, it is much faster for sulfur/selenium to diffuse along the van der Waals gaps. Therefore, the TMD layers naturally oriented perpendicular to the film, exposing van der Waals gaps for fast reactions. The assisted reduction process of MoO₃-x by carbon based materials is likely to alter the growth rate and thus provides a way to tune the surface structure of TMD layers.

In order to better understand the growth mechanism and further develop a method which is capable of engineering the surface structure of MoS₂ layers in a controlled manner. Carbon based materials were deposited directly on the growth substrates to tune the local growth condition. Graphene oxide (GO) prepared by modified Hummers method is generally accepted as a defective form of carbon and GO flakes with abundant function groups also show similar Raman feature with the carbon cloth used in our study (See Supporting Data). Therefore, GO was chosen to reveal the reaction between carbon and MoO₃-x, and its effects on the crystallization of MoS₂ crystallites. To investigate the growth mechanism and reveal the role of carbon promoter during MoS₂ formation, GO dispersed in DI water was drop casted on cleaned Si wafer with 300 nm SiO₂ top layer. The GO casted substrates were carried into CVD furnace and MoS₂ growth was then carried out. Figure 2 (a), (b) and (c) show the optical image of GO coated SiO₂/Si wafer after growth. The color contrast is due to the different layer thickness of deposited materials. Flakes with irregular shape can be found among the single layer MoS₂. We chose a location that fully covered with MoS₂ monolayer and GO flakes can be found distributed among the mono layer MoS₂. The Raman measurement clearly shows the distribution of monolayer and few-layer MoS₂. Spectrum in Fig. 2 (d) shows a typical comparison of PL and Raman peak intensity taken from an irregular shaped few layer MoS₂ and its surrounding. Note that the Raman peak of GO becomes very weak after CVD synthesis. The mapping in Fig. 2 (e) and (f) displays the peak intensity distribution on the sample surface. Moreover, it is worthy to mention that for the typical growth, most of the SiO₂/Si surface were covered with triangular monolayer MoS₂ crystallites or MoS₂ film. Meanwhile, all the MoS₂ Raman peaks taken from the GO surface have a large E₂g to A₁g peak distance suggesting they are mono layer MoS₂. The Raman measurement clearly shows the distribution of monolayer and few-layer MoS₂. Spectrum in Fig. 2 (d) shows a typical comparison of PL and Raman peak intensity taken from an irregular shaped few layer MoS₂ and its surrounding. Note that the Raman peak of GO becomes very weak after CVD synthesis. The mapping in Fig. 2 (e) and (f) displays the peak intensity distribution on the sample surface. Moreover, it is worthy to mention that for the typical growth, most of the SiO₂/Si surface were covered with triangular monolayer MoS₂ crystallites or MoS₂ film. Meanwhile, all the MoS₂ Raman peaks taken from the GO surface have a large E₂g to A₁g peak distance suggesting they are few-layers (see supporting information). These results are solid evidence that the GO tends to attract and promote MoS₂ growth. We also noticed that without sulfur supply, monolayer GO is more reactive and can be totally etched away by MoO₃ vapor (see supporting information) which also suggests the carbon MoO₃ reduction reaction takes place during the growth.

**Flower-shape MoS₂ growth, characterization and application.** Since it was reported that sulfurization process largely affects the layer orientations in the synthesized chalcogenide. As discussed, at high temperatures, carbon can dramatically enhance the reduction of MoO₃, thus promote the formation of MoO₃-x (x>1) to react with sulfur vapor which further converts to MoS₂ layers. Thereby under monolayer MoS₂ growth condition, the introduction of additional carbon materials is likely to create a localized sulfur diffusion limited process for MoS₂ growth. In order to investigate the effect of carbon on the layer orientations of synthesized chalcogenides, we intentionally apply more carbon based materials by utilizing filtered GO thin film as the growth template, and all the other growth conditions were kept unchanged. The as-grown samples possess a dramatically different morphology as shown in Fig. 3 (a) and (b). Interestingly, the synthesized MoS₂ layers tend to form in a micrometer flower shape as illustrated in Fig. 3 (c). Figure 3 (d) displays the energy-dispersive X-ray spectroscopy (EDS) mapping characterization, which confirms the chemical composition of the flower shape structure.

Further structural characterizations using transmission electron microscopy (TEM) provide additional insights into MoS₂/GO composite film. Figure 4 shows the typical TEM images of MoS₂/GO film. Figure 4 (a) displays a low magnification TEM image, where the MoS₂ layers show a darker color contrast.
on GO thin film. Figure 4 (b) exhibits a high-resolution TEM (HRTEM) image taken along the edge part of these composites. Stripe-like grains with ~10 nm in length and several nanometers in width were found, however these grains are densely packed and overlapped with each other preventing an accurate lattice structure analysis. In Fig. 4 (c), the HRTEM image on a single grain reveals individual atomic planes ordered in the S–Mo–S sequence to form each layer. The carbon surface with a lighter color contrast under TEM was confirmed to be graphene by performing the selected area electron diffraction (SEAD) and the FFT confirms the hexagonal arrangement of S-Mo-S atoms. As shown in Fig. 4 (d), both the HRTEM image and fast Fourier transform (FFT) pattern reveal that MoS2 flakes grown on GO retain the crystal symmetry with the lattice constant ~0.32 nm. Both of the EDS and TEM analysis suggests the MoS2 layers tend to form a layered flower-shape structure on GO substrates compared to monolayer in plan growth on SiO2/Si substrates. The morphology change is likely due to the promoted conversion rate of MoO3–x, where the chemical conversion occurs much faster than the diffusion of sulfur gas into the film, forcing the MoS2 layers naturally oriented perpendicular to the growth substrates, exposing van der Waals gaps for fast reaction 49.

As a proof-of-concept application, the electrochemical property of the MoS2/GO composite as an anode material of a Lithium ion battery (LIB) was further investigated by galvanostatic discharge/charge and cyclic voltammetry (CV) measurements. The measurement was based on a half-cell configuration as shown in the supporting materials. Figure 5 (a) illustrates the first, second and third discharge/charge voltage profiles of the flower shape MoS2/GO composite electrode grown by CVD method. The test were carried out in the voltage range from 0.01 to 3 V (vs. Li/Li⁺). The initial discharge and charge capacities were measured to be 1612 and 1149 mAh g⁻¹, respectively, with a corresponding initial Coulombic efficiency of 71.3%. The irreversible capacity loss for the first cycle could be mainly attributed to the electrolyte decomposition and inevitable formation of the solid electrolyte interface (SEI), which are commonly observed for nanosized anode materials 13. The second and third cycles show a decreased capacity but with a much higher Coulombic efficiency of 93.8% and 95.3%, respectively. In the first discharge process, the initial discharge capacity between 2.0 to 1.5 V can be attributed to the reaction of residual carbon surface functional group and the lithium insertion to MoS2 which forms LiₓMoS2. The following capacity between 1.0 to 0.5 V can be attributed to the conversion reaction process of MoS2, where the metal sulfide reacts with lithium ions forming metal nanoparticles and insoluble Li2S matrix, MoS2+4Li⁺+4e⁻→Mo+2Li2S 14. The formation of a SEI and the gel-like polymeric layer on the surface of the active materials contribute to the sloping plateau at the lower voltage region (< 0.5 V). In the charge
process, the plateau at ~1.3 V and the sloping region above 2.2 V can be attributed to the reverse reaction process, where oxidation of Mo particles to MoS₂ and the conversion of Li₂S to S and Li⁺ occur. It is noted that the lithium extraction from the LiₓMoS₂ phase should also be considered.

To further clarify the electrochemical process of MoS₂/GO composite, cyclic voltammogram (CV) measurements of the first three cycles in the voltage range of 0.01-3.0 V at a scan rate of 0.1 mV s⁻¹ were carried out as shown in Fig. 5 (b). In the initial cycle, two reduction peaks at 1.1 and 0.5 V were observed, which can be attributed to the formation of LiₓMoS₂ and the conversion reaction that leading to Mo metal nanoparticles embedded in a Li₂S matrix. In the reverse anodic scan, the oxidation peak at ~ 1.4 V can be partly attributed to the oxidation of Mo to MoS₂ and the peak at ~ 2.3 V can be assigned to the oxidation of Li₂S to S. In the 2nd CV scan, the reduction peak at 0.9 V can be attributed to the Li⁺ insertion into MoS₂ lattice to form LixMoS₂. The weak reduction peak at ca. 2.1 V indicates the formation of Li₂S. In the anodic sweeps, the oxidation peaks at 1.4 V and 2.3 V correspond to the extraction of Li⁺ from LixMoS₂ lattice and the oxidation of Li₂S, respectively. The results are in agreement with the above lithiation and delithiation profiles.

The MoS₂/GO composites also possess outstanding high-rate performance. Figure 5 (c) shows cycle performance of the composite electrodes under high current density of 1000 and 2000 mA g⁻¹. The initial discharge and reversible capacities are ca. 1484 and 779 mAh g⁻¹, respectively, at 1000 mA g⁻¹, which retain ca. 68% of capacities at 100 mA g⁻¹ (see supporting information). After the initial 36 cycles, the specific capacity slightly decreased to 542 mAh g⁻¹. However, a subsequent increase of specific capacity was observed for MoS₂/GO composites, which should be attributed to the gradual activation of the electrode during lithiation and delithiation and a formation of gel-like film resulting from decomposition of the electrolyte at a low voltage. Due to the vertical structure of MoS₂, the Li⁺ could get sufficient contact with the atomic layers of MoS₂. As a result, excellent electrochemical performance was achieved for vertical grown MoS₂ and GO film. The reversible capacity can retain 776 mAh g⁻¹ even after a long cycling
period of 500 cycles. When the current density increases to 2000 mA g\(^{-1}\), the reversible capacity after 940 cycles can still retain \(~727\) mAh g\(^{-1}\), which is about 94% of that at 1000 mA g\(^{-1}\).

The MoS\(_2\)/GO composites electrodes were further investigated by the electrochemical impedance spectroscopy measurement where the Nyquist plots of MoS\(_2\)/GO composite and MoS\(_2\):GO (commercial MoS\(_2\) and GO powder mixed in solution phase followed by freeze-dried to form a self-supporting film) powder blended electrode after 10 discharge/charge activation cycles are shown in Fig. 5 (d). The corresponding equivalent circuit is shown in the inset of Fig. 5 (d). The measurement indicates that the film resistance (R\(_f\)) and charge-transfer resistance (R\(_{ct}\)) of MoS\(_2\)/GO are ca. 27 and 112 Ω, respectively. Both the R\(_f\) (106 Ω) and R\(_{ct}\) (130 Ω) of MoS\(_2\):GO mixture are much larger than those of MoS\(_2\)/GO electrode. Since the MoS\(_2\)/GO composites electrode possesses lower charge-transfer resistance, the charge transfer is lower than that of MoS\(_2\): GO blends. The significantly improved charge capacity of MoS\(_2\)/GO composites could be attributed to the unique nanostructure of MoS\(_2\) sheets on the surface of GO film. The vertical structured MoS\(_2\) with extruding layers on GO has a much larger surface area, which provide more active sites during charging-discharging processes. In addition, lithium ions can be inserted/extracted into/out-of the vertical MoS\(_2\) flakes from both sides of MoS\(_2\), leading to a quick lithiation and delithiation process even under a large current density, as shown in the schematic diagram in Fig. 5 (e). Therefore, the MoS\(_2\)/GO composite electrodes show excellent rate performance.

**Conclusion**

In conclusion, we propose a carbon promoted process to synthesize large-area and highly crystalline MoS\(_2\) thin layers. The addition of carbon based materials during the high-temperature annealing drastically enhances the reduction of MoO\(_3\) vapor, as evidenced by various spectroscopic and microscopic characterizations including Raman, PL, TEM, and SAED. In particular, using GO thin film as the growth template results in an edge-terminated layered chalcogenide films forming in a flower shaped MoS\(_2\)/GO composite. These MoS\(_2\) thin layers tend to orientate perpendicular to the growth substrate due to the sulfur diffusion limited process. The synthetic approach is simple and scalable, providing not only an easy but also efficient way to manipulate the structure of chalcogenide films. The unique structure paves the way to use the edges of layered materials more effectively.
Figure 5. (a) Charge-discharge curves of MoS$_2$/GO composites at current density of 100 mAg$^{-1}$; (b) Representative cyclic voltammograms of MoS$_2$/GO composite at the 1st 3 cycles between 0.01 V and 3.0 V at scan rate of 0.1 mV s$^{-1}$; (c) The cycling performance of MoS$_2$/GO composite at various current densities of 1 Ag$^{-1}$ and 2 Ag$^{-1}$ (d) Nyquist plots of MoS$_2$/GO composite and MoS$_2$:GO powder blended electrode after 10 discharge/charge activation cycles. Inset shows the equivalent circuit model used for the fittings and the corresponding values are shown in Table 1. (e) Schematic illustration of the surface structure of MoS$_2$/GO composite for high current density lithium storage.

| Sample                  | R$_s$ (Ω) | R$_f$ (Ω) | R$_ct$ (Ω) |
|-------------------------|-----------|-----------|------------|
| MoS$_2$:GO powder       | 28        | 106       | 130        |
| MoS$_2$ flower/GO film  | 19        | 27        | 112        |

Table 1. Fitting results of the EIS curves in Fig. 5 (d) using the equivalent circuit.

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**Acknowledgements**
This work was supported by SUTD-MIT international design center (IDC) grant.

**Author Contributions**
Y. S. and H. Y. Y. designed research and analyzed data. Y. S., H. L. and J. I. W., carried out the material growth, synthesis and characterization. X. Z., H. S. and Y. W. performed the electrochemical measurement. H.Y. Y. supervised the project. All authors contributed to the writing and editing.

**Additional Information**
Supplementary information accompanies this paper at http://www.nature.com/srep

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

**How to cite this article:** Shi, Y. et al. MoS2 Surface Structure Tailoring via Carbonaceous Promoter. *Sci. Rep.* **5**, 10378; doi: 10.1038/srep10378 (2015).

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Corrigendum: MoS$_2$ Surface Structure Tailoring via Carbonaceous Promoter

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*Scientific Reports* 5:10378; doi: 10.1038/srep10378; published online 21 May 2015; updated on 20 January 2016

The Acknowledgements section is incomplete.

“This work was supported by SUTD-MIT international design center (IDC) grant.”

should read:

“This work was supported by SUTD-MIT international design center (IDC) grant and SUTD Temasek Seed funding (IGDSS1402031).”

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