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MoS₂ 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 (MoS₂) monolayers show promising applications in field effect transistors, optoelectronics and valleytronics. However, the controlled synthesis of highly crystalline MoS₂ remain a challenge especially the systematic approach to manipulate its structure and morphology. Herein, we report a method for controlled synthesis of highly crystalline MoS₂ by using chemical vapor deposition method with carbonaceous materials as growth promoter. A uniform and highly crystalline MoS₂ monolayer with the grain size close to 40 μm was achieved. Furthermore, we extend the method to the manipulation of MoS₂ morphology, flower-shape vertical grown MoS₂ layers were obtained on growth promoting substrates. This simple approach allows an easy access of highly crystalline MoS₂ layers with morphology tuned in a controllable manner. Moreover, the flower-shape MoS₂ 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 mobility³, excellent on-off ratio⁴ and good bendability⁵ are promising for future flexible and low-power consumer electronics^{5,6}. The fundamental studies on their electronic structures and valley-spin relations are also emerging^{7,8}. Being a member of the TMDs family, molybdenum disulfide (MoS₂) has already attracted considerable attention for its great potential in the fields of hydrogen evolution reaction (HER)^{9,10}, bio-sensing^{11,12} and energy storage^{13–15}. Recently, it has been demonstrated that ultra-thin MoS₂ crystals with a typical thickness of ~0.65 nm holds even more significant promise in electronics^{4,16,17} and optoelectronics^{7,18–22}.

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 MoS₂ 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^{13,14}. For the application of HER, only the edge sites of MoS₂ are catalytically active, which require the controllable synthesis of MoS₂ layers with abundant exposed edge sites^{10,23}. 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 MoS₂ synthesis^{8,24–26}. Among the various approaches for MoS₂ synthesis, those using MoO₃ and sulfur powder as solid state precursors become dominant^{26–30}, which is due to the simplified process and high yield of monolayers.

However, it is more challenging to grow single crystalline monolayer MoS₂ 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 MoS₂ by CVD does not involve any catalysts^{35,36} and the growth of MoS₂ is very sensitive to the substrate treatment prior to the growth^{18,22}. Previous reports demonstrate nucleation of MoS₂ can be facilitated by seeding

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the substrate with graphene-like species^{29,30,37}. Meanwhile Najmaei *et al.* have shown that the MoS₂ crystallines commonly nucleate on the step edges during growth without the present of seeding molecules²⁸. Recently, Van der Zande *et al.* proved that large MoS₂ 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 MoS₂²⁷. It was suggested that the MoS₂ growth normally follows an analogous layer-plus-island (or Stranski-Krastanov) growth mode⁸. The Stranski-Krastanov mode is a two-step process: initially, monolayer MoS₂ domains gather and interconnect with each other till the full coverage of monolayer is nearly completed. Beyond the critical layer number (1 for MoS₂), the growth of MoS₂ continues through the nucleation and coalescence of MoS₂ nanoparticles or few layers islands⁸. In other words, the thermodynamics favors the basal plane growth, which limits the tunability of surface structure.

Nevertheless, the widely used method for MoS₂ synthesis is based on the direct chemical vapor phase reaction of MoO₃ by S gas in which the MoO_x vapor generated from MoO₃ powder reacts with sulfur vapor at elevated temperatures to form monolayer MoS₂ on the collecting substrates^{26,29}. Thus, it is common to obtain molybdenum oxide microcrystals byproducts since the reduction of MoO₃ also produce MoO₂ crystals under similar growth condition³⁸. MoO₃ was selected by Li *et al.* as a precursor for MoS₂ growth on the basis that it has an evaporation temperature of ~700 °C²⁶. However, the growth dynamics of MoO_{3-x} and S are still not fully understood. It has been suggested in literatures^{39,40} that there are two channels for MoO_{3-x} to react with S, one is it adsorb and diffuse on the substrate, reacting with S to form MoS₂; the other is forming MoS₂ clusters in vapour phase and crystalize on substrate. Both these two channels require the forming of vapour phase MoO_{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 MoS₂ crystals, preventing the formation of MoO₂ byproducts, meanwhile controlling the surface structure of MoS₂ layers at the atomic scale.

Herein, we engineer the reduction process of MoO₃ precursor by carbon based materials. In a typical synthesis, the solid state precursor of MoO₃ 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. MoO₃ powder can be thermally evaporated and only the gas phase MoO₃ 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 MoO₃ and large MoO₂ crystals can be trapped by the carbon cloth which effectively prevents the co-deposition of MoO₂ and MoS₂ on the collecting substrates. Finally, continuous large-area MoS₂ thin films was successfully grown on substrate. The synthesized MoS₂ layers are in a well-defined triangular shape with a typical lateral size ~40 μm. We further investigated the effects of carbonaceous promoter in the growth of MoS₂ on various substrates. By simply replacing the SiO₂/Si substrates with GO film or GO flakes, few-layer MoS₂ preferentially form on the surface of GO under the same growth condition. The results suggest, the growth of MoS₂ is very sensitive to the substrate treatment and carbon based materials can significantly promote the growth rate and yield of MoS₂, which is due to the assisted reduction of MoO₃ by carbon.

This work elucidates how morphological control of MoS₂ at the nanoscale can be achieved by carbonaceous promoter. The surface morphology engineering of MoS₂ layers enables new opportunities for enhancing surface properties for catalysis, energy storage and other important technological applications. As a proof-of-concept, the MoS₂/GO composites were used as electrode materials to demonstrate its application in lithium ion batteries (LIBs). The surface structure engineering of MoS₂/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., > 1000 mAh g⁻¹) was achieved at the current density of 100 mA g⁻¹, which is much higher than theoretical value for either GO or MoS₂ alone (~566 and ~670 mAh g⁻¹, respectively). The MoS₂/GO composites also show an outstanding high-rate charge/discharge performance. Even at a very high current density of 1000 mA g⁻¹, the composite electrode can still deliver a capacity of 776 mAh g⁻¹ after 500 cycles. The reversible capacity only slightly decreases to 727 mAh g⁻¹ after an additional 440 cycles under 2000 mA g⁻¹. The high rate capability can be attributed to the unique nano-architecture engineering of MoS₂, which provides structural stability and transport advantages for both electrons and lithium ions.

Materials and Methods

Monolayer CVD-MoS₂ growth. CVD-MoS₂ was prepared using chemical vapor deposition method with carbon based materials as a growth promoter. High-crystal-quality MoS₂ can be grown on a silicon substrate with 300 nm SiO₂ layer on top inside a hot-wall horizontal tube furnace. To be brief, the MoS₂ films were synthesized using high purity MoO₃ (99%, Aldrich) and S powder (99.5, Sigma-Aldrich) as precursors. The precursors were placed in two separated Al₂O₃ 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 MoO₃ 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. MoS₂ 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 MoS₂ growth.

Flower shape MoS₂ 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 SiO₂/Si substrates and gently blow dried using N₂ gas. Self-supporting GO thin film was obtained by vacuum filtration of GO dispersion with a polymer filter membranes (pore size 0.02 μm, 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 MoS₂ synthesis.

Chemicals and precursors. Graphene oxide powder was purchased from Graphene Supermarket, Calverton, NY, USA. MoO₃ (purity 99%) and S powder (purity 99.5%) powder purchased from Sigma-Aldrich Co. (Singapore) were directly used for MoS₂ synthesis without further purification. Carbon cloth was purchased from Hesen Shanghai Co., Ltd, China.

MoS₂/GO transfer for TEM characterization. The CVD synthesized MoS₂/GO composite was transferred by coating the film with a thin layer (~100 nm) of Poly[methylmethacrylate] (PMMA). After etching the underlying SiO₂/Si substrates with NaOH aquariums (with a concentration of 3 M) at 80 °C, the PMMA/ MoS₂/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 H₂ 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 MoS₂/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. MoS₂/GO composites were directly used as cathodes. For control samples, the working electrode materials of GO and MoS₂ were prepared by mix GO and MoS₂ 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 MoS₂ growth. A schematically illustration of the experimental set-up used for MoS₂ synthesis is presented in Fig. 1 (a). MoS₂ monolayers were grown by CVD with solid MoO₃ and S precursors. In contrast to previous reports, the MoO₃ powder with a weight of ~15 mg was directly placed on a silicon wafer which is next to the collecting substrates for MoS₂ growth. A piece of carbon cloth (thickness: 0.34 ± 0.02 mm, surface area ~50 mm²) was put on the top of MoO₃ powder. Prior to the growth, argon gas was used to flush the quartz tube thoroughly in order to remove the oxygen and moistures. 10 sccm of argon was supplied during the synthesis of MoS₂ 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, MoO₃ powder evaporated and reacted with sulfur vapor to form a continuous MoS₂ films and isolated triangular MoS₂ 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 MoS₂ sheets were grown on the SiO₂/Si substrate. The triangular shape of the crystallites reflects the 3-fold symmetry of MoS₂ that suggests they are single-crystalline^{30,41}. Similar to previous work, the monolayer MoS₂ can be merged to form a large MoS₂ sheet²⁹, and among different growths the average size of MoS₂ 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 MoS₂ 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 MoS₂ crystallite. Figure 1 (g) displays the typical spectra taken from the MoS₂ crystallite that consisting

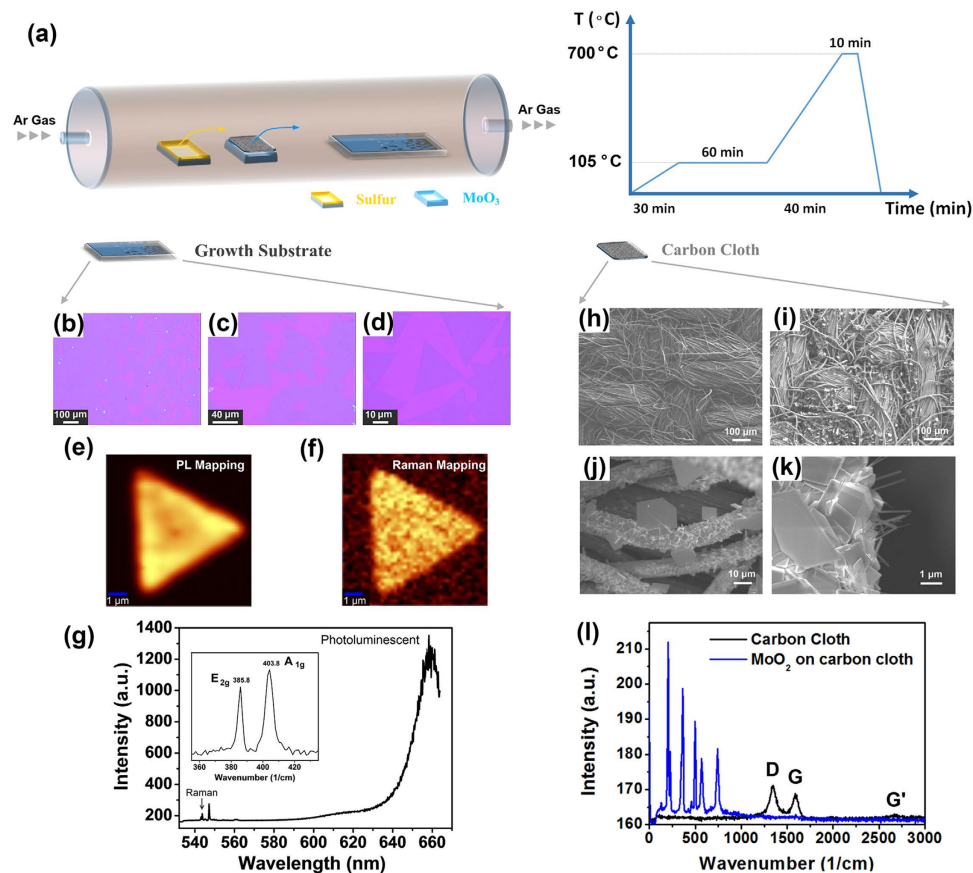


Figure 1. (a) Schematic illustration of the experimental set-up for CVD-growth of MoS₂; and illustration of temperature profile for the MoS₂ growth process at different stages. (b), (c) and (d) show the optical images for as-grown MoS₂ monolayer films and isolated monolayer crystallites. (e) Photoluminescence (PL) map of the synthesized MoS₂ monolayers, and (f) shows the corresponding Raman intensity map. The synthesized MoS₂ were grown on SiO₂/Si substrates. (g) Experimental results show the PL spectrum of MoS₂ films. Inset, typical Raman spectra collected from the area of the MoS₂ monolayer film. (h) and (i) SEM images of carbon cloth surface before and after 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.

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 MoS₂, 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 MoS₂ crystallites^{45,46}.

We note that without the carbon cloth, triangular shape MoS₂ can also be obtained but there will be few-layer MoS₂ and/or MoO₂ 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 MoS₂ growth. It is worthy to mention that, recently reports demonstrated aromatic molecules are helpful for the nucleation of the MoS₂ layers^{29,30}. However, it is still controversial that a larger single layer MoS₂ 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 MoO₃ powder reacts with sulfur vapor and being sulfurized to form monolayer MoS₂ on the collecting substrates, therefore the reduction of MoO_x is a critical step for the MoS₂ formation³⁸.

Accordingly we further investigated the surface reaction of carbon cloth with MoO_x during MoS₂ synthesis. Figure 1 (h) and (i) show the Scanning Electron Microscope (SEM) images of the carbon cloth surface before and after the growth. The pristine carbon cloth is manufactured in bundles of thousands of tiny fibers, and woven onto a fabric roll. After growth, the surface of carbon cloth facing the MoO₃ precursor are fully covered by micro size flakes or large crystals, as displayed in Fig. 1 (j) and (k). Figure 1 (l) compares the Raman spectrums from carbon cloth before and after the CVD process. These micro crystals deposited on the carbon cloth surface show strong Raman peaks and the carbon peaks

at around 1300 and 1600 cm^{-1} become comparatively weaker. According to the literature, the additional Raman peaks obtained after CVD process belongs to MoO_2 ^{47,48}. However, there are no detectable MoS_2 Raman peaks from carbon cloth.

The forming of MoO_2 crystals on the surface of carbon cloth suggests carbon is more reductive under elevated temperature to react with vapor phase MoO_3 . In our experiments, the carbon cloth directly contacted with MoO_3 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 MoO_{3-x} concentration change between the top and bottom layer of the carbon cloth. It is well known that the reduction of MoO_{3-x} by sulfur can produce MoO_2 and further sulfurization gives MoS_2 layers^{27,29,30,37}. Therefore, it is likely that during the growing process where the carbon layer provides a more steady and sustainable flow of MoO_{3-x} ($x > 1$) and results a more constant ratio of Mo and S to form stoichiometry MoS_2 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 MoO_3 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 MoO_{3-x} . Thus these carbon fibers assist the reduction of MoO_{3-x} for MoS_2 growth with improved reactivity and efficiency.

Recently, Kong *et al.* reported vertically aligned MoS_2 and molybdenum diselenide (MoSe_2) layers can be produced by a rapid sulfurization/selenization process at 550 °C⁴⁹. 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 reactions⁴⁹. The assisted reduction process of MoO_{3-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 MoS_2 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 MoO_{3-x} and its effects on the crystallization of MoS_2 crystallites. To investigate the growth mechanism and reveal the role of carbon promoter during MoS_2 formation, GO dispersed in DI water was drop casted on cleaned Si wafer with 300 nm SiO_2 top layer. The GO casted substrates were carried into CVD furnace and MoS_2 growth was then carried out. Figure 2 (a), (b) and (c) show the optical image of GO coated SiO_2/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 MoS_2 . We chose a location that fully covered with MoS_2 monolayer and GO flakes can be found distributed among the mono layer MoS_2 . The Raman measurement clearly shows the distribution of monolayer and few-layer MoS_2 . Spectrum in Fig. 2 (d) shows a typical comparison of PL and Raman peak intensity taken from an irregular shaped few layer MoS_2 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 SiO_2/Si surface were covered with triangular monolayer MoS_2 crystallites or MoS_2 film. Meanwhile, all the MoS_2 Raman peaks taken from the GO surface have a large E_{2g} to A_{1g} peak distance suggesting they are few-layers (see supporting information). These results are solid evidence that the GO tends to attract and promote MoS_2 growth. We also noticed that without sulfur supply, monolayer GO is more reactive and can be totally etched away by MoO_3 vapor (see supporting information) which also suggests the carbon MoO_3 reduction reaction takes place during the growth.

Flower-shape MoS_2 growth, characterization and application. Since it was reported that sulfurization process largely affects the layer orientations in the synthesized chalcogenide⁴⁹⁻⁵¹. As discussed, at high temperatures, carbon can dramatically enhance the reduction of MoO_3 , thus promote the formation of MoO_{3-x} ($x > 1$) to react with sulfur vapor which further converts to MoS_2 layers. Thereby under monolayer MoS_2 growth condition, the introduction of additional carbon materials is likely to create a localized sulfur diffusion limited process for MoS_2 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 filtrated 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 MoS_2 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 MoS_2/GO composite film. Figure 4 shows the typical TEM images of MoS_2/GO film. Figure 4 (a) displays a low magnification TEM image, where the MoS_2 layers show a darker color contrast

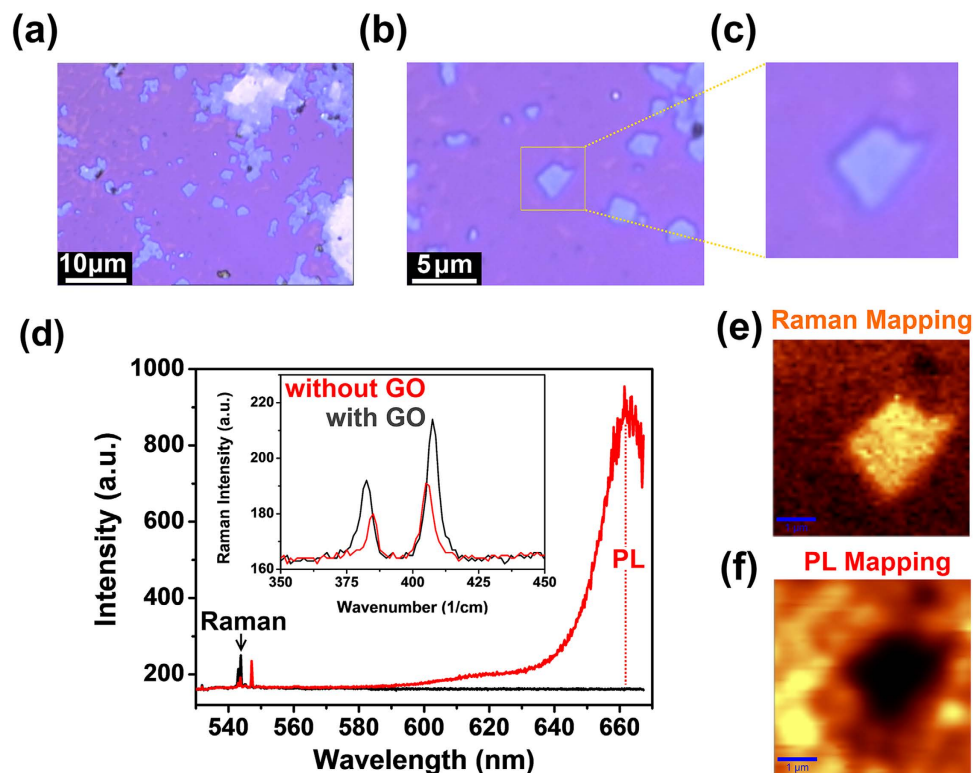


Figure 2. (a), (b) and (c) present the optical microscope images of GO coated SiO_2/Si substrates after CVD synthesis taken under various magnifications. (d) Typical PL and Raman spectrums taken from monolayer and few layer MoS_2 regions. (e) and (f) are the corresponding Raman and PL maps in Fig. (c), the rectangular shape present a few layer MoS_2 with monolayer MoS_2 surrounding it.

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 MoS_2 flakes grown on GO retain the crystal symmetry with the lattice constant ~ 0.32 nm. Both of the EDS and TEM analysis suggests the MoS_2 layers tend to form a layered flower-shape structure on GO substrates compared to monolayer in plan growth on SiO_2/Si substrates. The morphology change is likely due to the promoted conversion rate of MoO_{3-x} , where the chemical conversion occurs much faster than the diffusion of sulfur gas into the film, forcing the MoS_2 layers naturally oriented perpendicular to the growth substrates, exposing van der Waals gaps for fast reaction⁴⁹.

As a proof-of-concept application, the electrochemical property of the MoS_2/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 MoS_2/GO composite electrode grown by CVD method. The test were carried out in the voltage range from 0.01 to 3V (vs. Li/Li^+). The initial discharge and charge capacities were measured to be 1612 and 1149 mAhg^{-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 materials¹³. 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 1.5V can be attributed to the reaction of residual carbon surface functional group and the lithium insertion to MoS_2 which forms Li_xMoS_2 . The following capacity between 1.0 to 0.5V can be attributed to the conversion reaction process of MoS_2 , where the metal sulfide reacts with lithium ions forming metal nanoparticles and insoluble Li_2S matrix, $\text{MoS}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Mo} + 2\text{Li}_2\text{S}$ 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

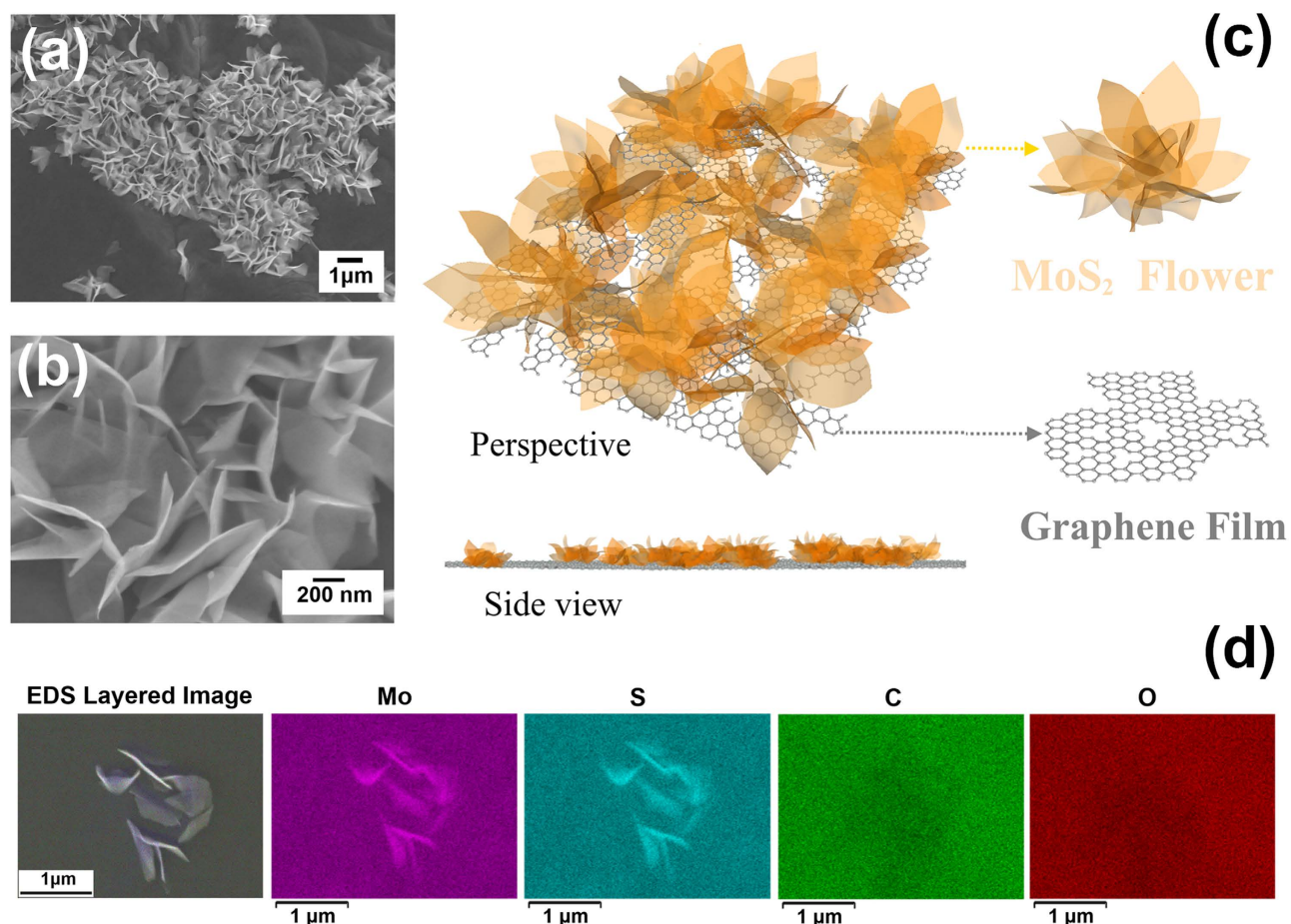


Figure 3. (a) and (b) show the SEM images of samples obtained by using GO thin film as growth templates. (c) Schematic illustration of flower-shape MoS_2 grown on GO thin film. (d) EDS mapping of a layered structure region. The EDS intensity maps confirm the chemical composition of these layered structures to be MoS_2 .

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 MoS_2 and the conversion of Li_2S to S and Li^+ occur^{14,52,53}. It is noted that the lithium extraction from the Li_xMoS_2 phase should also be considered.

To further clarify the electrochemical process of MoS_2/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 Li_xMoS_2 and the conversion reaction that leading to Mo metal nanoparticles embedded in a Li_2S matrix. In the reverse anodic scan, the oxidation peak at ~ 1.4 V can be partly attributed to the oxidation of Mo to MoS_2 and the peak at ~ 2.3 V can be assigned to the oxidation of Li_2S to S. In the 2nd CV scan, the reduction peak at 0.9 V can be attributed to the Li insertion into MoS_2 lattice to form Li_xMoS_2 . The weak reduction peak at ca. 2.1 V indicates the formation of Li_2S . In the anodic sweeps, the oxidation peaks at 1.4 V and 2.3 V correspond to the extraction of Li^+ from Li_xMoS_2 lattice and the oxidation of Li_2S , respectively. The results are in agreement with the above lithiation and delithiation profiles.

The MoS_2/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 MoS_2/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 MoS_2 , the Li^+ could get sufficient contact with the atomic layers of MoS_2 . As a result, excellent electrochemical performance was achieved for vertical grown MoS_2 and GO film. The reversible capacity can retain 776 mAh g^{-1} even after a long cycling

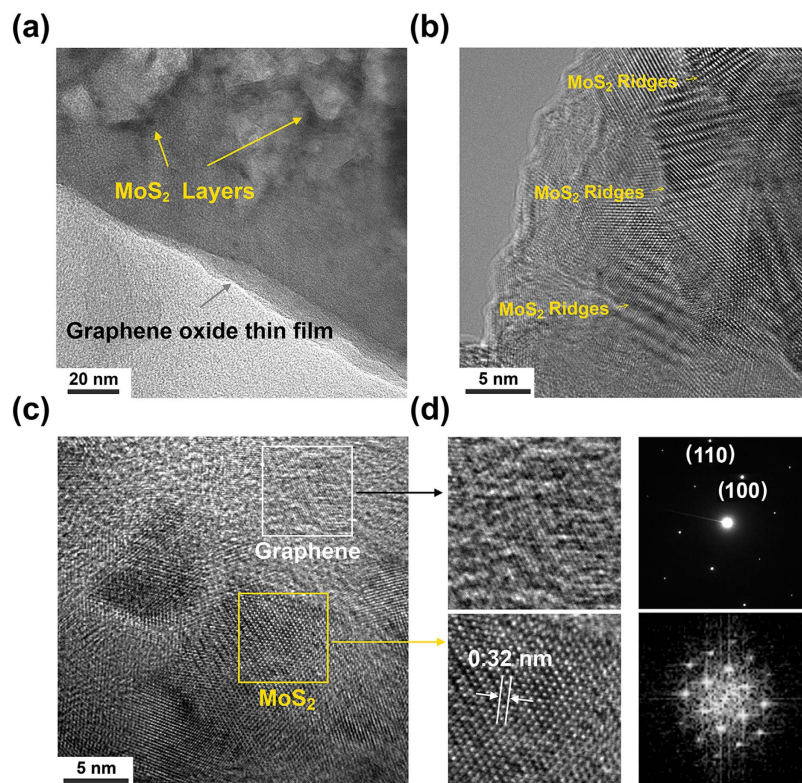


Figure 4. (a) and (b) TEM images of MoS₂/GO composite under different magnifications; (c) HRTEM image shows both graphene and MoS₂ regions; (d) enlarged HRTEM images display the corresponding carbon and MoS₂ lattice structures. SAED in upper right confirms the background is graphene. FFT in the bottom right, suggests the hexagonal arrangement of S-Mo-S elements in MoS₂ layers.

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 MoS₂/GO composites electrodes were further investigated by the electrochemical impedance spectroscopy measurement where the Nyquist plots of MoS₂/GO composite and MoS₂:GO (commercial MoS₂ 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 MoS₂/GO are ca. 27 and 112 Ω , respectively. Both the R_f (106 Ω) and R_{ct} (130 Ω) of MoS₂:GO mixture are much larger than those of MoS₂/GO electrode. Since the MoS₂/GO composites electrode possesses lower charge-transfer resistance, the charge transfer is lower than that of MoS₂:GO blends. The significantly improved charge capacity of MoS₂/GO composites could be attributed to the unique nanostructure of MoS₂ sheets on the surface of GO film. The vertical structured MoS₂ 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 MoS₂ flakes from both sides of MoS₂, 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 MoS₂/GO composite electrodes show excellent rate performance.

Conclusion

In conclusion, we propose a carbon promoted process to synthesize large-area and highly crystalline MoS₂ thin layers. The addition of carbon based materials during the high-temperature annealing drastically enhances the reduction of MoO₃ 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 MoS₂/GO composite. These MoS₂ 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.

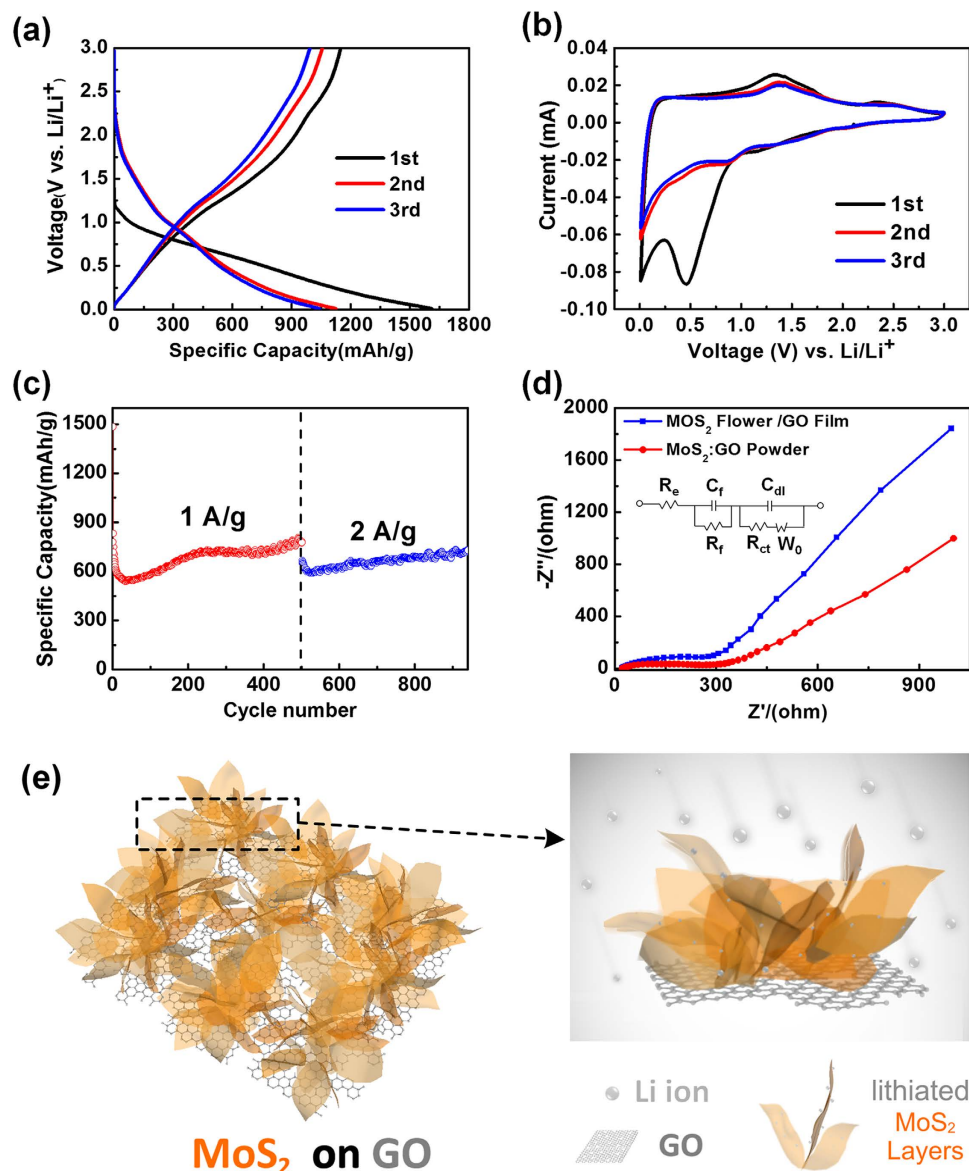


Figure 5. (a) Charge-discharge curves of MoS₂/GO composites at current density of 100 mA g⁻¹; (b) Representative cyclic voltammograms of MoS₂/GO composite at the first 3 cycles between 0.01 V and 3.0 V at scan rate of 0.1 mV s⁻¹; (c) The cycling performance of MoS₂/GO composite at various current densities of 1 A g⁻¹ and 2 A g⁻¹ (d) Nyquist plots of MoS₂/GO composite and MoS₂/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 MoS₂/GO composite for high current density lithium storage.

Sample	R _e (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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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

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