Thickness Tunable Wedding-Cake Like MoS₂ Flakes for High Performance Optoelectronics

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Abstract

Atomically thin transition metal dichalcogenides (TMDCs) have received substantial interests due to their typical thickness-dependent optical and electronic properties, and related applications in optoelectronics. However, the large-scale, thickness tunable growth of such materials are still challenging. Herein, we report a fast growth of thickness tunable wedding-cake like MoS₂ flakes on 6-inch soda-lime glass, by using NaCl-coated Mo foils as metal-precursors. The MoS₂ thicknesses are tuned from one layer (1L) to >20L by controlling the concentrations of NaCl promoter. To attest the ultrahigh crystal quality, related devices based on 1L–multilayer MoS₂ lateral junctions have been constructed and displayed relatively high rectification ratio ($\sim 10^3$) and extra high photoresponsivity ($\sim 10^4$ A/W). Thanks to the scalable sizes, uniform distributions of the flakes and homogenous optical properties, the applications in ultraviolet (UV) irradiation filtering eyewear are also demonstrated. Our work should hereby propel the scalable production of layer-controlled TMDC materials, as well as their optical and optoelectrical applications.

Keywords

thickness tunable, molybdenum disulfide, glass, large-area, optoelectronics

Atomically thin layered two-dimensional (2D) transition metal dichalcogenides (TMDCs) have received intensive attentions due to their intriguing properties such as the valley related physics, magnetism, and superconductivity,¹⁻³ as well as their promising potentials in electrical, optoelectrical applications. To optimize the optical and electrical properties of TMDCs-based devices, various techniques such as applying strain,⁴ external fields,⁵ and chemical doping⁶ have been attempted. Essentially, modulating their layer thicknesses contributes a more facile strategy for such a purpose. This is inspired by the fact that, TMDCs have presented sensitive thickness-dependent properties, such as tunable bandgap (1.8 to 1.2 eV, from monolayer to bulk in MoS₂),⁷ and relatively high carrier mobility in the multilayer field-effect transistors relating to the high density of states.⁸ So far, multilayer TMDC flakes/films have been utilized in various prototype devices, including ultrathin optical windows,⁹ ultrabroadband photodetectors,¹⁰ electrochemical actuators¹¹ and triboelectricity generators.¹² Evidently, for further expanding the practical applications, the batch production of TMDC flakes/films with tunable thicknesses should be an essential topic.

Chemical vapor deposition (CVD) has been recognized as the most promising route to achieve large-area, large-domain, and thickness tunable TMDCs with relatively high crystal quality.¹³⁻¹⁷ Although great efforts have been made on the wafer-scale syntheses of continuous TMDC films with controlled thicknesses, by sulfurization (or selenization) of predeposited metal (or metal oxide) thin films¹⁸ or by thermal decomposition of thiosalts,¹⁹ the as-grown films are usually polycrystalline with small domain sizes (less than 0.1 μm). Recently, Ajayan *et al.*²⁰ and Jiao *et al.*²¹ demonstrated the syntheses of

multilayer MoSe₂ and MoS₂ domains (tens of microns sizes) on SiO₂, under relatively high growth temperature (800–900 °C) or rather long growth period (20–55 min). These multilayer flakes were then employed to construct 2D heterojunctions and high mobility electronics, respectively. However, it is still challenging to obtain TMDC flakes with precisely controlled thicknesses. And the sample size (now limited to 1 cm scale) still cannot meet the requirements for practical applications. In this regard, synthesizing high-quality multilayer flakes with controlled thicknesses on a large scale (up to several inch scales) is highly desirable for multi-range applications from individual flakes to their macroscopic aggregates.

Recently, our group have designed a “face-to-face” metal-precursor supply route to synthesize 6-inch uniform, monolayer MoS₂ on a low-cost soda-lime glass substrate.²² The trace concentration of sodium in glass was confirmed as efficient catalyst for the fast growth of monolayer MoS₂. However, nucleation and growth of additional MoS₂ on top of monolayer was extremely difficult, due to the limited catalysts on the surface and the surface catalytic growth mechanism.²³ Recently, alkali metal halides have been proved to be perfect promoters in facilitating the growth of TMDC materials. Eda *et al.* adopted alkali metal halides to synthesize WSe₂ and WS₂ monolayers innovatively, at a lowered growth temperature by ~150 °C.²⁴ Lately, Liu *et al.* applied the molten-salt-assisted strategy for synthesizing almost all TMDC compounds, and demonstrated the effect of salt on decreasing the melting point of metal reactants.²⁵

Herein, we have developed a NaCl-promoter assisted low-pressure CVD (LPCVD) route for the synthesis of large-area, thickness tunable MoS₂ flakes on a commonly used transparent, low-cost soda-lime glass surface. The superiorities of this route can be summarized as follows: i) the face-to-face metal-precursor-feeding route with an over-placed NaCl-coated Mo foil as metal-precursor guarantees a homogenous release of Mo precursors on the substrate surface in the CVD process. ii) the concentrations of NaCl promoter can be varied in a more wide range towards releasing abundant metal precursors, allowing a fast growth rate even at a low temperature ~730 °C (around the softening point of soda-lime glass), and more significantly, achieving a precise control of MoS₂ thickness. As a result, wedding-cake like multilayer MoS₂ flakes with variable MoS₂ thicknesses were synthesized on glass within only 8 min, with the sample size scalable to a 6-inch scale. The large-area multilayer MoS₂ flakes samples with excellent optical and electrical properties were then readily used for various prototype devices and daily-life related applications, such as high performance photodetectors and UV filtering eyewear, *etc.*

Results and Discussion

To achieve multilayer growth, more rapid and continuous feeding of Mo precursor is highly needed. Herein, a special design using NaCl-coated Mo foils as metal-precursors is proposed. The coated NaCl is utilized to promote the release of abundant Mo-based precursors, as well as for catalysing the surface growth of MoS₂, as depicted in **Figure 1a** and **Figure S1**. In order to maintain the original morphology of soda-lime glass, the growth temperature is set at ~730 °C, close to the softening point of glass. The sublimed

sulfur was transported downstream by mixed Ar (50 sccm) and O₂ (3 sccm) carrier gases, and then sulfurized Mo precursors to a supersaturation state around the substrate, leading to the nucleation of the first layer MoS₂.²⁶ Notably, the concentration of the Mo precursor was usually oversaturated due to the introduction of NaCl promoter, facilitating the nucleation and growth of bilayer and multilayers.

By increasing the concentrations of NaCl, the thicknesses of the obtained MoS₂ flakes were tuned from 1L to >20L at ~730 °C for 8 min. In comparison, without the assistance of NaCl, monolayer MoS₂ domains with an average edge length ~200 μm were usually achieved under the same growth condition (Figure 1b). However, when NaCl was introduced into the growth process, multilayer wedding-cake like MoS₂ flakes evolved under the same growth condition (Figure 1c, e and **Figure S2**). Upon increasing the NaCl concentrations from 0.05 to 0.10, 0.15 mmol/L, the layer numbers of MoS₂ flakes were precisely tuned from ~2L, ~5L to ~21L, respectively. Particularly, the optical contrasts become gradually brighter with increasing MoS₂ thicknesses. OM images at low magnification presented a uniform distribution of the MoS₂ flakes and thus a homogeneous contrast over the whole region (**Figure S3**). Statistics based on a large number of thickness measurements by atomic force microscopy (AFM) are presented in **Figure S4**, confirming the narrow thickness distributions of the derived MoS₂ flakes. A representative AFM image of a MoS₂ flake in Figure 1e reveals the multiple concentric triangles morphology. The height profile shows a thickness ~2.9 nm, in line with a four layer flake.²⁷ Notably, with increasing growth time, as illustrated in **Figure S5**, the bottom layers of the MoS₂ flakes are gradually merged, while the top layers are still seen

as isolated islands because of its lower growth rate. The average layer number of MoS₂ flakes as a function of NaCl concentration is also plotted in Figure 1h, showing a monotonic increase of layer thicknesses with increasing NaCl concentrations. The X-ray photoelectron spectroscopy (XPS) spectra on such samples further confirm the formation of MoS₂ (**Figure S6**).²⁸ Besides, the controllable growth of multilayer MoS₂ flakes can also be achieved by using other alkali halides compounds (NaBr, NaI and KCl) as promoters (**Figure S7**). The proper concentrations of the promoters are varying for different alkali halide compounds under the similar CVD conditions.

As mentioned above, by using the “face-to-face” metal-precursor supply route, the size of the CVD-derived multilayer MoS₂ sample is only limited by the size of the furnace. To demonstrate this, MoS₂/glass samples with different thicknesses (~1L, ~2L, ~5L, corresponding to Figure 1b-d, respectively) on glass are displayed in Figure 1i, which show gradually deepening yellow colour with increasing layer number. Notably, the highest edge growth rate of our multilayer MoS₂ flake on glass is estimated as ~20 μm/min (of the bottom layer), which is at least five times faster than that of the multilayer TMDCs growth reported previously (4.75 μm/min and 0.6 μm/min for MoSe₂ and MoS₂ on SiO₂, respectively).^{20,21} The current growth route thus allows a fast growth of multilayer MoS₂ on a functional glass substrate, which is compatible with batch production and future practical applications.

Both theoretical and experimental studies indicated that, the bandgap of semiconducting TMDCs can be tuned by changing their layer thicknesses.⁷ Photoluminescence (PL)

combined with Raman are perfect tools to evaluate the band gap variations and the layer-dependent optical properties. Herein, five representative Raman spectra of 1L, 2L, 4L, 5L and 21L transferred MoS₂ on SiO₂ were obtained and displayed in **Figure 2a**, with the typical morphology and thickness characterizations shown in Figure S4. The two typical peaks correspond to the in-plane vibrations of Mo and S atoms (E_{2g}^1), and out-of-plane vibration of S atoms (A_{1g}), respectively. The frequency differences (Δ) of the two characteristic peaks are increased from $\sim 18.3\text{ cm}^{-1}$ to $\sim 25.7\text{ cm}^{-1}$ with increasing layer numbers (Figure 2c), in good agreement with that reported for monolayer and multilayer MoS₂.²⁹ As shown in Figure 2b, the PL peak red shifts with the increasing layer thicknesses (from 655 to 678 nm in wavelength, from 1L to 21L). The strong peak at 655 nm (exciton A) is attributed to the monolayer sample. And its full-width at half-maximum (FWHM) $\sim 58\text{ meV}$ is comparable with that of the mechanically exfoliated MoS₂ (50–60 meV),^{30,31} confirming the rather high crystallinity of our CVD-derived MoS₂ samples. Moreover, the PL emission intensity decreases significantly with increasing layer number, due to the transition from direct to indirect bandgap semiconductors. To further access the interfacial effect of the MoS₂ multilayers, Raman and PL intensity mapping were also performed on the $\sim 4\text{L}$ MoS₂ flake (shown in Figure 1e). The step region exhibits stronger Raman and weaker PL intensities than that of the surrounding monolayer platform, clearly indicating the thickness dependency (Figure 1f, g).

Due to the existence of interlayer van der Waals interactions in 2D layered materials, stacking significantly governs the crystal symmetry and the physical/chemical properties,

like magnetism,³² superconductivity,³³ second harmonic generation (SHG),³⁴ *etc.* In this work, scanning transmission electron microscopy (STEM) and selected area electron diffraction (SAED) were then performed to access the stacking configuration and crystalline quality of the derived samples. The wedding-cake morphology of a typical MoS₂ flake is evidently shown by the low-magnification STEM image (Figure 2d). The SAED patterns from the numbered layers (1, 2, and 3 in Figure 2d, from bottom to upper layers) present only one set of lattice orientation, strongly indicating a non-twisted stacking arrangement (Figure 2e). Moreover, a large-scale atomic resolution STEM image on a monolayer MoS₂ region clearly displays a well-organized honeycomb structure with an interatomic distance ~ 0.32 nm (Figure 2f), in accordance with the documented lattice constant of MoS₂.³⁵ The negligible defect effect also justifies the rather high crystal quality of our CVD-derived MoS₂ on glass. To precisely identify the stacking geometry, atomic resolution STEM images were also captured at the edge of MoS₂ bilayers showing an AB stacked configuration (Figure 2g, h). The Mo (S) atoms from the upper layer MoS₂ overlap with the S atoms (centre of the hexagon) from the lower layer, the same as that of the simulated model in Figure 2i. Additionally, a magnified image of the 1L–2L area reveals an atomically sharp boundary, as evidenced by the TEM image shown in Figure 2h. Notably, such AB-stacked layers usually exhibit strong SHG intensity due to the broken inversion symmetry,³⁶ which makes it a perfect platform to explore symmetry-dependent properties, such as optical nonlinearity and valley polarization physics.³⁷

During the NaCl-assisted CVD growth process, it was intriguing to find that, the colour of Mo foil changed from silver to grey rather than to black purple (without loading NaCl) (**Figure 3a**). This may indicate the distinct compositional transformation of the Mo foil in the current growth strategy. To understand this, the Mo foils used for MoS₂ growth with and without NaCl assistance (towards multilayer and monolayer MoS₂ growth, respectively) were compared in detail. First of all, the as-prepared commercial Mo foil is found to be relatively flat with slight oxidations (Figure 3b). After monolayer MoS₂ growth (without the assistance of NaCl), the surface of Mo foil is oxidized heavily and becomes compactly packed with MoO_x nanoparticles (size: 100–600 nm) (Figure 3c). However, after the NaCl-assisted multilayer MoS₂ growth process, numerous vertical nanosheets springs up on the Mo foil surface, along with the formation of high density MoO_x nanoparticles (Figure 3d).

To identify the accurate compositions, X-ray diffraction (XRD) measurements were then conducted on the two kinds of Mo foil precursors (**Figure S8**) after the CVD growth processes. For the NaCl-coated Mo foil for multilayer growth, two main diffraction peaks appear to be attributed to MoS₂ and MoO₂, respectively, according to PDF database (#37-1492 and #32-0671). However, for the pure Mo foil used for monolayer growth, only the MoO₂ diffraction peak emerges, suggesting the insufficient sulfurization of the Mo-O oxide precursors.

For more details, the vertical nanosheets were transferred onto SiO₂/Si by simply pressing the substrate facedown onto the Mo foil. A typical AFM image of a transferred

nanosheet is presented in Figure 3e, and the corresponding height profile analysis reveals a thickness ~ 300 nm. From Raman characterizations, two characteristic peaks are prominent at ~ 382.1 cm^{-1} (E_{2g}^1) and ~ 408.2 cm^{-1} (A_{1g}), respectively, with the frequency difference (Δ) ~ 26.1 cm^{-1} , which are in good agreement with that of thick MoS_2 reported previously.³⁸ In this regard, the Mo foil used in the NaCl-promoted growth process is sulfurized to a larger extent than that without introducing NaCl. The formation of vertical MoS_2 on Mo foils suggests that, the concentration of Mo precursor is pretty excessive on the Mo foil surface and inside the growth zone. Thereby, it is reasonable to assume that, NaCl could facilitate the volatilization of Mo vapour to provide sufficient metal-precursors, and thus accelerate the surface reaction rate in the growth of MoS_2 .^{24,25}

To attest this deduction, XPS measurements were performed on the NaCl-coated Mo foil after a typical CVD process at ~ 730 $^\circ\text{C}$ but without introducing sulfur (Figure 3f). The signals of Na_2MoO_4 , MoCl_4 , and MoO_2 are detected, similar with that from the literatures.^{39,40} The possible reaction route is as follows:

Volatile MoOCl_4 species with high chemical activities²⁵ serve as the main gas phase metal-precursors. The NaCl promoter is proposed to be removed by the gas flow in the CVD process (**Figure S9**). The Gibbs free energy for this reaction calculated by density functional theory (DFT) is estimated as -20.2 eV (see Experimental Section), suggesting its exothermic characteristic. Specifically, at the initial stage, monolayer MoS_2 flakes with small sizes were preferentially grown on the substrate from the energetically favourable point of view.⁴¹ Meanwhile, under the promotion of NaCl, the vapour pressure

of Mo precursor was significantly increased due to the formation of volatile MoOCl_4 . Nucleation and growth occurred frequently on the pre-deposited flake, leading to the formation of bilayer and multilayers. Accordingly, a layer-by-layer growth behaviour should dominate the synthesis of the wedding-cake like multilayer MoS_2 under a Mo precursor over-saturated condition.

Vertical or lateral semiconducting heterojunctions are the basic building blocks of modern optoelectronic devices, such as photodetectors,⁴² light emitting diodes⁴³ and solar cells.⁴⁴ Current methods of constructing in-plane lateral or vertically stacked van der Waals heterostructures based on TMDC materials often require deliberate alignment, stacking, or doping of the composite layers.^{45–48} Nevertheless, lateral heterojunctions of a specific TMDC material are easy to be fabricated, based on thin layer and in-plane stitched thick layers possessing different bandgaps. Javey *et al.* presented the formation of a type I lateral junction in as-exfoliated 1L–14L MoS_2 flakes from both theoretical and experimental results.⁴⁹ Furthermore, Ajayan *et al.* demonstrated layer-engineered MoSe_2 junctions achieved by direct CVD routes, and defined its rectification and photovoltaics characteristics as that of type II junctions.²⁰

To evaluate the electrical and optoelectronic properties of our CVD-grown multilayer MoS_2 , monolayer–multilayer (1L–ML) MoS_2 heterojunctions were also fabricated with the schematic shown in **Figure 4a**. The source electrode is in contact with 1L MoS_2 , while the drain electrode is in contact with ML MoS_2 . Figure 4b shows the gate-tunable $I_{\text{ds}}-V_{\text{ds}}$ characteristics of a typical 1L–25L MoS_2 heterojunction on a semi-log plot,

exhibiting excellent rectifying characteristics. The rectification ratio $I_{\text{fwd}}/I_{\text{rev}}$ (the ratio of the forward/reverse current) can be controlled by a gate voltage to $\sim 5 \times 10^3$ at $V_{\text{gs}} = 0$ V (Figure 4c), which is comparable with that reported in previous TMDC-based heterostructures (Table S1).^{20,45,48,50–52} The 1L–8L, 1L–2L MoS₂ heterojunctions presented rectification ratios $\sim 9 \times 10^2$ and $\sim 3 \times 10^2$, respectively (Figure S10, 11). Accordingly, an enhanced trend in rectification behaviour with the increasing thickness offset can thus be determined.

To better understand this issue, the energy band profile of a 1L–ML MoS₂ junction is depicted in Figure 4d. According to the theoretical bandgap values (1L: 1.8 eV, 2 L: 1.5 eV, 8 L: 1.3 eV, 25 L: 1.2 eV) (Figure S11),⁵³ the 1L–ML MoS₂ band alignment introduces a type I junction, where the conduction band minimum (CBM) and the valence band maximum (VBM) of ML MoS₂ are located lower or higher than that of monolayer MoS₂, respectively.⁵² Electrons transfer from the MoS₂ layer with a higher Fermi level to the layer with a lower one (from 1L to ML), affording a built-in electric field between the junction. When a forward bias is applied, the built-in potential decreases, promoting the flow of electrons from 1L to ML. On the contrary, the build-in potential increases and much less electrons can overcome the relatively large potential barrier.⁵⁴ As a rule, the band offsets are increased accordingly, with the increasing layer number differences (for 1L–2L, 1L–8L and 1L–25L MoS₂ junctions), accounting for the gradually increased rectification ratios.

Furthermore, photoresponse properties of these devices were also recorded by examining the photocurrent generation at the heterojunction. A comparison of different samples is shown in Figure S12. Herein, the 1L–25L MoS₂ sample is listed as an example, considering of the larger light absorption. The transfer curve (I_{ds} - V_{gs}) (under 660 nm light illumination) is presented in Figure 4e, which shows a typical n-type behaviour. Moreover, photoresponsivity (R) and detectivity (D^*) are important parameters to evaluate the ability of photodetectors to convert light into electrical signals, and to measure the detector sensitivity under a certain wavelength. Herein, $R = (I_{light} - I_{dark})/P_{incident}$, $D^* = A^{1/2} R/(2qI_{dark})^{1/2}$, where I_{light} , I_{dark} , $P_{incident}$, A and q are photocurrent, dark current, incident power, absorbing area and electronic charge, respectively.¹⁰ Based on this, R and D^* are estimated by varying the applied V_{gs} (Figure 4f and **Figure S13**), presenting maximum values as $\sim 1 \times 10^4$ A/W (at $V_{gs} = 0$ V) and $\sim 1.6 \times 10^{13}$ Jones (at $V_{gs} = -18$ V), respectively. These two data are much higher than the vertical and lateral TMDC-based heterojunctions reported previously (**Table S2**).^{46,47,54–60} This rather high device performance, in return, indicates the extra high crystal quality of our CVD-derived MoS₂ multilayers. Briefly, 1L–ML MoS₂ lateral heterojunctions with tunable band alignments can serve as perfect candidates for constructing high performance electronics and optoelectronics. The layer controlled synthesis of high quality, large domain size, large-scale multilayer MoS₂ flakes makes this concept device becomes more realistic.

Due to the narrower bandgap (< 1.8 eV) of multilayer MoS₂, higher light absorbance and wider spectrum response than that of monolayer MoS₂ can be realized from UV to near

infrared (NIR) wavelength regions, thus possessing great advantages in a variety of photoprotection applications. As is well-known that, UV-A (315–400 nm) and UV-B (280–315 nm) are the two main solar radiations reaching the earth's surface, which can induce dose-related damage to our eyes.⁶¹ Hereby, contact lenses and spectacles have been designed as effective UV absorbers, and offered good protection to us. Considering of the prominent UV and visible light absorption property of multilayer MoS₂, combined with its flexibility and transparency, it is promising to utilize multilayer MoS₂ as an active component in UV irradiation filtering glasses. A key advantage of this proposal is to allow for the scalable production capability of thickness tunable MoS₂ flakes on low-cost soda-lime glass, which has balanced UV and visible light absorption properties and optical transparency.

To explore the living organisms related applications, the first step is to examine the biocompatibility of the CVD-derived MoS₂ materials. To achieve this, the adhesion, viability and proliferation behaviours of NIH-3T3 mouse fibroblasts were investigated using our monolayer MoS₂. Notably, considering the hydrophilicity nature of the glass substrate, the multilayer MoS₂ samples were transferred onto the hydrophobic PDMS substrate to prevent being peeled off by the nutrient solution. NIH-3T3 cell is commonly used as a typical cell line for testing the cytocompatibility of biomaterials through examining cell adhesion, spreading and proliferation behaviours.⁶² In this work, early adhesion behaviour of NIH-3T3 fibroblast was characterized by imaging optical phase contrast image of adhered cells on MoS₂/PDMS at early culture time ~1.5 h (**Figure 5a**). Surprisingly, the fibroblasts are more prone to adhere and spread on the MoS₂ covered

surface rather than on the bare substrate, which can be ascribed to the properties of MoS₂, like wettability, absorbability, and topological structure.⁶³ Furthermore, it was confirmed that, MoS₂ had no adverse effect on cell viability, since almost all the cells were stained with calcein-AM (green; indicates live cell), while no cell was stained with ethidium homodimer (EthD-1, red; indicates dead cell) after culturing for ~24 h (Figure 5b, c). The F-actin filament was also labelled with phalloidin to characterize the spreading and cytoskeleton structure of cultured cells (Figure 5d). All cultured NIH-3T3 fibroblast exhibited clear and typical stress fibre structures, suggesting a favourable spreading behaviour. Moreover, as illustrated in **Figure S14**, the thickness of MoS₂ layer makes negligible difference to the viability and proliferation behaviours of the cells. A good biocompatibility of our CVD-derived MoS₂ can thus be derived, which may be engineered for versatile applications in related fields.

For the sunglass lenses, except for biological safety, it is crucial to provide desired UV blocking while maintaining sufficient transmittance in the visible region. Figure 5e first demonstrates the use of MoS₂ films as optical windows with colour-tunable transparencies. Photographs from front to back correspond to bare glass and MoS₂-coated glass with variable thicknesses (~1L, ~2L, ~5L, ~21L), respectively. As described by the gradual colour contrast changes, the transparencies are accordingly decreased. Specifically, at a wavelength of 550 nm, the transmittance is ~85.0% for the ~1L MoS₂, and gradually declines to ~57.7%, ~50.1% and ~24.8% for ~2L, ~5L and ~21L MoS₂, respectively (Figure 5f). The UV-B absorptions for the four types MoS₂ flakes films are beyond ~95%, and the average UV-A absorptions are larger than that of the visible

absorptions, adequately meeting the requirements of China National Standards for Sunglasses QB 2457-99 for practical production. The wide choice of transmittance offered by thickness tunable MoS₂ could afford different levels of protection. In particular, the ~2L and ~5L MoS₂ flakes films are more appropriate for practical applications owing to the perfect balance between visible transmittance and UV absorbance. Besides, it is worthwhile to note that, such discontinuous MoS₂ flakes films with micrometer-scale distances/gaps are superior to continuous films for providing natural channels for the permeability of salt ions (ionic diameter: 0.6–4 Å) and oxygen (molecular diameter: ~3.6 Å), which are necessary to maintain corneal health.

The sufficient optical transmittance in the visible region along with a high UV absorbance makes multilayer MoS₂ perfect candidate for transparent, flexible photoprotection applications. To demonstrate this, prototype UV filtering spectacles and contact lenses were fabricated using the as-grown multilayer MoS₂ films, as shown in Figure 5h,i (detailed fabrication route shown in Experimental Section). In practical applications, the soft contact lens offer more protection than the rigid ones, for their full contact with entire cornea. Notably, only a few UV filtering contact lenses are currently available at the market, and the main components are the typical hydrophobic silicone hydrogels added with UV absorbents, such as benzophenone and benzotriazole. Although the effects of many other factors still need to be well addressed before practical use, our flexible atomically thin MoS₂ with good hydrophilicity, biocompatibility and optimal optical properties could serve as promising UV absorbents with much improved degree of comfort in use, which may be readily applicable to UV filtering contact lenses.

Conclusion

In summary, by using the face-to-face metal-precursor supply route, we have successfully synthesized large-area, thickness tunable MoS₂ flakes on solid soda-lime glass with the assistant of NaCl promoter. Such a synthetic strategy guarantees the batch production of MoS₂ with homogenous thickness distribution considering of the efficient and homogenous delivery of molybdenum precursors. The NaCl promoter is confirmed to play a crucial role in the multilayer MoS₂ growth by increasing the vapour pressure of metal-precursors. The layer-controlled MoS₂ synthesized using this method is already found to be a perfect candidate for a next generation of multifunctional optical material, *e.g.*, in high performance photodetectors and in UV-filtering eyewear. This research hereby provides a robust pathway for the scalable production of high-quality, layer-controlled TMDCs, and offering insights into their daily life related applications.

Experimental Section

NaCl-Assisted Synthesis of Multilayer MoS₂. The growth of multilayer MoS₂ on soda-lime glass was performed inside a 3-inch diameter quartz tube of a CVD system. A 14×6 cm² Mo foil (99.95%; 0.025 mm thick) was immersed into the NaCl solution for 5 min and pulled out slowly. After baking on the hot plate at 100 °C for 10 min, the NaCl-coated Mo foil was folded into a bridge and placed over the glass substrate with a distance ~1 cm. The sulfur powder (99.5%) were placed on the upstream region, ~20 cm away from the glass substrate. Then, the soda-lime substrate and Mo foil were heated to ~730 °C in Ar (50 sccm) and O₂ (3 cm) atmosphere in 25 min. After CVD growth for ~8 min, the furnace was cooled to room temperature naturally.

Etching-Free Transfer of MoS₂ Flakes. First, the as-grown MoS₂/glass was spin-coated with polymethyl methacrylate (PMMA) (950 K, Allresist, AR-P 679.04) at 80 rpm for 1 min followed by curing at 80 °C for 10 min. Then, the edge of the PMMA film was scored using a knife for the water penetration. Next, the PMMA/MoS₂/glass was inclined against the edge of a petri dish, and deionized water was injected slowly to separate the PMMA/MoS₂ stack from the glass substrate. The delaminated stack was then transferred to target substrates. Finally, the PMMA was removed by soaking in acetone.

Characterizations. OM (Nikon ECLIPSE, LV100ND), Raman spectroscopy (HORIBA, Lab-RAM HR-800, with an excitation wavelength 532 nm), AFM (Bruker, Dimension Icon), XPS (Kratos Analytical AXIS-Ultra with monochromatic Al K α X-ray), UV-Vis-NIR spectrophotometer (Shimadzu UV3600Plus), TEM (JEOL JEM-2100F) and STEM (Titan Cubed Themis G2) were used to characterize the optical and structural properties of the MoS₂ samples.

Fabrication and Characterization of 1L–ML MoS₂ Devices. Multilayer MoS₂ samples were first transferred onto 90 nm SiO₂/Si substrates using the abovementioned etching-free transfer method. Metal source/drain contacts were deposited on the 1L and ML regions of MoS₂, respectively. The devices were then fabricated by a standard e-beam lithography and metallization processes. The electrodes were made of Ti/Au (10/50 nm). The resulting structure is shown in Figure 4a, with channel length (L) $\sim$ 3 μ m and width (W) $\sim$ 13 μ m. The electronic and optical properties of 1L–ML MoS₂ heterojunction were characterized with an Agilent B1500 parameter analyser at room temperature in air

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2
3 ambient conditions. The monochromatic lights with different wavelengths were provided
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5 by CEL-LEDS35 LED illuminant system (CEAULIGHT).
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7 ***Cell Culture Experiment.*** NIH-3T3 cells were cultured in the 37 °C, 5% CO₂ incubator
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9 with Dulbecco's modification of Eagle's medium (DMEM) supplemented with 10% (v/v)
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11 fetal bovine serum (FBS), 100 U/mL streptomycin, and 100 U/mL penicillin. In order to
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13 assess the effect of MoS₂ on the adhesion behaviour of NIH-3T3 cells, the early adhesion
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15 of NIH-3T3 cell was measured (after the cells were seeded for 1.5 h) through acquiring
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17 the optical phase contrast images of adhered cells on MoS₂ samples. In order to test the
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19 cytotoxicity effect of MoS₂ flakes, dead NIH-3T3 cells were identified with Live/Dead
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21 viability/cytotoxicity assay kit (Molecular Probes, Thermo Fisher Scientific) according to
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23 the manufacture's instruction. Briefly, NIH-3T3 cells were incubated with a live/dead
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25 cells staining solution (2 µM acetol methoxy derivative of calcein (calcein AM, green;
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27 live) and 4 µM ethidium homodimer (EthD-1, red; dead)) for 35 min at room temperature.
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29 Then, fluorescence images of live and dead cells were obtained from twenty random
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31 fields for each sample by fluorescence microscopy (IX71, Olympus, Japan). To label F-
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33 actin and cell nucleus with fluorescent probe, NIH-3T3 cells cultured on MoS₂ flakes for
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35 24 h were fixed with 4% paraformaldehyde for 30 min, and permeabilized with 0.1%
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37 Triton X-100 for 10 min. Then, the fixed cells were stained with TRITC-Phalloidin and
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39 DAPI, respectively. Subsequently, the labeled cells were imaged by laser confocal
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41 scanning microscopy (PerkinElmer, Massachusetts, USA).
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49 ***Fabrication of Multilayer MoS₂ UV Filtering Eyewear.*** For the MoS₂ UV filtering
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51 spectacles, a ~5L MoS₂ flakes films were transferred to commercial spectacles using the
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53 etchant-free transfer strategy mentioned above. For the MoS₂ UV-absorbing contact
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lenses, as described in **Figure S15**, a Parylene-C film with a thickness of $\sim 25\ \mu\text{m}$ was first deposited onto the as-grown hemispherical $\sim 2\text{L}$ $\text{MoS}_2/\text{glass}$ complex and then detached by water to keep the shape of contact lens, which is the same as the graphene contact lens made in the literature.⁶⁴

Theoretical Calculation. The calculations were performed within the framework of DFT with electron project augmented wave (PAW) method,⁶⁵ which was implemented in the Vienna *Ab-initio* Simulation Package (VASP).⁶⁶ The exchange-correlation potentials were treated by the Perdrew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA). A $9\times 9\times 9$ and $1\times 1\times 1$ k-point grid was adopted for solid and gas-phase material, respectively. The plane-wave cutoff energy was chosen at 500 eV and all the structures were fully relaxed with the convergence criteria set to 10^{-5} eV/cell in energy and 0.01 eV/Å in force. For detailed calculations and parameter settings, please see the SI.

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Associated Content

Supporting Information Available. Figures S1–S15 and Table S1, S2. This material is available free of charge *via* the Internet at <http://pubs.acs.org>

Conflict of Interest. The authors declare no competing financial interest.

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Figure 1. LPCVD growth of layer-controlled, wedding-cake like MoS₂ flakes on soda-lime glass with the assistance of NaCl. (a) Schematic diagram of the NaCl-assisted growth process. (b–d) OM images of ~1L, ~2L, ~5L MoS₂ synthesized at ~730 °C in 8 min, with variable NaCl concentrations of 0, 0.05, 0.10 mmol/L, respectively. (e) AFM image of a typical wedding-cake like MoS₂ flake showing a thickness ~2.9 nm. (f, g) Raman and PL mapping images of the MoS₂ flake in (e). (h) Average thickness variations of MoS₂ multilayers with varied NaCl concentrations. Insets are corresponding optical images of MoS₂ flakes on soda-lime glass, showing gradually darker contrasts with increasing thicknesses. (i) Photographs of the achieved 6-inch MoS₂/glass samples with layer number of ~1L, ~2L, ~5L, in line with that of Figure 1b–d, respectively. The relative uniform distributions of the flakes can be observed from the uniform colour contrasts.

Figure 2. Layer-dependent optical properties and stacking configurations of MoS_2 flakes. (a,b) Raman and PL spectra of the MoS_2 flakes shown in Figure 1(h). (c) Frequency differences between E_{2g}^1 and A_{1g} Raman peaks (left panel) and the PL peak positions (right panel) as a function of layer thickness. (d) STEM image of a typical multilayer MoS_2 flake transferred on a TEM grid. (e) Typical SAED pattern of the regions numbered 1–3 in (d) (in line with 1L, 2L, 3L, respectively). (f) Atomic-scale STEM image of the monolayer MoS_2 region, revealing a honeycomb structure with the interatomic distance ~ 0.32 nm. The blue and yellow balls present Mo and S atoms, respectively. (g) STEM images of the 1L–2L stacked edge showing an atomically sharp step. (h) Enlarged view of the stacked edge in (g). (i) Atomic model of AB-stacked bilayer MoS_2 . The Mo (S) atom from the upper layer MoS_2 overlaps with the S atom (centre of the hexagon) from the lower layer.

Figure 3. The role of NaCl in promoting the multilayer growth of MoS₂. (a) Photographs of the as-prepared Mo foil (left) and after used for MoS₂ growth, without and with NaCl-coated (middle, right), respectively. (b–d) SEM images of the as-prepared Mo foil, and the Mo foils used for MoS₂ growth without and with NaCl-coating, respectively. (e) AFM image and corresponding height profile of the vertical nanosheets in (d) transferred on SiO₂/Si. The inset Raman spectrum confirms it is bulk-like MoS₂. (f) XPS data of Mo foil used for the NaCl-assisted CVD route but without introducing sulfur precursor.

Figure 4. High performance photodetector applications of 1L-ML MoS₂ heterojunctions. (a) Schematic of the photodetector device. (b) Gate tunable I_{ds} – V_{ds} characteristics of the 1L–25L MoS₂ lateral junction. (c) Rectification ratio I_{fwd}/I_{rev} of the 1L–2L, 1L–8L, 1L–25L MoS₂ heterojunctions as a function of V_{gs} . (d) Band diagram of the 1L–ML MoS₂ heterojunction in the off state ($V_{gs}=0$, $V_{ds}=0$). Red and blue spheres correspond to electrons and holes, respectively. (e) I_{ds} – V_{gs} curves of the 1L–25L MoS₂ heterojunction with and without 660 nm light illumination. The inset shows the OM image of the device. (f) V_{gs} -dependence of photoresponsivity.

Figure 5. Application of uniformly distributed few-layer MoS₂ flakes as coating layer in UV irradiation filtering eyewear. (a) Representative optical image of early adhesion of 3T3 cells on monolayer MoS₂ flakes. Inset: enlarged view of cultured cells on a typical MoS₂ domain, scale bar: 80 μm. (b, c) Fluorescent image of live and dead 3T3 cells cultured for 24 h labelled by Calcein-AM and EthD-1, respectively. (d) Fluorescent image of cytoskeleton (red) of 3T3 cells cultured on MoS₂ covered PDMS. (e) Photographs of bare glass and MoS₂-coated glass with ~1L, ~2L, ~5L and ~21L MoS₂, respectively (from front to back). (f) UV-visible absorption spectra of different MoS₂ layers. (g) Schematic drawing of MoS₂ UV filtering eyewear. (h) Prototype UV-absorbing spectacle fabricated by transferring a ~5L MoS₂ film onto a commercial plain glasses. (i) Photograph of a flexible ~2L MoS₂/Parylene-C UV-absorbing contact lens.

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