

CVD synthesis of large-area, highly crystalline MoSe₂ atomic layers on diverse substrates and application to photodetectors†

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Synthesis of large-area, atomically thin transition metal dichalcogenides (TMDs) on diverse substrates is of central importance for the large-scale fabrication of flexible devices and heterojunction-based devices. In this work, we successfully synthesized a large area of highly-crystalline MoSe₂ atomic layers on SiO₂/Si, mica and Si substrates using a simple chemical vapour deposition (CVD) method at atmospheric pressure. Atomic force microscopy (AFM) and Raman spectroscopy reveal that the as-grown ultrathin MoSe₂ layers change from a single layer to a few layers. Photoluminescence (PL) spectroscopy demonstrates that while the multi-layer MoSe₂ shows weak emission peaks, the monolayer has a much stronger emission peak at ~1.56 eV, indicating the transition from an indirect to a direct bandgap. Transmission electron microscopy (TEM) analysis confirms the single-crystallinity of MoSe₂ layers with a hexagonal structure. In addition, the photoresponse performance of photodetectors based on MoSe₂ monolayer was studied for the first time. The devices exhibit a rapid response of ~60 ms and a good photoresponsivity of ~13 mA/W (using a 532 nm laser at an intensity of 1 mW mm⁻² and a bias of 10 V), suggesting that MoSe₂ monolayer is a promising material for photodetection applications.

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1. Introduction

The experimental realization of graphene has triggered a worldwide upsurge in research interest on other two-dimensional (2D) layered materials such as VS₂, CoS₂, GaSe, h-BN and NbSe₂.^{1–7} These 2D crystals exhibit a variety of electrical characteristics including metallic, semimetallic, semiconducting, insulating, and charge density wave behaviour. In particular, atomically-thin group-VIB transition metal dichalcogenides (TMDs) (MX₂; M = W, Mo; X = S, Se) are a new class of 2D semiconductors with extraordinary properties and tremendous application potential.^{8–11} For example, while the bulk of TMDs have an indirect bandgap, the monolayers show a sizable direct bandgap around 1–2 eV, making them appealing materials for ultrathin, lightweight, and flexible device applications such as field effect transistors (FETs), photovoltaic cells, light emitting diodes (LEDs) and photodetectors.^{8,12–15} Interestingly, the

electronic structures of these materials can be effectively modulated by partially substituting the metal or nonmetal atoms with their congeners, forming 2D TMD alloys (Mo_{1–x}W_xS₂, Mo_{1–x}W_xSe₂, MoS₂(1–x)Se_{2x}, etc.).^{16–19} The availability of various alloys with tunable bandgaps will not only promote fundamental studies of these materials, but will also allow their practical application in electronics and optics. Recent studies have demonstrated that the breaking of inversion symmetry together with the spin-orbit interaction could result in the coupling of spin and valley physics in monolayer TMDs, making it possible to manipulate the spin and valley degrees of freedom in these novel 2D crystals.^{20–22}

Until now, most studies on group-VIB TMDs have concentrated on MoS₂. Other group-VIB TMDs such as MoSe₂, however, possess attractive properties. For instance, monolayer MoSe₂ has a direct bandgap of ~1.5 eV, which is close to the optimal bandgap value of single-junction solar cells and photoelectrochemical cells.^{23,24} Few-layer MoSe₂ has nearly degenerate indirect and direct bandgaps, and an increase in temperature can effectively push the system towards the 2D limit.²⁴ In contrast to MoS₂, monolayer MoSe₂ has a larger spin-splitting energy of ~180 meV at the top of the valence bands, which makes MoSe₂ more applicable than MoS₂ in spintronics.^{25,26} While some methods including exfoliation (chemical or mechanical) from the bulk,^{27–29} hydrothermal synthesis,^{27,30} and selenization of metals^{31,32} have been used to produce MoSe₂ nanosheets, none of these approaches are able

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to synthesize large-area, uniform, and highly-crystalline MoSe₂ atomic layers. Although molecular beam epitaxy (MBE) is a facile method to grow large-scale ultrathin MoSe₂ layers of high quality,²⁶ it is not suitable for industrial production because of its high cost. Until recently, CVD has been used to successfully grow large-area ultrathin MoSe₂ layers on SiO₂/Si substrates.^{33–35}

For different applications such as flexible devices^{36–39} and heterojunction-based devices,^{40–43} however, the growth of MoSe₂ atomic layers on SiO₂/Si substrates is not sufficient; different functionalities require the integration of MoSe₂ with different kinds of materials. Therefore, the synthesis of large-scale, high-quality, ultrathin MoSe₂ layers on diverse substrates is necessary. To this end, we herein report a simple CVD method to directly grow a large area of highly-crystalline MoSe₂ atomic layers on SiO₂/Si, mica and Si substrates at atmospheric pressure using MoO₃ and Se powders as starting materials. Scanning electron microscopy (SEM), optical microscopy (OM), AFM, Raman spectroscopy, PL spectroscopy, and TEM have been used to systematically study the samples. In addition, photodetectors based on monolayer MoSe₂ were fabricated and studied for the first time. The devices exhibited a fast response and a good photoresponsivity.

2. Experimental section

Growth of MoSe₂ atomic layers

We obtained MoSe₂ layers by the selenization of MoO₃ powder (99.99%, Beijing Lanyi Chemical Co., Ltd) in a high temperature CVD furnace (GSL-1400X tube furnace, Hefei Kejing Material Technology Co., Ltd). In a typical CVD growth, a ceramic boat containing 10 mg of MoO₃ powder located at the centre of the heating zone and another ceramic boat with 0.5 g of Se powder (99.99%, Beijing Lanyi Chemical Co., Ltd) located upstream of the furnace 10–20 cm away from the MoO₃ powder were placed in the furnace. Cleaned 300 nm SiO₂/Si, mica and the newly-cleaved side-wall of SiO₂/Si substrates were placed downstream close to the MoO₃ powder along the quartz tube. The furnace chamber was vacuum pumped to expel the air and then filled with high-purity Ar to atmospheric pressure. Next, the centre of the heating zone was heated to 820 °C within 41 min and kept for 15 min before being allowed to cool naturally. During the growth process, high-purity Ar with a flow rate of 10 standard cubic centimeters per minute (sccm) was used as the gas carrier.

Characterization

SEM characterization was carried out on a Hitachi S-4800 with an acceleration voltage of 5–10 kV. Optical images were obtained using an optical microscope (Nikon Inverted Microscope Eclipse Ti-U with a CCD of Nikon Digital Sight). The thickness profile was determined using an atomic force microscope (Veeco Nanoscope V) at a scanning rate of 0.976 Hz with 512 scanning lines. Raman spectra and PL spectra were recorded with a Renishaw InVia Raman microscope with a 50× objective. The Si peak at 520 cm^{−1} was used as a reference for wavenumber calibration. For the Raman and PL measurements, we used a 532 nm laser and an 1800 I mm^{−1} grating. The laser

was focused on the sample at a power of ~250 μW to minimize the laser-induced thermal effect. The structure and composition of MoSe₂ samples were investigated by a JEOL JEM-2100F at an acceleration voltage of 200 kV and energy dispersive X-ray spectroscopy. For TEM characterization, an ultrathin carbon film supported on a copper grid was used. The method for transferring the MoSe₂ sample is similar to that in the previous report on the direct transfer of graphene.⁴⁴ In our experiments, we didn't wet the sample with isopropanol; instead, 1% HF solution was used directly as the etchant. The detailed procedures are shown in ESI Fig. S2.†

Photodetectors based on monolayer MoSe₂ were fabricated by evaporating 100 nm Au directly on the top of MoSe₂ layers patterned by electron beam lithography (Raith 150). Photocurrent measurement was performed at room temperature under atmospheric conditions. The illuminating 532 nm laser was generated by Spectra-Physics Laser. A laser attenuator was used to obtain different laser intensities, which were confirmed by a laser power meter. The electrical measurement was carried out using a Keithley-4200SCS semiconductor parameter analyser.

3. Results and discussion

In this work, a high-temperature tube furnace was used for the CVD synthesis of MoSe₂ atomic layers; the schematic representation of the growth setup is displayed in Fig. 1a. During the CVD growth, the centre of the heating zone was heated to 820 °C under Ar atmosphere (see details in the experimental section). At such a high temperature, MoO₃ powder was partially reduced by Se vapour to form volatile suboxide MoO_{3−x} species that were transported downstream by the Ar carrier gas.⁴⁵ Selenization of vapour-phase MoO_{3−x} could then produce MoSe₂ species, which nucleated on the substrate and grew into large MoSe₂ atomic

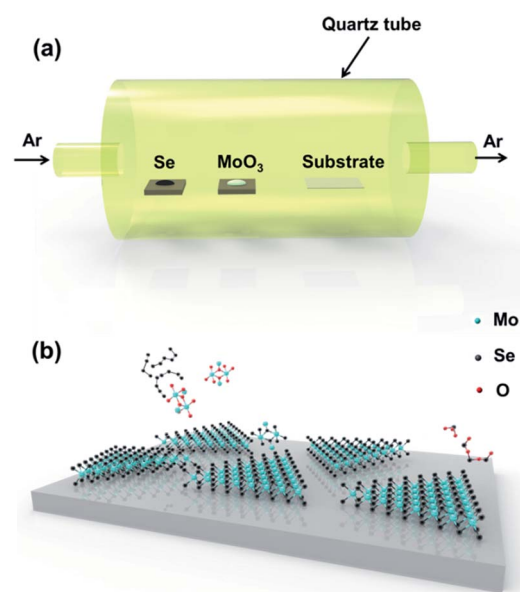


Fig. 1 (a) Growth setup for synthesizing MoSe₂ atomic layers. (b) A schematic view illustrating the growth of MoSe₂ layers.



layers.^{45–47} The corresponding schematic is illustrated in Fig. 1b. Recent reports on the growth of MoSe₂ atomic layers have used a similar CVD approach.^{33–35} In their syntheses, the growth was performed at 750 °C or 800 °C under an Ar–H₂ gas mixture environment in which H₂ gas acted as an indispensable reducing agent. Interestingly, in our method, the CVD growth could take place efficiently without the use of H₂.

Fig. 2a–c show typical SEM images of large-area MoSe₂ layers grown on SiO₂/Si, mica and Si substrates, respectively. The spatial distribution of MoSe₂ layers (darker contrast in Fig. 2a–c) indicates that MoSe₂ nucleates randomly on the substrates. For samples grown on SiO₂/Si and mica substrates, most of the isolated MoSe₂ islands have equilateral triangle morphologies with edge lengths ranging from a few microns to 40 μm (Fig. 2a and b), suggesting the single crystalline nature of these domains.^{35,48} In contrast, MoSe₂ layers synthesized on the cleaved side-wall of SiO₂/Si substrates show irregular shapes with sizes larger than 50 μm (Fig. 2c). This result indicates that the substrates have an important influence on the morphology of TMDs.^{48,49}

Fig. 2d and e display OM images of MoSe₂ layers grown on SiO₂/Si and mica substrates, respectively. The sharp colour contrast between the triangular crystallites (greyish triangular

flakes in Fig. 2d; white triangular flakes in Fig. 2e) and the substrates (violet area is the bare SiO₂/Si substrate in Fig. 2d; black regions represent the mica in Fig. 2e) demonstrates the high uniformity of the MoSe₂ domains. The thickness-dependent contrast observed in the OM images reveals single-, bi-, tri- and multi-layered MoSe₂ flakes, as marked in Fig. 2d. To determine the thicknesses of these MoSe₂ layers, they were characterized with AFM. Fig. 2f shows the AFM image and height profile of a monolayer MoSe₂ triangle. The homogeneous colour contrast signifies that this flake has a flat and uniform surface, and its thickness (0.71 nm) confirms that this MoSe₂ triangular flake is a monolayer.^{24,29} AFM images and height profiles are also shown for bilayer and trilayer MoSe₂ (Fig. S1†).

In order to investigate the crystal structure of the MoSe₂ flakes, a direct transfer approach was used to prepare TEM samples. The approach is not only suitable for 2D MoSe₂, but also other 2D crystals such as MoS₂, WS₂ and WSe₂ grown on SiO₂/Si, mica and Si substrates. Unlike PMMA-assisted transfer technology,³⁵ the direct transfer method is much more rapid and convenient. The detailed procedure can be found in Fig. S2.† Fig. 3a displays a bright-field TEM image of a monolayer MoSe₂ triangular flake with an edge length of ~3.5 μm. The lattice fringe measured from the high-resolution TEM

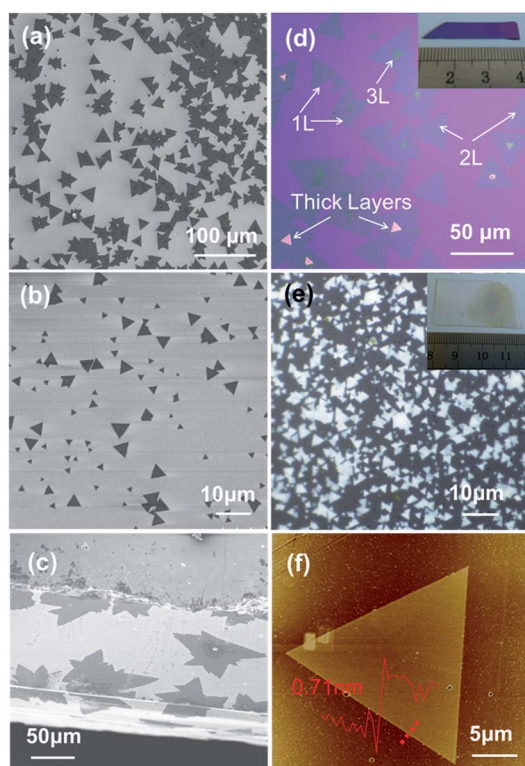


Fig. 2 SEM images of MoSe₂ layers synthesized on (a) SiO₂/Si, (b) mica and (c) Si substrates. (d) Optical image of MoSe₂ layers on a SiO₂/Si substrate. The violet area is the bare SiO₂/Si substrate; the greyish, light green and pink triangles represent MoSe₂. The inset shows a photograph of 2D MoSe₂ grown on the SiO₂/Si substrate. (e) Optical image of MoSe₂ layers on a mica substrate. The inset shows a photograph of 2D MoSe₂ grown on the mica substrate. White triangular flakes represent MoSe₂; the black area is the mica. (f) AFM image and height profile of an MoSe₂ monolayer.

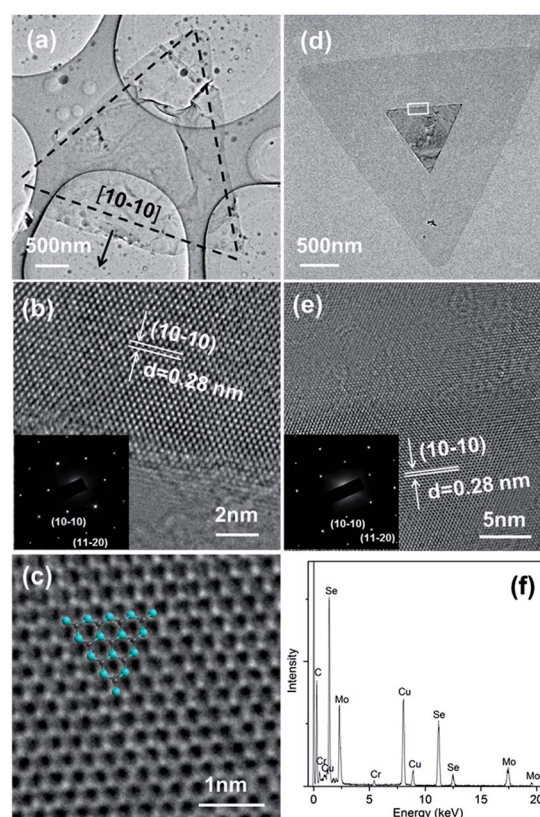


Fig. 3 (a) Bright-field TEM image of a monolayer MoSe₂ triangle. (b) HRTEM image of the MoSe₂ triangle. The inset shows the SAED pattern. (c) HRTEM phase-contrast image of the MoSe₂ triangle. The inset shows the hexagonal arrangement of Mo and Se atoms. (d) Bright-field TEM image of a few-layer MoSe₂ triangle. (e) HRTEM image and corresponding SAED pattern of the marked region in Fig. 3d. (f) EDX spectrum of the MoSe₂ layers.



(HRTEM) image in Fig. 3b is 0.28 nm, corresponding to the $\{10\bar{1}0\}$ planes. The selected area electron diffraction (SAED) pattern (inset in Fig. 3b) from the MoSe₂ triangle exhibits one set of six-fold symmetry diffraction spots, confirming the single-crystalline nature of this flake with a hexagonal structure. By analysing the HRTEM image in Fig. 3b, we see that the edge of the MoSe₂ triangle is perpendicular to the $[10\bar{1}0]$ direction, indicating that the sample has zigzag edges.^{50,51} The HRTEM phase-contrast image (Fig. 3c) of the MoSe₂ triangle shows a honeycomb-like structure, which is consistent with previous reports.^{47,51}

Few-layer MoSe₂ was characterized in addition to monolayer MoSe₂ (Fig. 3d and e). The bright-field TEM image in Fig. 3d shows a few-layer MoSe₂ triangle with a small triangular island on the top. Intriguingly, the small triangular island is located both at the centre of the bottom triangle and parallel to it, indicating an AB stacking growth mode.^{33,52} The HRTEM image of the marked region in Fig. 3d is displayed in Fig. 3e. The interface between adjacent layers can be distinguished due to the contrast difference. The corresponding SAED pattern in Fig. 3e demonstrates the single-crystallinity of the few-layer MoSe₂ with a hexagonal structure. Furthermore, energy dispersive X-ray spectroscopy (EDX) equipped in TEM was applied to study the composition of the MoSe₂ samples. As shown in Fig. 4f, the intense peaks of Mo and Se confirm that MoO₃ has been successfully converted into MoSe₂.

The as-synthesized MoSe₂ layers were further investigated by Raman spectroscopy using a 532 nm excitation laser (Fig. 4a). Two typical Raman active modes, *i.e.*, the prominent A_{1g} Raman mode and the weak E_{2g} Raman mode, are observed in the Raman spectra. The A_{1g} mode relates to the out-of-plane vibration of Se atoms, and the E_{2g} mode is associated with the in-plane vibration of Mo and Se atoms (see the inset in Fig. 4a). In general, the location of Raman modes can be used to determine the thickness of 2D materials.^{6,45,53} In this study, the A_{1g} and E_{2g} modes of single-layer MoSe₂ are located at 240.6 cm⁻¹ and 287.5 cm⁻¹, respectively (Fig. 4a). As the layer thickness increases, the A_{1g} Raman mode is blueshifted to 242.3 cm⁻¹ for 2–3L, and to 243.9 cm⁻¹ for thick MoSe₂; the E_{2g} Raman mode exhibits a redshift to 285.9 cm⁻¹ for ≥ 2 L. The stiffening of the A_{1g} mode may result from the increasing van der Waals interaction between layers, while the softening of the E_{2g} mode may be caused by the presence of long-range coulomb interactions between layers.^{54–56} Similar phenomena have been previously reported in other 2D materials including graphene, h-BN, MoS₂ and GaSe.^{5,6,45,53} The frequency difference between the E_{2g} and A_{1g} modes is another important indicator of the thickness of 2D materials, although different substrates may have an effect. In our case, the peak spacing between E_{2g} and A_{1g} modes decreases as the layer number increases. The spacings are 46.9 cm⁻¹, 43.6 cm⁻¹ and 42 cm⁻¹ for MoSe₂ monolayers, 2–3L and thick samples, respectively.

Recent studies have demonstrated that the electronic structure of MoSe₂ varies with its thickness.^{8,11} To confirm this behaviour in the CVD-grown samples, PL experiments (532 nm laser) were carried out. Fig. 4b shows the room-temperature PL spectra of MoSe₂ layers of different thicknesses. It can be seen that

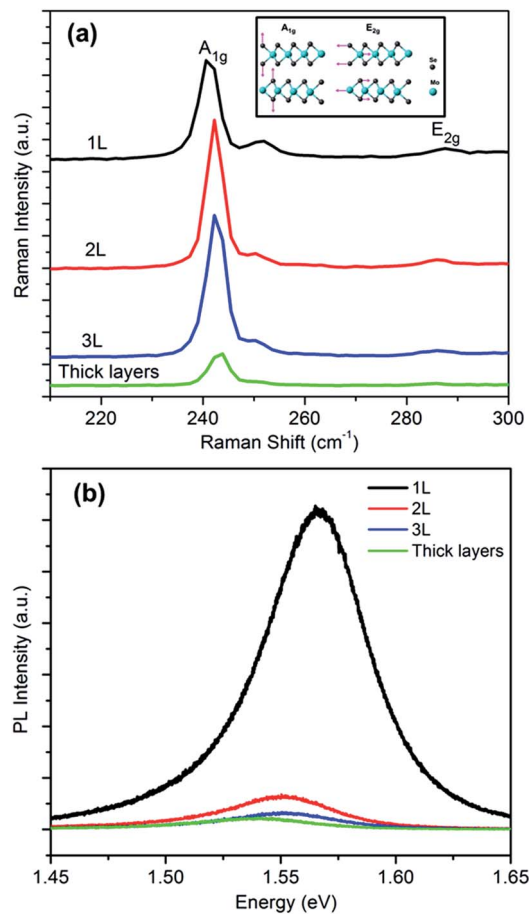


Fig. 4 (a) Raman spectra of MoSe₂ layers with different thicknesses. The inset shows schematic representations of the A_{1g} and E_{2g} modes. (b) Room-temperature PL spectra of MoSe₂ layers with different thicknesses.

monolayer MoSe₂ exhibits a single emission peak at ~1.56 eV with a very strong PL intensity; which can be ascribed to the direct bandgap at the K high symmetry point of the Brillouin zone.²⁴ With increasing layer number, PL intensity declines sharply. For example, the PL intensity of bilayer MoSe₂ is approximately 10-times weaker than that of the monolayer (Fig. 4b). As the thickness increases, the PL peak is also redshifted to ~1.54 eV for thick MoSe₂ layers. The change in PL intensity and bandgap should be attributed to the transition from direct to indirect bandgap, which has been previously reported.²⁴ Generally, Raman spectra and PL spectra demonstrate the high quality of the as-grown MoSe₂ atomic layers in this study.

Due to its sizeable direct bandgap of ~1.56 eV, monolayer MoSe₂ could be a promising candidate for photodetection applications. In view of this, photodetectors based on monolayer MoSe₂ were fabricated using electron beam lithography and metal evaporation, as illustrated schematically in Fig. 5a. In this study, Au was used as the metal electrode due to its large work function.^{57,58} In general, 100 nm of Au was deposited on the top of the MoSe₂ monolayers by electron beam evaporation. The as-fabricated devices were then annealed at 200 °C for 2 h in an Ar atmosphere to improve the contact.



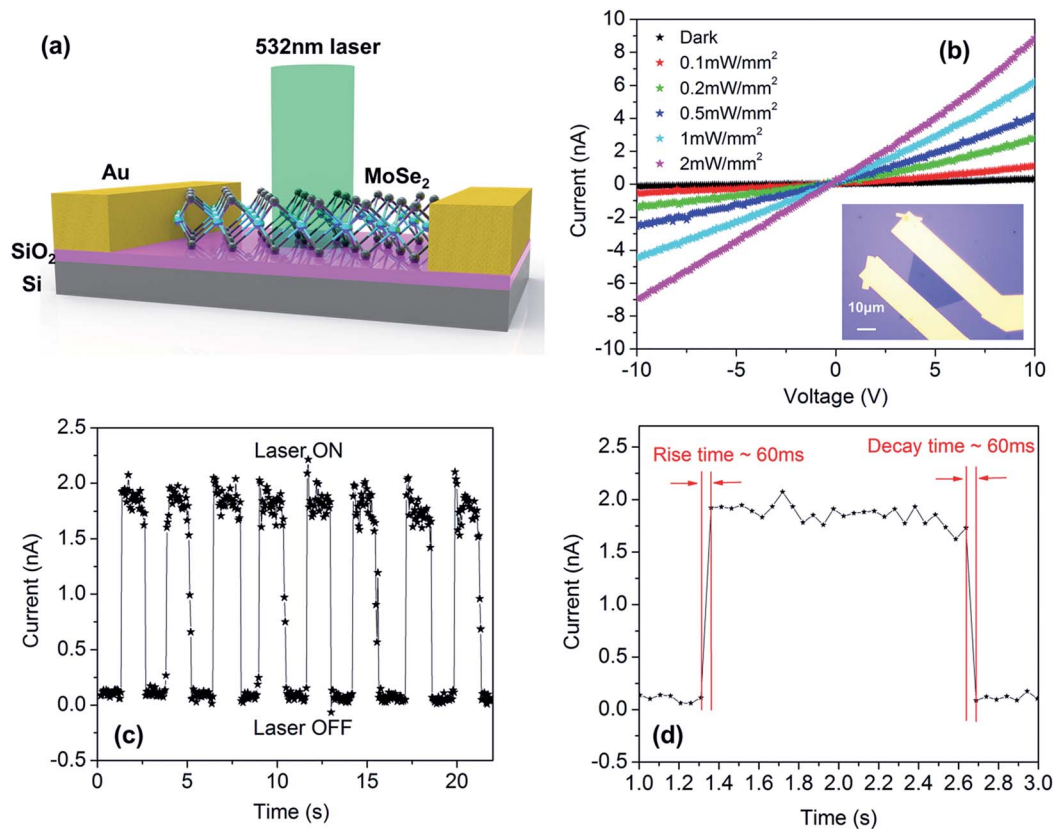


Fig. 5 (a) Three-dimensional schematic view of a monolayer MoSe₂ photodetector and the 532 nm laser beam used for illumination. (b) *I*–*V* characteristics of the device in the dark and in the presence of an illuminating laser with different laser powers. The inset shows the optical image of a monolayer MoSe₂ photodetector. (c) Time-resolved photoresponse of the device at a bias voltage of 5 V and a laser power of 0.5 mW mm^{−2}. (d) A single cycle response of laser on and off.

Electrical measurements were performed in the dark and in the presence of an illuminating laser with different powers ranging from 0.1 mW mm^{−2} to 2 mW mm^{−2} (Fig. 5b). The quasilinear *I*–*V* plots of the device (see inset in Fig. 5b) demonstrate good contact between MoSe₂ and the Au electrodes. In contrast to the dark current, the current is significantly increased when the device was illuminated. The *I*–*V* curves also indicate that the current is strongly dependent on the power of the illuminating laser. At a fixed bias, a larger laser power could lead to a larger current due to the increased number of photon-generated carriers. As a consequence, the photocurrent I_{ph} ($I_{ph} = I_{illuminated} - I_{dark}$) also increases. Photoresponsivity is a critical factor used to evaluate the performance of photodetectors. For the device produced in this study, the effective exposure area is approximately 446 μm². At a laser power of 1 mW mm^{−2} and a bias voltage of 10 V, the photoresponsivity is calculated to be approximately 13 mA W^{−1}, which is comparable to the graphene-based photodetector.⁵⁹

Photoresponse time is another critical parameter used to judge device performance. We investigated the time-resolved photoresponse of the device by switching the laser on and off. Fig. 5c shows the current of the device as a function of time at a bias voltage of 5 V and a laser power of 0.5 mW mm^{−2}. The device exhibits a repeatable and stable response to the laser illumination. As the laser is switched on and off, the device

shows a low off-state current of ~0.09 nA and a high on-state current of ~1.9 nA, giving a good on/off ratio of ~20. Fig. 5d displays a single cycle response of laser on and off. The measured rise and decay times are ~60 ms, indicating the fast response performance of the device. It should be noted that the performance of the device might be further improved by optimizing the contact or using a phototransistor mode;^{57,58} further study is currently underway.

4. Conclusion

In conclusion, a large area of highly crystalline MoSe₂ atomic layers has been directly synthesized on SiO₂/Si, mica and Si substrates using a CVD method at atmospheric pressure without the assistance of H₂ gas. Characterization by AFM and Raman confirmed that the thickness of the as-grown MoSe₂ ranges from a single layer to a few layers. By using a direct transfer method, we successfully obtained TEM samples. HRTEM together with the SAED pattern demonstrated that the ultrathin MoSe₂ flakes are single-crystalline and possess a hexagonal lattice structure. Room-temperature PL indicated that monolayer MoSe₂ has a direct bandgap of ~1.56 eV with a strong emission peak. Photodetectors based on monolayer MoSe₂ were fabricated and studied for the first time. The devices exhibited a fast response of ~60 ms and a good



photoresponsivity of 13 mA W^{-1} . We believe that this simple CVD approach can be scaled up to produce wafer-scale ultrathin MoSe_2 layers on diverse substrates, expanding the applications of this 2D crystal.

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