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Sub-millimeter size high mobility single crystal MoSe₂ monolayers synthesized by NaCl-assisted chemical vapor deposition

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Monolayer MoSe₂ is a transition metal dichalcogenide with a narrow bandgap, high optical absorbance and large spin-splitting energy, giving it great promise for applications in the field of optoelectronics. Producing monolayer MoSe₂ films in a reliable and scalable manner is still a challenging task as conventional chemical vapor deposition (CVD) or exfoliation based techniques are limited due to the small domains/nanosheet sizes obtained. Here, based on NaCl assisted CVD, we demonstrate the simple and stable synthesis of sub-millimeter size single-crystal MoSe₂ monolayers with mobilities ranging from 38 to 8 cm² V⁻¹ s⁻¹. The average mobility is 12 cm² V⁻¹ s⁻¹. We further determine that the optical responsivity of monolayer MoSe₂ is 42 mA W⁻¹, with an external quantum efficiency of 8.22%.

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Introduction

Recently, transition metal dichalcogenides (TMDCs) have received considerable attention owing to their narrow direct bandgaps and great potential for use in electronics and optoelectronics, catalysts, capacitors, and novel heterostructures.^{1–3} MoSe₂ is a TMDC with many unique properties and is a route to explore their applications.^{4–6} Phototransistors based on MoSe₂ have been shown to display a very quick response time (<25 ms) at room temperature under ambient conditions.^{7,8} The edge sites of MoSe₂ nanofilms and nanosheets have been found to be electrochemically active for H₂.^{9,10} It has also been shown that mesoporous MoSe₂ based anodes are an alternative for lithium

ion batteries, with a reversible and stable storage capacity of 630 mA h g⁻¹.^{11,12} Heterostructures incorporating MoSe₂ have been reported to exhibit a strong photocurrent response and photovoltaic effect with high quantum efficiency.¹³ MoSe₂ monolayers are the most promising candidate, among these materials, for applications in the field of optoelectronics due to the narrow direct bandgap (1.55 eV), high optical absorbance and large spin-splitting energy.^{2,4,11,14}

There are many different ways to produce MoSe₂.^{4,14–16} However, producing monolayer MoSe₂ films in a reliable and scalable manner is still a challenging task. The most common approaches are mechanical exfoliation and CVD.^{17–20} Although simple and convenient, exfoliation as a method usually suffers from some drawbacks. The product is usually multilayered, meaning it has an indirect bandgap and relatively weak optoelectronic performance.²¹ The lateral dimensions of exfoliated monolayer TMDCs are as small as a few tens of nm to several micrometers, which poses difficulties for its laboratory investigation and use.² Furthermore, contamination in the exfoliation processes is unavoidable. Comparatively, CVD can produce larger, purer and monolayer materials.^{20,22} Reports on the CVD growth of MoSe₂ suggest that it is extremely difficult to synthesize large area continuous monolayer films with solid-phase precursors because of the low chemical reactivity of Se.^{23–25} The CVD synthesis of MoSe₂ results in triangular-shaped discontinuous domains of either single-layer MoSe₂ or mixtures of single- and few-layer MoSe₂.^{20,26,27} In addition, CVD is known to suffer from a lack of steady and durable output, which prevents its more widespread use for the production of monolayer MoSe₂ films.²⁸ To overcome some of the challenges

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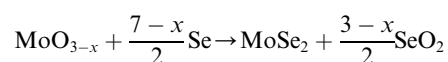
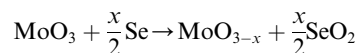
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associated with the CVD growth of TMDs using solid-phase precursors, recently NaCl has been used to assist the CVD growth of MoS₂ and WS₂ monolayers.^{29–31} It was found that the addition of NaCl led to an enhancement of the growth rate, reduced growth temperature and more continuous film production, due to formation of intermediate Na-containing species that reduce the energy of the reaction. The size of MoS₂ and WS₂ monolayers grown by this method were found to reach 300 μm (ref. 29) and 500 μm (ref. 31) respectively. However, to the best of our knowledge, there is little data on electrical and photoelectrical properties of TMDs monolayers prepared by the NaCl assisted CVD method. In this work, we extended the above methodology to MoSe₂ monolayer synthesis. Using NaCl assisted CVD, we have developed a simple and stable CVD method to synthesize large-scale, single crystal and monolayered MoSe₂, whose size can be up to 250 μm. We also study the electrical and optoelectronic properties of the MoS₂ monolayers in a four fingered back-gated field-effect transistor (FET) and find that they are n-type with an average mobility of 12 cm² V⁻¹ s⁻¹ and responsivity of 42 mA W⁻¹.

Results and discussion

Fig. 1(a) shows a schematic of the CVD growth system. MoO₃ powder and Se particles were used as precursors. NaCl was used to assist the reaction. A SiO₂ (300 nm)/Si substrate was put on the boat containing MoO₃ powder with its polished surface facing downward in the quartz boat to receive sufficient mass flux of metal precursor. In conventional CVD, the process of MoSe₂ monolayer growth is a step-by-step nucleation.²⁹ The two main reactions involved in MoSe₂ growth are:



The first reaction occurs mainly during the temperature ramp-up period while the second reaction, which is called an epitaxial process, takes place in the steady temperature period.

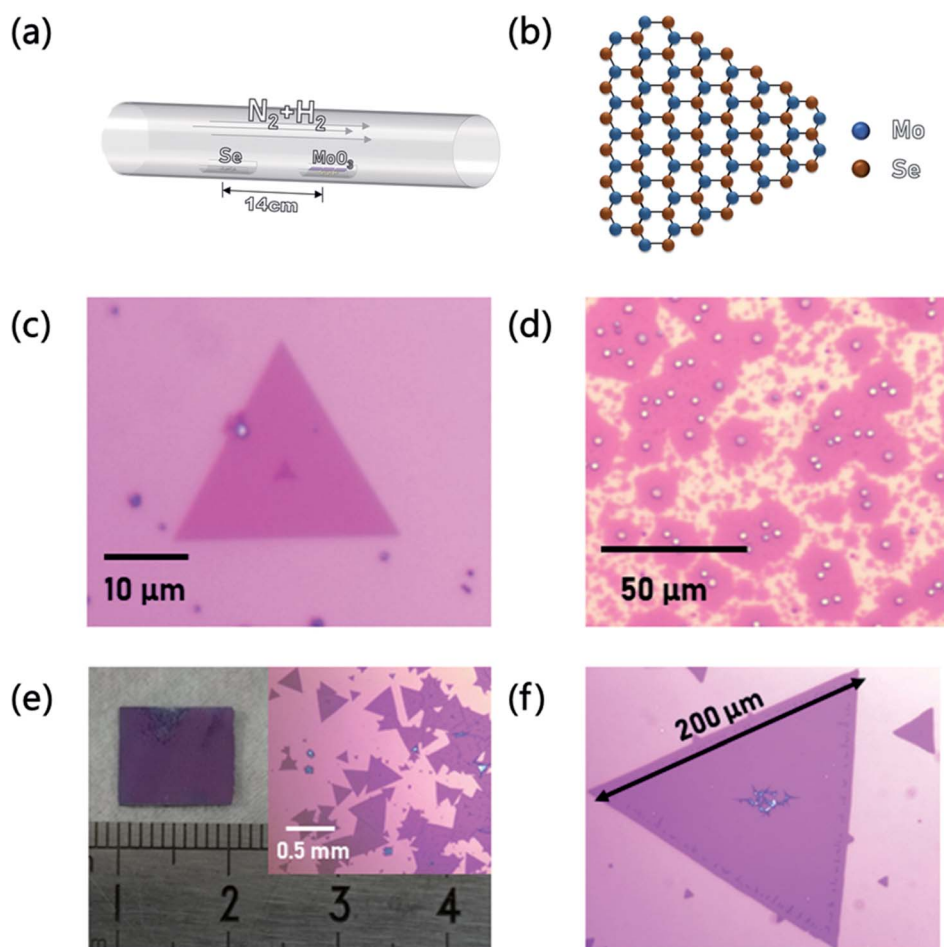


Fig. 1 (a) Schematic of CVD growth system. (b) Atomistic model of monolayer MoSe₂. (c) Image of MoSe₂ grown by standard conditions without NaCl, using 15.6 mg MoO₃ as the precursor. (d) Image of MoSe₂ grown with the same conditions without NaCl, using 16.6 mg MoO₃ as the precursor. (e) Typical appearance of prepared MoSe₂ on the substrate. The dark purple layers, contrast with the pink substrate, are visible monolayers of MoSe₂. (f) MoSe₂ triangle of typical size of grown with the assistance of NaCl.

As a result, the core-like dots at the center of many of the MoSe₂ monolayers are essentially suboxide compounds, MoO_{3-x}Se_y, rather than the MoSe₂ at the core. Moreover, the anisotropic growth of MoSe₂ proceeds by different modes when there is a different ratio between Mo and Se, resulting in two kinds of edges, Mo-edges and Se-edges (Fig. 1(b)).³¹ When the ratio between Mo and Se atoms is close to 1 : 2, the shape of the MoSe₂ flakes looks like a regular hexagon. If Mo atoms are greater in abundance, the Mo-edge grows relatively faster.^{15,27,32} Following standard practice, when we use a relatively small quantity of MoO₃ powder, the process yields low density small monolayer MoSe₂ triangles. When more MoO₃ is used, there is densely distributed isotropic MoSe₂ (Fig. 1(c and d)). Clearly, the change of ratio between Mo and Se in the reaction, created by the great abundance of MoO₃, results in the change in observed morphology.

To overcome above issues, NaCl has been used to assist the CVD growth. In the NaCl assisted CVD method, NaCl has a two-fold effect on the growth process as below:³³



First, it can accelerate the growth of MoSe₂, with the formation of MoO₂Cl₂, which provides an opportunity for gas-gas phase reactions among MoO₂Cl₂, Se and H₂. Secondly, it can increase the mass flux of the metal precursors by decreasing the melting point of MoO₃, producing higher

nucleation density. To avoid over-nucleation, a small quantity of MoO₃ powder is used. Fig. 1(e) shows a typical optical image of a monolayer MoSe₂ film grown by NaCl assisted CVD. It shows both large-scale and dense monolayer MoSe₂ coverage. The typical lateral size of MoSe₂ grown with the NaCl assisted CVD is more than 200 μm (Fig. 1(f)), and some can reach up to 500 μm.

Fig. 2(a) shows an atomic force microscopy (AFM) image of as-prepared MoSe₂. Clear contrast between the SiO₂/Si substrate and MoSe₂ indicates that the thickness is ~0.82 nm. In addition to verifying the uniformity of the layers, we also identify the phase of the complete monolayer as MoSe₂ using the Raman spectroscopy (Fig. 2(b)).²⁸ The Raman spectra consists of two main peaks at 240 cm⁻¹ and 520 cm⁻¹. The peak at 520 cm⁻¹ is the characteristic Raman peak of the Si, while the one at 240 cm⁻¹ indicates the dominance of the A_{1g} mode, the out of plane vibration, of MoSe₂.^{34,35} We also find Raman peaks at 169 cm⁻¹, 289 cm⁻¹ and 361 cm⁻¹, corresponding the E_{1g}, E_{2g} and A_{2g}, modes of MoSe₂ respectively. We used transmission electron microscopy (TEM) to verify the monolayer nature and crystal structure of the MoSe₂. The measured width of the lattice fringes is 0.27 nm which is in agreement with reports on the distance between the adjacent atoms.⁵ Selected-area-electron-diffraction (SAED) images of MoSe₂ (inset of Fig. 2(c)) exhibit one set of six-fold symmetry diffraction spots, confirming its highly crystalline monolayer nature. From energy-dispersive X-ray spectroscopy (EDS) mapping of a MoSe₂ sample exposed to atmosphere, the ratio between Mo and Se atoms is determined to be close to 1 : 2, displaying the stability of MoSe₂. The stability of MoSe₂ and its adhesion to the Si/SiO₂ substrate was

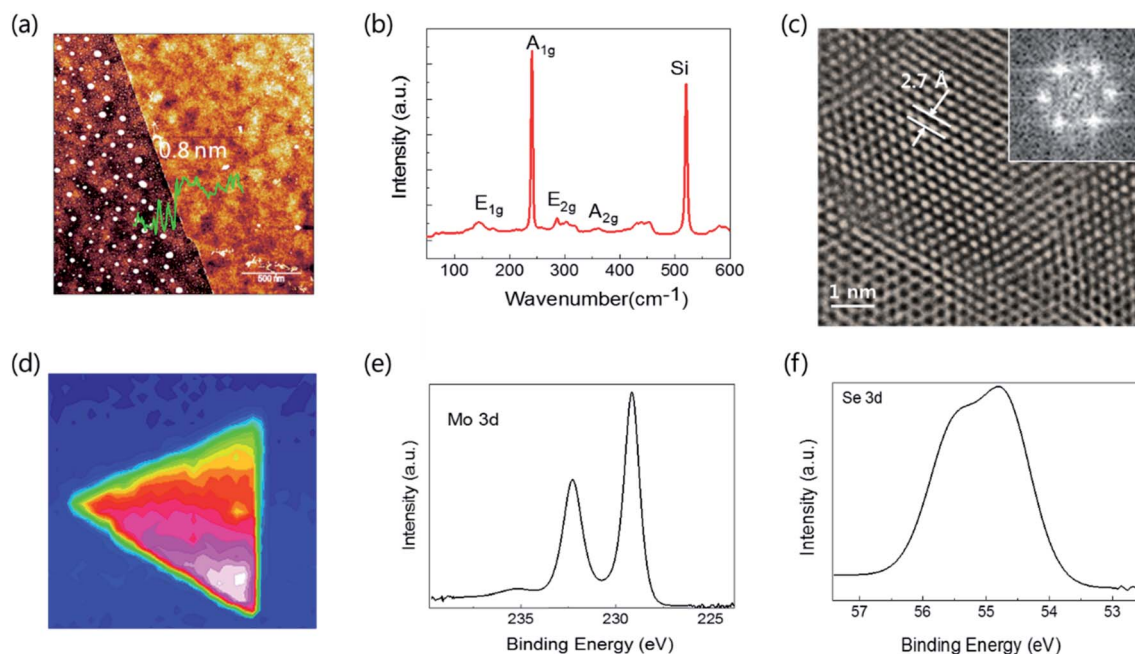


Fig. 2 (a) AFM height map of MoSe₂ sample on growth substrate. Also shown in the figure is the height profile near the edge of a MoSe₂ domain. (b) Raman spectra of MoSe₂ sample, showing the major observed peaks. (c) High resolution TEM image of MoSe₂ sample with its selected area diffraction pattern shown in the inset. (d) Raman mapping of MoSe₂ sample. (e and f) XPS spectra recorded for Mo 3d and Se 3d edges at room temperature for monolayer MoSe₂ sample.

further checked by soaking it in water, ethanol and acetone. Fig. 2(e) shows X-ray photoelectron spectroscopy (XPS) core level spectra of the Mo-3d and Se-3d core-levels of the as grown MoSe₂ monolayer films measured at 300 K. From the data we can determine that there is only one major state for the Mo and two states for Se atoms, the binding energy for the Mo–Se Mo 3d_{5/2} state is 229.1 eV. While the corresponding values for the Se 3d_{5/2} 55.5 eV. Both elements showed minor components at higher binding energies attributed to surface oxygen absorption as the sample was exposed to ambient conditions for an extended period.³⁶

In order to study the electrical and optoelectronic properties of MoSe₂, we fabricated four-finger back-gated field-effect transistors. The output and transfer characteristics of a MoSe₂ FET is shown in Fig. 3. The output and transfer characteristics are evidence of the n-type nature of the MoSe₂, which is in-line with the previous studies.^{16,31,37,38} Fig. 3(a and b) shows the I_d – V_d characteristic under gate voltages ranging from –16 V to +4 V. The curve shows the obvious semiconducting nature of MoSe₂, whose resistance decreases as the bias voltage increases. In contrast with conventional FETs, there is no apparent saturation in the drain current the FETs fabricated from MoSe₂. The switching voltage without a gate voltage is about 12 V, while the positive/negative gate voltage can decrease/increase the switching voltage. As expected, gate voltage can modulate the conductivity of the FET. Fig. 3(c) exhibits the I_d – V_g characteristic measured under different bias voltage. The FET is depleted from free carriers when V_g is lower than 0 V. The switch ratio, I_{on}/I_{off} , under +4 V of bias voltage, can reach 10⁵.^{39–42} The transfer characteristic offers the opportunity to compute the mobility of the FET. Using the

formula $\mu = \frac{dI_d L}{dV_g W C_{SiO_2} V_d}$, we find that the mobility μ is 20.1 cm² V^{–1} s^{–1}. In this formula, L and W are the length and width of the conduction channel, respectively, and $C_{SiO_2} = \epsilon_0 \epsilon_r / d$ is capacitance per unit area estimated for the gate dielectric, with ϵ_0 being the free-space permittivity, ϵ_r , the relative permittivity for SiO₂, being 3.9, and d , the thickness of the SiO₂, being 300 nm. More than 20 devices were fabricated and characterized. It was found that the mobility ranged from 38 to 8 cm² V^{–1} s^{–1} (Fig. 3(d)), with an average 12 cm² V^{–1} s^{–1}. The highest mobility found for our samples is very close to the reported value (50 cm² V^{–1} s^{–1}) for mechanically exfoliated ultra-thin MoSe₂.⁴³ The reduced mobility can be attributed to imperfections in the monolayers, such as Se vacancies, which might be improved by reducing nuclei density, controlling the mass flux or growth rate, *etc.*³¹

In order to realize the potential of monolayer MoSe₂ for applications in solar cells, photosensitive sensor and other devices,^{18,44} it is also necessary to investigate its optoelectronic properties. We measured the optoelectronic responsivity in ambient conditions with different voltages and light sources of different wavelengths. Fig. 4(a) exhibits the quick response time of the FET under the 200–500 mW cm^{–2} power laser with a 635 nm wavelength. The bias voltage is 10 V and the gate voltage is 10 V. Under such conditions, the photocurrent ranges between a few to hundreds of nanoamperes. When the laser power is increased sufficiently, there is saturation of the photo-enhancement of the drain current as can be seen in Fig. 4(b). We also investigate the time response of the gated FET under pulsed 400 mW cm^{–2} illumination (Fig. 4(c)). It is apparent that a positive gate voltage not only elevates the drain current in both

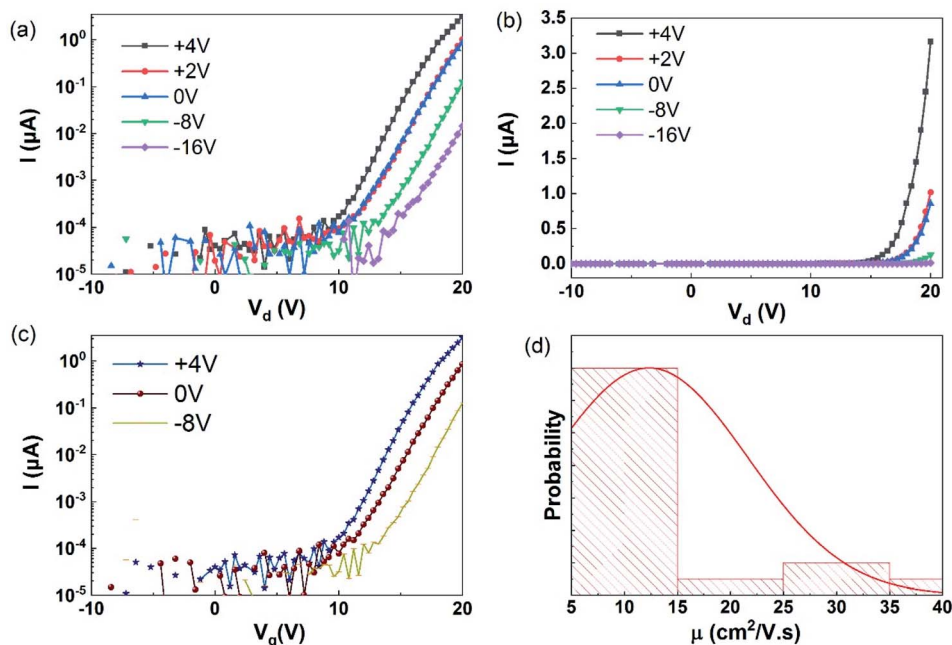


Fig. 3 (a) The I – V_d curves of the MoSe₂ FET under various gate voltages plotted on a log scale and (b) on a linear scale. (c) Transfer characteristic curve of the FET under various bias voltages. (d) Distribution of the mobility of all devices measured.

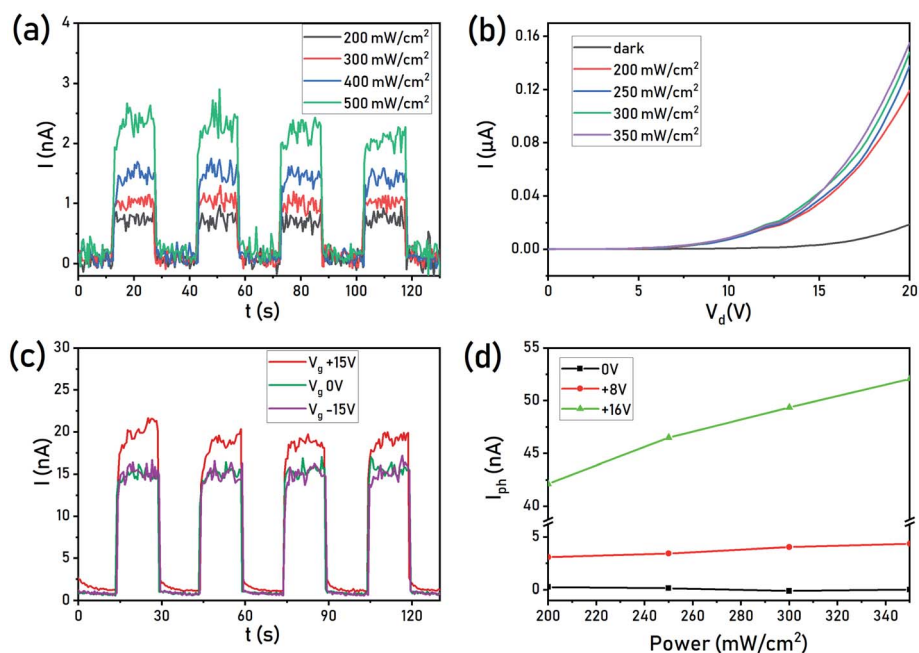


Fig. 4 (a) I - t characteristic plots for FET for a variety of power intensities of a 635 nm laser. (b) The output characteristic of the FET under different power intensities of 635 nm laser. (c) I - t characteristic curve of the FET under different gate voltages for the 635 nm laser. (d) The I_{photo} -power curve of the FET under different bias voltages.

Table 1 List of electrical and optoelectronic properties from other studies

Type	Method	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Responsivity (mA W^{-1})	Size (μm)	Reference
Monolayer	CVD	23	—	~ 5	8
Film	CVD	0.02	—	~ 0.2 (grain size)	26
Multilayer	CVD	121	—	Several hundred	37
Monolayer	CVD	50	—	135	34
Multilayer	Micromechanical exfoliation	50	—	1–3	16
Monolayer	CVD	—	13	> 50	21
Ultra-thin	Mechanical exfoliation	50.5	—	$< 44 \mu\text{m}$	43
Multilayer	Mechanical exfoliation	19.7	97 100	~ 30	45
Multilayer	Atomic layer deposition	—	11.7	Several hundred	46
Multilayer	Mechanical exfoliation	30–35	—	~ 10	47
Monolayer	CVD	42	—	Several hundred	48
Multilayer	CVD	10	93 700	3–4	49
Multilayer	Mechanical exfoliation	50.6	519 200	~ 10	50
Few layer	Mechanical exfoliation	5.1	238 000	~ 25	51
Monolayer	CVD	38	42	Several hundred	Our work

dark and lit condition, but also increases the photo current, while a negative gate voltage has no such effect. We show the power dependence of the I_{photo} in Fig. 4(d) derived from the Fig. 4(b), which intuitively presents the modulation of the bias voltage and the laser power. When the bias voltage climbs into a certain range, the photo current can be modulated by the power intensity, which is shown in Fig. 4(d). We determine the responsivity of the FET to be 42 mA W^{-1} , and the external quantum efficiency (EQE) of the device is 8.22%. Table 1 summarizes the electrical and optoelectronic properties of MoSe_2 from other studies from literature. Clearly, it is rather difficult to synthesize both high-mobility and large-scale

monolayer MoSe_2 . Using NaCl assisted CVD method, it is relatively easy to synthesize large monolayer MoSe_2 with sound electrical and optoelectronic properties.

Conclusion

In conclusion, we have found an effective and convenient method to synthesize large-scale monolayer MoSe_2 and investigated the optoelectronic properties of derived FETs. When as-prepared MoSe_2 was used to fabricate FETs, it had a mobility up to $38 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a responsivity of 42 mA W^{-1} , which is promising for its practical application.

Materials and methods

Sample preparation and characterization

For the reaction, 0.5 g of selenium granules and 5–7 mg of a mixture of MoO₃ powder and 1 mg of sodium chloride powder, were prepared as precursors. We used a quartz boat containing selenium granules and another boat with the mixed NaCl and MoO₃ powder to obtain layered MoSe₂ by the selenization of MoO₃. Before heating the furnace, 100 standard cubic meter per minute (sccm) of the mixture of H₂/N₂ (10 : 90) carrier gas was used to purge the tube for 20 minutes. The furnace was heated to 750 °C in 15 minutes with the rate of 50 °C per minute, and a reaction dwell time of 15 minutes was used, after which the furnace was allowed to cool naturally. During the heating and reaction process, the flow rate of the carrier gas was kept at 50 sccm, giving a H₂ flow of 5 sccm. The pressure inside the tube was maintained at 30 Torr. Atomic force microscopy (Bruker Multi-mode 8, in peak force tapping mode), Raman spectroscopy (Bruker Senterra confocal spectrometer with an excitation wavelength of 532 nm), Transmission electronic microscopy (JEOL JEM-2100F at 200 kV with a probe size under 0.5 nm), and XPS (micro-XPS, PHI Versa Probe III) were used to characterize the MoSe₂ samples, identifying its single-layer and high-quality nature. In Raman spectroscopy measurements, the wavelength of the laser used was 532 nm.

Device fabrication and measurement

The MoSe₂ films were transferred onto new 300 nm SiO₂/Si substrates using a PMMA assisted transfer method. Ultraviolet lithography was then used to pattern the electrodes. We deposited Ti–Au electrodes with 15 nm of Ti and 55 nm of Au using electron beam evaporation. The channel lengths and widths were 4 μm and 50 μm respectively. For electrical measurements, the devices was placed in a darkness, except for when required, and at room-temperature. In all experiments the source was grounded.

Author contributions

H. C. W. conceived the study. J. C. L., and J. L. grew the sample. W. J. Y., Y. H. L. and D. Z. performed the Raman measurements. C. C. conducted the AFM characterization. C. P. C., T. S., and G. S. D. performed the XPS characterization. J. C., M. C., and B. S. C. carried out the TEM measurements. Y. F. Z., C. Z. L. and S. K. A. helped with device fabrication and data analysis. H. C. W. and J. C. L. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There is no conflicts to declare.

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