Ultrathin transition metal dichalcogenides (TMDs), MX$_2$ (M = Mo, W; X = S, Se, Te), have been attracting great interest because of their unique properties associated with lateral anisotropy, intrinsic bandgaps, and mechanical flexibility. Their emerging properties are feasible for future electronics on flexible substrates. With success in easy synthesis of high quality TMD thin films, the potential applications will become more viable in electronics, optics, energy storage, and catalysis. Synthesis of TMD thin films has been mostly performed in vacuum or by thermolysis. So far, there is no solution phase synthesis to produce large-area thin films directly on target substrates. Here, this paper reports a one-step quick synthesis (within 45−90 s) of TMD thin films (MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$, etc.) on solid substrates by using microwave irradiation on a precursor-containing electrolyte solution. The numbers of the quintuple layers of the TMD thin films are precisely controllable by varying the precursor's concentration in the electrolyte solution. A photodetector made of MoS$_2$ thin film comprising of small size grains shows near-IR absorption, supported by the first principle calculation, exhibits a high photoresponsivity (>300 mA W$^{-1}$) and a fast response (124 µs). This study paves a robust way for the synthesis of various TMD thin films in solution phases.

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To grow a thin film on a substrate, it is essential to restrict the three-dimensional growth of the material. Here, we have utilized microwave-assisted selective heating of the substrate (Figure 1a). Very recently, pulsed microwave was used to convert graphene oxide to graphene.[18] When a precursor solution is covered by a conductive substrate, the microwave energy absorbed by the substrate quickly increases substrate temperature. The temperature increase rate (dT/dt) is a function of electrical conductivity (σ), thickness (l), and area of the substrate.[19] If temperature of the substrate ($T_{\text{sub}}$) is higher than the critical temperature ($T_c$) of precursor thermolysis, while the precursor solution temperature ($T_{\text{sol}}$) is lower than $T_c$, the formation of TMD thin films can take place only on the substrate surface. As there is no crystal formation in the bulk solution in such situation the solution phase can be removed by solvent washing after the thin film synthesis.

In this study, we used a p$^{++}$ Si wafer ($\sigma$ = 1.000 S m$^{-1}$, 0.5 mm in thickness, 2 × 2 cm$^2$ in area) as the top substrate (Figure 1b). Since the microwave penetration depth ($\delta$) of the Si wafer, $\delta = (2/\omega \sigma \mu)^{1/2}$ where $\omega$ is the radian frequency of the microwave and $\mu$ is the free space permeability, is calculated to be $\approx$0.33 mm,[19] the microwave energy is mostly absorbed by the substrate.
Under microwave irradiation (700 W), the substrate temperature increases theoretically at a rate of 7.8 °C s⁻¹ (see Supporting Information for details). The measured surface temperature of the wafer increased to 240 °C in 40 s. Depending on the target TMD thin films, the microwave irradiation time was adjusted from 45 to 90 s. Liquid electrolyte (1-butyl-3-methylimidazolium tetrafluoroborate) was used as the solution medium to facilitate the convective distribution of the thermal energy caused by its active microwave energy absorption. Since the electrolyte is thermally stable up to 393 °C, it maintains the liquid phase during the synthesis. Moreover, as the viscosity of the liquid electrolyte reduces with increasing temperature, its thermal conductivity increases significantly, facilitating the convective heat transfer through the liquid electrolyte. The enhanced convective heat transfer prevents localized heating of the substrate, which may cause the formation of nonuniform films. With an insulating bottom substrate, morphology, and thickness of the film synthesized on the top substrate was not controllable because the temperature increase was too fast. Additionally, although there was a simultaneous film formation on the conducting bottom substrate also, however, the film quality in terms of uniformity, roughness, and crystallinity, was not good because the heat on the bottom substrate was not enough for precursor decomposition. After the film formation, the electrolyte solution was washed with ethanol and deionized (DI) water.

This simple process allowed the formation of various TMD thin films including MoS₂, MoSe₂, WS₂, and WSe₂. Figure 1c presents an optical image of the monolayer WSe₂ thin film, showing a continuous and uniform thickness over the entire area of the specimen (inset image). The thickness of the WSe₂ layer was 0.81 nm measured by atomic force microscope (Figure 1d), confirming its monolayer character. The Raman spectra of the as-synthesized MoS₂, MoSe₂, WS₂, and WSe₂ in Figure 1e exhibits the typical characteristic phonon modes.

As an example analysis of the thin films, the as-synthesized MoS₂ film was characterized in detail (Figure 2a–f). X-ray photoelectron spectroscopy (XPS) spectra (Figure 2a,b) exhibit that the binding energies (Mo 3d₃/₂, Mo 3d₅/₂, S 2p₃/₂, S 2p₁/₂) are in excellent accordance with those of hexagonal MoS₂ crystals. Energy-dispersive X-ray spectroscopy (EDS) analysis (Figure 2c;
Figure S1 and Table S1, Supporting Information) confirms an atomic ratio of Mo:S = 1:2.06. Synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS) (Figure 2d) presents two broad out-of-plane reflection arcs with a diploid relationship at \( q_z = 0.62 \) and 1.24 Å\(^{-1} \). The circular diffraction image in the inset indicates the polycrystalline character of the thin film. The 2D GIWAXS pattern (Figure 2e) obtained from the 2D image reveals that the peaks corresponding to the (001) and (002) reflections match with the calculated diffraction pattern of a \( c \)-axis expanded cell (JCPDS file No. 37–1492). The domain spacing (10.12 Å) of the (001) plane indicates an enlarged interlayer compared with that of the bulk crystal (6.15 Å). The expanded interlayer spacing can be attributed to the oxygen incorporation in the MoS\(_2\) layers, as recently reported for hydrothermally synthesized MoS\(_2\) nanosheets (9.5 Å).

The deconvoluted XPS spectrum of the O 1S peak (Figure S2, Supporting Information) shows two peaks, a peak (530 eV) corresponding to the binding energy of Mo\(^{4+}\)=O bonds and an intense peak (532 eV) corresponding to the H\(_2\)O molecule adsorbed at the surface. The EDS analysis (Figure S3, Supporting Information) also shows uniform incorporation of oxygen with 3.74 at\% in the MoS\(_2\) film. Figure 2f (and Figure S4, Supporting Information) shows a high-resolution transmission electron microscope (HR-TEM) image of the MoS\(_2\) thin film transferred onto a TEM grid. It reveals a lattice spacing of 0.27 and 0.16 nm, which is consistent with the (100) and (110) planes of MoS\(_2\), respectively.

Figure 2g,h and Figure S5 (Supporting Information) show the cross-sectional TEM images of the MoS\(_2\), MoSe\(_2\), and WS\(_2\) thin films, respectively. They clearly exhibit that crystals have the horizontally grown layered structure. A series of cross-sectional TEM images of the WSe\(_2\) thin films (Figure 2i) emphasizes the precise control of the number of layers. The corresponding optical microscopic (OM) images of the samples display slight difference in color with the film thickness. The uniform color over the whole sample area indicates that the uniformity in thickness can be readily achieved simply by adjusting the concentration of the precursors in the electrolyte...
Precise control of the number of quintuple layers over the whole substrate was readily achieved in the WSe$_2$ thin films, whilst thickness control by the same degree was difficult in the other thin films (MoS$_2$, MoSe$_2$, WS$_2$). When the other films were less than 5 nm, the thicknesses were locally variant. We suppose that interface control of the conductive substrate and the kinetic control of the nucleation and growth are the key elements to achieve the precise control of the thickness.

On the basis of the cross-sectional TEM images and XRD results of the synthesized TMD thin films, metal sulfides had smaller grains than their corresponding metal selenides. Scherrer analysis of the (001) planes indicates the average grain size of the MoS$_2$ thin film was $\approx$4.5 nm. As the heat of formation of MS$_2$ (M = Mo or W) compounds$^{[26]}$ so it takes longer microwave exposure for the synthesis of MS$_2$ compounds, which in turn may induce more defects during the growth process and restrict the grains growth more in case of MS$_2$ compounds. The intense sharp peak at 575 nm in the deconvoluted photoluminescence (PL) spectrum (Figure S6, Supporting Information) can be interpreted by the quantum size effect of the crystal domains, whereas the two low-intensity broad peaks at 614 and 678 nm can be assigned to the PL corresponding to the direct excitonic transitions.$^{[27]}$ Formation of an ultrathin film constructed with small grains can be a uniqueness of the solution phase synthesis because thin films with large grains can be prepared via the CVD process.

We investigated the effect of small grain size on the optical absorption of the MoS$_2$ thin film. We have observed near-IR optical absorbance with a local maximum at $\approx$867 nm, which is additional to the reported two peaks between 350–500 nm and 600–700 nm (Figure 3a)$^{[28]}$. As shown in the previous report, the optical absorbance of MoS$_2$ flakes is not layer-dependent in the NIR region and the peak intensity in the UV–vis region increases with increasing the number of absorbing species (from of 1L to 6L), maintaining their relative positions same.$^{[29]}$ In this experiment, too, thickness dependence of the absorption profile was not observed. So, to account for the NIR absorption, we theoretically examined optical absorptions of a monolayer MoS$_2$ film containing many S|7 line defects (Figure 3b) and a film constructed with grain line-type defects (grain diameter = 9.37 $\text{Å}$, intergrain distance = 6 $\text{Å}$) (Figure 3c).$^{[30]}$ Figure 3d compares the theoretical UV–vis absorbance of the MoS$_2$ films without defects (black line), with the S|7 line defects (red line), and the grain line-type defects (blue). The film with the grain line-type defects has the transition at the NIR region ($\approx$1.41 eV) from the localized Mo 4d and S 2p states of the outermost Mo and S atoms (labeled as Mo1, Mo2, S1, and S2 in Figure 3e) near the grain boundaries. Hence, the NIR absorbance increases as the grain size decreases. The theoretical absorbance depends on the grain size, defect type, and intergrain distance. Details of the theoretical calculations are in the Supporting Information (Figures S7–S9, Supporting Information).

We took advantage of the enhanced NIR absorbance of the MoS$_2$ thin film to fabricate a photodetector with a wide spectral range. The energy band diagram for the synthesized MoS$_2$ is illustrated in Figure 4a. Details can be found in the Supporting Information. Figures 4b–f demonstrate the optoelectronic characteristics of the MoS$_2$ thin film photodetector.

Figure 3. Comparison of experimental absorbance with calculated optical property of different MoS$_2$ structures. a) Measured vis–NIR absorption spectrum of the as-synthesized MoS$_2$ thin film. b) The S|7 line defect structure of a MoS$_2$ thin film. c) The grain line-type defect structure of an MoS$_2$ thin film. d) Calculated absorbance spectra from single layer MoS$_2$ thin films without defects (black), with the S|7 line defects (red), and with grain line-type defects (blue). e) Partial electron density of the grain line-type defect structure. Mo atom and S atom are depicted in gray and yellow sphere, respectively. Translucent red region shows the partial electron density. The energy difference of the outermost atoms counts for the absorbance in the NIR region.
Figure 4. Energy band diagram and photoresponse of the MoS₂ thin film. a) Schematic of the energy band diagram for the MoS₂ thin film, as deduced from the UPS data (Figure S11, Supporting Information). Note that the bandgap energy (Eg) used in the diagram is the optical bandgap as calculated in Figure S10, Supporting Information. b) Current (I)–voltage (V) characteristic of the photodetector in the dark and under light illumination (λ = 633 nm) at different powers (1–100 μW). c,d) Spectral EQE and the corresponding calculated photoresponsivity curve of the photodetector. e) Stability of the photoswitching characteristics of the photodetector under repeated on–off illumination from three different laser sources (λ = 488, 532, and 633 nm). The bias voltage (2 V) and the illumination power (100 μW) were kept constant. f) Time-resolved photocurrent measurement shows a response time (t_r) of 124 μs and a decay time (t_d) of 487 μs.

Figure 4b shows the photoresponse of the device under different laser illumination powers (λ = 633 nm) in the 1–100 μW range. The dark current was 104 nA (bias voltage = 2 V), and the device current increased to 1.25 μA at 10 μW. Figure 4c exhibits the external quantum efficiency (EQE) at 2 V. The device exhibits high EQEs in a wide spectral range of 300–1100 nm. From the relationship between the spectral photoresponsivity (R_λ) and EQE_λ, EQE_λ = (R_λ/λ) x (1240 W nm A⁻¹). R_λ was calculated as shown in Figure 4d. The device shows a high photoresponsivity in a wide range: 100 mA W⁻¹ at λ = 375 nm, 315 mA W⁻¹ at λ = 610 nm, and 140 mA W⁻¹ at λ = 1000 nm. The overall photoresponsivity in the visible and NIR region was significantly higher than the reported values for the single layer MoS₂ (R_λ = 7.5 mA W⁻¹ at V_g = 50 V and λ = 550 nm)[32] and a multilayer MoS₂ (20 mA W⁻¹ at V_g < 5 V and λ = 800 nm).[13] The photodetector exhibited stable photoswitching behavior under a pulsed irradiation of monochromatic visible lasers (λ = 488, 532, and 633 nm) (Figure 4e). A time-resolved measurement indicates a short rise time (t_r = 124 μs) and a decay time (t_d = 487 μs) at λ = 633 nm and 100 μW (Figure 4f). These response times are much faster than those reported previously for MoS₂ photodetectors (t_r = 50 ms or 4 s).[5,12]

In summary, the solution phase one-step synthesis under microwave irradiation enables the formation of various TMD thin films with a precisely controlled film thickness. Because of the simple process, quick synthesis, and easy scalability, the proposed synthesis can be extended as a generalized concept to prepare various TMD thin films. A photodetector fabricated with the MoS₂ thin film exhibits excellent optoelectronic characteristics, including stable and fast optical switching, and a high broadband photoresponsivity.

Experimental Section

Molybdenum (V) chloride (MoCl₅, 99.99%), tungsten (IV) chloride (WCl₆, 95%), thiourea (99.99%), selenourea (98%), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]), 98%), poly(methyl methacrylate) (PMMA, M_w = 350 000), chloroform, dichloromethane (DCM), and toluene were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. Potassium hydroxide was purchased from Duksan Chemicals, Korea. p++ Si and 300 nm SiO₂/Si wafers were purchased from Waniqiang Silicon-Peak Electronics Co., LTD, China. Indium tin oxide and fluorine doped tin oxide coated glass slides were purchased from Sigma-Aldrich.

All the substrates were precleaned and plasma treated using the following steps: (1) ultrasonic cleaning in acetone and ethanol alternatively three times for 10 min, (2) drying at 100 °C over hot plate, (3) O₂ plasma treatment of the wafer at 200 W for 90 s. In a typical synthesis, 25 × 10⁻³ μ MoCl₅/WCl₆ and 125 × 10⁻³ μ thiourea/selenourea were dissolved in 5 mL of [Bmim][BF₄] electrolyte under magnetic stirring. After 1 h, Argon gas was bubbled through the reaction mixture for 30 min to remove any dissolved O₂ in the mixture. Next, required amount of this precursor solution was dropped on the polished side of a p++ Si wafer and polished side of another wafer of same size was placed downward over the precursor mixture. The sandwiched precursor solution was then heated in a single-mode variable-power 700 W domestic microwave oven for 45–90 s (depending on the substrate size and intended material), at minimum power. Average surface temperature of the p++ Si wafer, measured using a hand held infrared thermometer during the reaction, was ~240 °C at 40 s. After microwave irradiation, the reaction mixture was allowed to cool to room temperature naturally and
finally the wafers were washed with ethanol and DI water alternatively for several times before drying in vacuum desiccators.

To control the number of quintuple layers of the thin films, the concentrations of the precursors were adjusted in the liquid electrolyte solution. The relative concentration of the metal precursor and halocarbon precursor was fixed at (25:125) \times 10^{-3} \text{m}, and the stock solution was diluted further with the liquid electrolyte solvent. All the other experimental conditions were the same, such as substrate size, volume of the precursors solution, microwave exposure time, microwave power, and position of the sample on the microwave glass turntable plate. Afterward, a new substrate (based on requirements), was used to fish out the PMMA and the MoS\textsubscript{2} film. Finally, after several washing with DI water (to remove KOH), the PMMA film was dissolved by DCM.\textsuperscript{134)

MoS\textsubscript{2} photodetector devices were fabricated using the synthesized multilayer MoS\textsubscript{2} thin film. Multilayer MoS\textsubscript{2} thin film was transferred to 20 nm thick ALD deposited HfO\textsubscript{2} on a p+ doped Si wafer. To define the device pattern over the thin film, standard photolithography technique was used and 50 nm thick Au electrode pads were then deposited over the thin film.\textsuperscript{135} Finally, the device was thermally annealed at 200 °C for 30 min, to reduce the contact resistance.

Samples were analyzed using optical microscope (Olympus BX-51), field emission scanning electron microscope (S-4200, Hitachi), scanning transmission electron microscopy (STEM, JEM-2100F and JEM-2011HC, JEOL) at an accelerating voltage of 200 kV, and EDS (INCA X-sight 7421, Oxford Instruments). XPS measurements were carried out in K-alpha (Thermo VG, U.K.) equipped with monochromated Al K\textalpha\ sources (Al K\textalpha line: 1486.6 eV run at 12 kV and 3 mA, fixed analyzer transmission). The topologies of the thin film were examined by atomic force microscopy (AFM, Dimension 3100, Digital Instruments Co.). Raman and PL spectra were obtained by a Micro-Raman spectrometer (Witec Alpha 300 RA Confocal Raman), with the wavelength and spot size of the laser excitation of 532 nm and 1\ \mu m. UV–vis–NIR absorption spectroscopy was performed on a PerkinElmer Lambda 9 UV–vis–NIR spectrophotometer. GIWAXS was performed at beam line 3C in the Pohang Accelerator Laboratory (South Korea). The thin film was illuminated by X-rays (\lambda = 1.2565 \AA) with a photon energy of 9.8673 keV at an incidence angle of 0.1°. Samples were prepared using all of the same processing methods as described above. A focused ion beam/EBSD (Helius, Pegasus, FEI) was used to prepare cross-sectional samples. The current–voltage (I–V) and the current–time (I–t) characteristic of the photodetectors were measured by a semiconductor parameter analyzer (Agilent 4156A) and Keithley 2400 source meter controlled by a LabView program, using either a 483 nm Ar\textsuperscript{+} laser, a 532 nm Nd:YAG laser or a 633 nm He-Ne laser. A laser power meter (PM100D, THORLABS) was used to measure the exact power of the incident laser illumination. The incident photon-to-current conversion efficiency (EQE) was measured using a photomodulation spectroscopy setup (Merlin, Oriel IQE-200) with monochromatic light from a xenon lamp. The power density of the monochromatic light was calibrated using an Si photodiode certified by the National Institute for Standards and Technology.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
photodetectors, solution-phase synthesis, transition metal dichalcogenides, thin films

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One-Step Solution Phase Growth of Transition Metal Dichalcogenide Thin Films Directly on Solid Substrates

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SUPPORTING INFORMATION

One-Step Solution Phase Growth of Transition Metal Dichalcogenide Thin Films Directly on Solid Substrates

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Computational methodology

Density-functional theory (DFT) calculations are performed with the projector-augmented wave (PAW) method as implemented in Vienna Ab initio Simulation Package (VASP).\textsuperscript{[1-3]} A plane wave kinetic energy cut off of 500 eV is applied, and the local-density approximation (LDA) to the exchange-correlation functional is used. The Brillouin-zone integration is performed with a Γ-centered k-point grid equivalent to a grid spacing of 0.2 Å\textsuperscript{-1} between the reciprocal points. For the geometry relaxation of the structures, the atomic positions are relaxed until the forces acting on the atoms are less than 0.02 eV/Å. For the optical response calculations, we have applied the independent-particle approximation (IPA) within the random-phase approximation (RPA), \textsuperscript{[4]}where excitonic and local-field effects are neglected. We carefully checked the effect of atomic relaxation on the calculated optical spectra, and were found to be negligible. Thus, for the optical absorbance calculations of the line-type grain boundaries, we used the unrelaxed geometry.

Supplementary Text

Calculation of substrate temperature rise under microwave irradiation

When a conducting substrate is placed under the microwave (MW) field, electromagnetic field of the microwaves is inductively coupled to the substrate, and temperature of the substrate increases according to its resistivity, i.e. due to ohmic losses in the substrate.\textsuperscript{[5]} The heating uniformity in the depth of the wafer depends on the microwave penetration depth \( \delta \) defined by,

\[
\delta = (2/\sigma \omega \mu)^{1/2}
\]  

(1)

where, \( \sigma \) is the electrical conductivity of the substrate, \( \omega \) is the radian frequency of the microwave and \( \mu \) is the free space permeability. So, based on the electrical conductivity (\( \sigma \)) of a substrate,
MW radiation can be either fully reflected (when substrate thickness $>\delta$), completely absorbed (where $\delta < \lambda_{MW}$) or penetrated (where $\delta > \lambda_{MW}$) without any interaction with the substrate.

To estimate the temperature rise in a substrate under MW irradiation, here we have employed the mathematical model developed by Bosman et al. to calculate the temperature rise of a contaminant thin film on a microwave window.[6] The temperature rise of the contaminant can be represented by the following equations:

$$\lambda = \frac{2\pi c}{\omega} \quad (2)$$

$$\delta/\lambda = s/2\pi\delta \quad (3)$$

$$L/s = L\lambda/2\pi\delta^2 \quad (4)$$

$$\Delta T = 100K \times \frac{a}{1\ mm} \times \frac{L_s}{(1 + \frac{L_s}{s})^2} \times \frac{A}{10^8\ W/m^2} \times \frac{1}{k} \frac{1}{10^3\ Wm^{-1}K^{-1}} \quad (5)$$

where $\Delta T$ is the rate of temperature rise, $\lambda$ free space wavelength of microwave, $c$ the speed of light in vacuum, $a$ is the radius of the thin film disk, $A$ is the average incident flux of MW, and $k$ is the thermal conductivity of thin film disk.

When $a$, $A$ and $k$ are constant in eq. (5), $\Delta T$ depends on $L/s$. Substituting eqs. (1), (2) and $\rho=1/\sigma$ (where $\rho$ is the resistivity of the contaminant) into eq. (4),

$$L/s = 60\pi L/\rho \quad (6)$$

As a result, $\Delta T$ depends on $L/\rho$ pas the following equation:

$$\Delta T = 100K \times \frac{a}{1\ mm} \times \frac{60\pi L}{\rho} \times \left(1 + \frac{60\pi L}{\rho}\right)^2 \times \frac{A}{10^8\ W/m^2} \times \frac{1}{k} \frac{1}{10^3\ Wm^{-1}K^{-1}} \quad (7)$$

Replacing the square shaped $p^{++}$ Si substrate used in the present study by a disk with equivalent area, we can obtain the value of $a$. By using the value of the respective parameters in eq. (7) we
can get the estimation of ΔT, which is in our case ~ 7.78 K/s for a 2 x 2cm² p++ Si substrate with an electrical conductivity of 1000 S/m under a 700 W microwave irradiation.

Study of defect structure dependent optical property

Several types of defect structure can be adopted in monolayer MoS₂, mainly line defects with different domain contact angles, and nano-grain boundary defects with corner-to-corner (grain void-type) or edge-to-edge (grain line-type) arrangement of different hexagonal MoS₂-grains (Fig. S7a-f). In Fig. S8a, DFT-LDA absorbance spectra of the pristine single-layer, the 5|7 line defect, the grain void-type, and the grain line-type defects in MoS₂ are plotted. We find that the pristine single-layered MoS₂ and the 4|4 or 5|7 line defects show very similar profile in their absorbance spectra – absorbing strongly in the visible light region (~ 2 to 3 eV). This is in contrast to that of the void- and line-type grain boundary defects in 2D MoS₂ where a very strong intense absorption peak is found for low photon energies (i.e. corresponding to the NIR region). Our theoretical finding strongly correlates with our experiments, and supporting that our MoS₂ films consist of small MoS₂ grains within a network of either void- and/or line-type grain boundary line defects.

To understand how the line defect width (LD) and the grain diameter (d) may influence the absorbance spectra, we have varied LD and d, and calculated their corresponding absorbance spectra, as shown in Fig. S8b and S8c. Surprisingly, void- and line-type grain boundary defects show very negligible differences in the absorption spectra, lending support that the strong IR absorbance may not be influenced by these two parameters. To investigate how the grain size may influence the absorbance spectra, we have varied the diameter of the grain (d) in line-type grain boundary structures, and calculated their corresponding absorbance spectra, as shown in Fig. S8d.
As the diameter of grain in line-type grain boundary structure increases, the absorbance at IR region is lowered while the absorbance peak at the UV-vis region increases.

To account for the observed low-energy IR absorption peaks, we calculate and examine the imaginary part of the frequency-dependent dielectric function, the electronic band structure, and the partial electron density of pristine MoS$_2$ and the grainline-type defects, as shown in Fig. S9. In Fig.S9a, pristine single-layered MoS$_2$ shows the first absorption peak at about 2 eV (peak A), which corresponds to the vertical transition at the K k-point (i.e. the direct band-gap energy), whereas the highest absorption peak positioned at about 3 eV (peak B) may be accounted by the vertical transition between the $\Gamma$ and M k-points. From the atomic orbital analysis (via DFT partial electron density calculations), we find that the orbital character responsible for the first absorption peak A (~ 2 eV) originates from Mo 4d states (with a minute participation of the S 2p states), in good agreement with previous reports.$^{[7-8]}$ The vertical transition (labeled as B) is found to contain more S 2p character in the conduction band. Both the calculated optical and electronic band structure may explain the reported near-UV absorption in pristine, defect-free MoS$_2$. However, in case of grain line-type defects, in Fig.S9b, the vertical transition for the first absorption peak at $\Gamma$ k-point (~ 0.3 eV, labeled as A’) is accounted for by the localized Mo 4d and S 2p states of the outermost Mo and S atoms near the grain boundaries. The inner bulk-like Mo and S atoms do not contribute to this low-energy IR optical vertical transition, as clearly shown in our orbital analysis via partial electron density calculations. So, the outermost Mo and S atoms (labeled as Mo1, Mo2, S1, and S2 in Fig.S9b) participate differently in the low-energy IR region. Specifically, for the A’ vertical transition, only the 4d states of both Mo1 and Mo2 contribute to valence band edge states, while within the conduction states, we find that only the 4d states of Mo2 and 2p states of S2 are dominant.
Details of band gap calculation

The optical band gaps for direct and indirect transitions of MoS$_2$ were found to be 1.72 and 0.87 eV, respectively, from the “Tauc” plot (Fig. S10) of the UV-vis-NIR absorption.$^{[9]}$ Ultraviolet photoemission spectroscopic (UPS) analysis indicates that the maximum of the valence-band energy ($E_V$) and work function ($\Phi$) for MoS$_2$ were 0.54 and 4.27 eV, respectively (Fig. S11). Based on these values ($E_V$&$\Phi$) and the optical band gap energy, we drew an energy band diagram for the synthesized MoS$_2$, as shown in Fig. 4a in the main text.

![Fig. S1](image1.png)

**Fig. S1.** EDS analysis. EDS spectrum of the MoS$_2$ thin film showing the presence of Mo and S as the principle element. The peak due to the supporting Cu grid can be seen around 8 eV.
**Fig. S2.** XPS analysis of MoS$_2$ thin film. XPS spectrum the MoS$_2$ thin film showing the binding energies of oxygen (O 1S).

**Fig. S3.** Elemental mapping of MoS$_2$ thin film. STEM-EDS elemental mapping of MoS$_2$ thin film showing the uniform presence of O along with Mo and S in the entire detection range of the thin film.
**Fig. S4.** High resolution TEM image of MoS$_2$ thin film. HRTEM of MoS$_2$ thin film showing periodic atomic arrangements. Inset is a fast Fourier transform (FFT) pattern from the entire area of the figure, clearly indicating the presence of a highly crystalline hexagonal MoS$_2$ phase.

**Fig. S5.** Layered structure of WS$_2$ thin film. Cross-sectional TEM image of WS$_2$ showing the layer structure formation with an interlayer spacing of 0.63 nm.
**Fig. S6.** Photoluminescence study of MoS$_2$ thin film. PL spectrum of the thin film measured at room temperature using 532 nm laser excitation.
Fig. S7. Additional atomic structures used for DFT calculations. a) Pristine single-layered MoS$_2$ without any defect. b) 4|4 line defect structure. c) Grain void-type defect structure. d) Grain void-type defect structure with increased grain diameter. e) Grain line-type defect structure with increased line defect (LD) width. f) Grain line-type defect structure with increased grain diameter ($d$).
**Fig. S8.** Calculated optical absorbance of MoS$_2$ structures. 

a) Absorbance spectra of pristine MoS$_2$ without defects, with 4|4 line defect, with 5|7 line defect, with grain void-type defect, and with grain line-type defect MoS$_2$ structure. 

b) Absorbance spectra of grain void-type defect structure with different grain diameter ($d$) and line defect (LD) width. 

c) Absorbance spectra of grain line-type defect structure with different $d$ and LD widths. 

d) Absorbance spectra of grain line-type defect structure with different grain diameter ($d$).
Fig. S9. Calculated optical and electronic structure of MoS$_2$ monolayer and grain line-type defect structures. a) Imaginary part of dielectric function, electronic band structure, and partial electron density of pristine single-layered MoS$_2$. b) Imaginary part of dielectric function, electronic band structure, and partial electron density of grain line-type defect structure. Mo atom and S atom is depicted in grey and yellow sphere, respectively. Translucent red region shows the partial electron density.
Fig. S10. Determination of optical band gap. 'Tauc' plot of $(\alpha h \nu)^n$ versus $h \nu$ ($n = 2$ and 0.5 for direct allowed and indirect allowed transitions, respectively), to determine the band gap from the UV-vis-NIR absorption onset for MoS$_2$ thin film. a-b) Plots for direct and indirect band gap determination, respectively.
Fig. S11. UPS analysis of MoS\(_2\) thin film. a) Onset level (E\(_{\text{onset}}\)) of the UPS (ultraviolet photoelectron spectroscopy) spectra, where the work function (\(\Phi\)) can be calculated by \(\Phi = h\nu - E_{\text{onset}}\), \(h\nu\) is the incident photon energy of 21.2 eV. b) UPS spectra near the Fermi level energy and valence band maximum, of the MoS\(_2\) thin film.
Table S1. EDS elemental analysis of MoS$_2$ thin film.

<table>
<thead>
<tr>
<th>Atomic ratio of Mo: S</th>
<th>Atomic % of oxygen</th>
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<tr>
<td>1: 2.06</td>
<td>3.74</td>
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References