Interstitial Mo-Assisted Photovoltaic Effect in Multilayer MoSe_2 Phototransistors

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Thin-film transistors (TFTs) based on multilayer molybdenum diselenide (MoSe_2) synthesized by modified atmospheric pressure chemical vapor deposition (APCVD) exhibit outstanding photoresponsivity (103.1 A W^{-1}), while it is generally believed that optical response of multilayer transition metal dichalcogenides (TMDs) is significantly limited due to their indirect bandgap and inefficient photoexcitation process. Here, the fundamental origin of such a high photoresponsivity in the synthesized multilayer MoSe_2 TFTs is sought. A unique structural characteristic of the APCVD-grown MoSe_2 is observed, in which interstitial Mo atoms exist between basal planes, unlike usual 2H phase TMDs. Density functional theory calculations and photoinduced transfer characteristics reveal that such interstitial Mo atoms form photo-reactive electronic states in the bandgap. Models indicate that huge photo-amplification is attributed to trapped holes in subgap states, resulting in a significant photovoltaic effect. In this study, the fundamental origin of high responsivity with synthetic MoSe_2 phototransistors is identified, suggesting a novel route to high-performance, multifunctional 2D material devices for future wearable sensor applications.

2D layered materials such as transition metal dichalcogenides (TMDs) are significant contenders for future photosensors\cite{1} due to their superior electrical and optical properties as well as mechanical stability,\cite{2} and the optical properties of 2D materials can be even modulated by using metal nanostructures.\cite{3} Over the years, the photoresponsivity – a figure of merit for photosensors – of multilayer TMDs has remained relatively low, unlike that of monolayer TMDs, due to their indirect bandgap and inefficient photoexcitation process.\cite{2a,4} However, multilayer TMDs have clear advantages over their monolayer counterparts for practical applications in terms of favorable fabrication processes, large density of states (DOS), and wide spectral responses.\cite{4b,5} Recently, it has been reported that multilayer molybdenum diselenide (MoSe_2) can exhibit large photoresponsivity,\cite{6} while that of multilayer molybdenum disulfide (MoS_2) is significantly limited under photodetecting device architectures.\cite{4b,7} Notably, it is known that natural MoSe_2 flakes do not exist,\cite{8} and therefore, all previous measurements have been based on synthetic MoSe_2.\cite{9} Here, our central interest lies in the fundamental origin of large photoresponsivity with synthesized MoSe_2, compared to naturally occurring TMDs such as MoS_2 flakes. If it can be identified, a novel route can be paved for highly sensitive photodetectors by engineering synthetic MoSe_2, which is, however, inherently unachievable with natural MoS_2 flakes due to the uncontrolled growth condition and possible variations.

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Interestingly, although typical natural MoS$_2$-based photo-transistors exhibit significantly low photoresponsivity, we found that a limited number of devices based on the same material show remarkably better optical behaviors. Such performance deviation can be expected with MoS$_2$ flakes due to nonuniform growth conditions in the natural environment (where high-pressure and high-temperature environments are typically achieved). Since this can provide us a clue to understand the optical properties of synthetic MoSe$_2$, first we have investigated the microstructure of natural MoS$_2$. As a result, we could observe additional atomic layers between the basal planes, which are normally empty regions in the 2H hexagonal structure, for the MoS$_2$ flakes showing relatively high photoresponsivity. More importantly, similar interstitial atoms can also be found with MoSe$_2$ synthesized by modified atmospheric pressure chemical vapor deposition (APCVD). To identify the interstitial atoms observed in the synthetic MoSe$_2$, we have performed density functional theory (DFT) calculations, and the results suggest that the interstitial atoms are Mo interstitials (Moint). DFT simulations further reveal that gap states can be induced by Moint, which is also experimentally supported from the measurement of photoinduced transfer characteristics. Moreover, we modeled the conductivity increase with illumination (photoconductive (PC) effect) and the threshold voltage shift due to the local accumulation of charges (photovoltaic (PV) effect) independently to further understand the measured data, and found that the trap states induced by Moint are the origin of high photoresponsivity in APCVD-grown MoSe$_2$ phototransistors, where the PV effect is predominant over the PC effect. In this study, we systematically identified the origin of high photoresponsivity in synthetic MoSe$_2$ phototransistors based on our comprehensive approach, including material growth, device fabrication, advanced experimental analyses, as well as DFT simulations and modeling, thereby suggesting a novel route to realize highly sensitive phototransistors using APCVD-grown multilayer MoSe$_2$.

**Figure 1a** shows the average photoresponsivity ($R$; the ratio of photocurrent to the incident power) from 10 representative MoS$_2$ (■) and MoSe$_2$ (Δ) phototransistors, which turns out to be $0.17 \pm 0.05$ and $85.3 \pm 11.86$ A W$^{-1}$, respectively. Relatively lower $R$ of multilayer MoS$_2$ is in good agreement with previous reports.$^{[4b,7]}$ However, we could also find a MoS$_2$ phototransistor exhibiting an unusually high $R$ value of $10.1$ A W$^{-1}$ ( ), which is about two orders of magnitude larger than the typical values from multilayer MoS$_2$ devices. While any noticeable interstitial defect was not observed in a scanning transmission electron microscope (STEM) image (Figure 1b) for a typical multilayer MoS$_2$ phototransistor, distinct interstitial atoms (red-dashed ellipse) could be clearly observed from a cross-sectional high-resolution transmission electron microscopy (HRTEM) image.

![Figure 1](image_url)

**Figure 1.** Relation between photoresponsivity and interstitial atoms in MoX$_2$ (X = Se, S). a) Comparison of the measured photoresponsivity ($R$) of natural MoS$_2$ flakes with and without interstitial atoms as well as that of synthetic MoSe$_2$ with Mo interstitial (Moint). b) Cross-sectional STEM image of MoS$_2$ without interstitials. c) Aberration-corrected HRTEM image of MoS$_2$ with interstitials (red-dashed ellipses). d) Aberration-corrected HRTEM images of MoSe$_2$, exhibiting interstitial Mo atoms. Red-dashed ellipses indicate additional atomic layers between the MoSe$_2$ basal planes. A total of 5 layers of 2H stacking structure in MoSe$_2$ are clearly identified, which were denoted by braces and corresponding italicized characters. Blue and pink arrows designate atomic lines of Mo and Se, respectively.
(Figure 1c) for the MoS₂ device showing a relatively large \( R \) value. Similarly, the layered structure of our synthetic MoSe₂ is also exhibited in the aberration-corrected HRTEM image (Figure 1d). Each layer is stacked following the ABABAB sequence, which is consistent with the X-ray diffraction (XRD) and Raman spectroscopy analyses as shown in Figure S1 (Supporting Information), confirming that as a whole our APCVD-grown MoSe₂ has a 2H hexagonal structure. In Figure 1d, a total of 5 layers of 2H stacking structure are clearly identified with braces and corresponding italicized characters, and a couple of interstitial atoms were found between \( a \)- and \( b \)-layers (red-dashed ellipse) and also another group of interstitials between \( b \)- and \( c \)-layers.

Figure 2a,b shows the transfer characteristics of multilayer MoSe₂ and MoS₂ thin-film transistor (TFT), respectively, under illumination with various incident optical power densities (\( P_{inc} \))

![Figure 2](image_url)

**Figure 2.** Photoresponsive behavior of APCVD-grown MoSe₂ TFTs. a,b) \( I_{ds} - V_{gs} \) characteristics of multilayer (a) MoSe₂ and (b) MoS₂ phototransistors under illumination with a wavelength of 405 nm and various incident optical power densities. c) Measured (symbols) and modeled (dashed lines) photoresponsivity (\( R \)) as a function of \( P_{inc} \) for the MoSe₂ and MoS₂ phototransistors. A maximum value of 103.1 A W⁻¹ is obtained at \( P_{inc} = 20 \) mW cm⁻² and \( \lambda_{ex} = 405 \) nm with MoSe₂. d) The modeled \( I_{ph, PV} \) (solid lines) and \( I_{ph, PC} \) (dashed lines) plotted independently for the devices shown in (a) and (b) (the same colors are used as in (c) for various wavelengths). The symbols are taken from the measurements in the off states (\( V_{gs} = -40 \) V) for \( I_{ph, PC} \).

e) (Main panel) Calculated specific detectivity (\( D^* \)) for MoSe₂ and MoS₂ photodetectors at \( \lambda_{ex} = 405 \) nm. (Inset) Schematic energy band diagram, showing the mechanism of the photovoltaic (PV) effect. Filled and open circles denote electrons and holes, respectively. f) Photocurrent response to light intensity at \( \lambda_{ex} = 405 \), 638 nm (main panel) and 852 nm (inset).
at an excitation wavelength ($\lambda_{\text{ex}}$) of 405 nm and $V_{\text{ds}} = 1$ V. It should be noted that a typical natural flake of MoS$_2$ (as shown in Figure 1b) has been used here to provide representative optical behaviors of multilayer MoS$_2$ TFTs. While both materials show significant increase of off-state current (at low $V_{\text{gs}}$) under light compared to the dark states, only MoSe$_2$ exhibits clear response to illumination at on state (high $V_{\text{gs}}$) as shown in Figure 2a, whereas on current of the MoS$_2$ TFT remains nearly unchanged under the exposure to light (Figure 2b). In Figure 2c, we compare the photoresponsivity of MoSe$_2$ and MoS$_2$ for various $P_{\text{inc}}$, where symbols represent the experimentally obtained values. A maximum photoresponsivity of 103.1 A W$^{-1}$ was achieved with MoSe$_2$ at $P_{\text{inc}} = 20$ mW cm$^{-2}$ and $\lambda_{\text{ex}} = 405$ nm, which is $\approx 40$ times larger than that of natural multilayer MoS$_2$ phototransistors.

In order to understand the large photoresponsivity in the synthetic multilayer MoSe$_2$ TFTs, we have investigated the photocurrent induced by the PC effect ($I_{\text{ph,PC}}$) and the PV effect ($I_{\text{ph,PV}}$) independently in Figure 2d. Under illumination, electron–hole pairs are generated and the conductivity of the channel material is increased. This conductivity increase due to photoinduced excess carriers is the PC effect, and the consequent photocurrent is calculated by $I_{\text{ph,PC}} = \left( \frac{W}{L} \right) V_{\text{gs}} \Delta \sigma$, where $W$, $L$, $V_{\text{gs}}$, and $\Delta \sigma$ are the width and length of the device, the source–drain voltage, and the conductivity increase due to light illumination, respectively.$^{[10]}$ On the other hand, the PV effect is modeled with the threshold voltage ($V_{\text{th}}$) shift caused by accumulation of holes and barrier lowering, which is given by $I_{\text{ph,PV}} = g_{\text{m}} \Delta V_{\text{th}}$, where $g_{\text{m}}$ is the transconductance in the dark and $\Delta V_{\text{th}}$ is the threshold voltage shift induced by illumination.$^{[11]}$ While the excess electrons in the conduction band can easily move from the channel to the drain, the motion of the excess holes in the valence band can be hampered by a barrier near the source–channel junction, leading to the local accumulation of holes. Moreover, these excess holes can be captured by trap states, resulting in the suppression of the potential barrier and the increase of electron injection from the source, as depicted in the inset of Figure 2e.

To analyze the measured data using our models (details of the models are described in the Experimental Section), first we have plotted $I_{\text{ph,PC}}$ in Figure 2f (dashed lines) by fitting $\tau_\text{t}$, $\tau_\text{g}$, and $P_{\text{tr}}$ with experimental data (symbols; obtained from Figure 2a,b and Figure S3 (Supporting Information) in the off state), where $\tau_\text{t}$ is the recombination lifetime, $P_{\text{tr}}$ is the trap density, and $\tau_\text{g}$ are the trapping and escaping time of holes into and from the trap states, respectively.$^{[10]}$ Then, photoresponsivity values are fitted in Figure 2f (dashed lines), where both $I_{\text{ph,PC}}$ and $I_{\text{ph,PV}}$ are considered $I_{\text{ph}} = I_{\text{ph,PC}} + I_{\text{ph,PV}}$, by introducing a parameter $\chi$ describing barrier-lowering efficiency. Finally, we obtained $I_{\text{ph,PV}}$ from $I_{\text{ph}} - I_{\text{ph,PC}}$ and plotted it in Figure 2d (solid lines) to compare with $I_{\text{ph,PC}}$. Interestingly, our results indicate that, although the photoconductive current is larger with MoS$_2$, the synthetic MoSe$_2$ shows a significantly larger PV effect, resulting in remarkably higher photoresponsivity in the MoSe$_2$ TFTs. Notably, $I_{\text{ph,PV}}$ is larger than $I_{\text{ph,PC}}$ by 92 times with MoSe$_2$ at $P_{\text{inc}} = 20$ mW cm$^{-2}$ and $\lambda_{\text{ex}} = 405$ nm, whereas $I_{\text{ph,PV}}/I_{\text{ph,PC}}$ of MoS$_2$ remains much lower for the entire range of $P_{\text{inc}}$ considered. The fitted parameters ($\tau_\text{t}$, $\tau_\text{g}/\tau_\text{g}$, $P_{\text{tr}}$, $\chi$, $\chi$) are provided in the Experimental Section) indicate that the greater number of states exists energetically deeper in the bandgap region for the synthetic MoSe$_2$, resulting in shorter recombination lifetime (hence smaller $I_{\text{ph,PV}}$) and longer escaping time for holes from the trap states (hence larger $I_{\text{ph,PC}}$), compared to those in MoS$_2$ flakes.

Specific detectivity ($D^*$) is another figure of merit for photodetectors, which indicates the sensitivity of detectors and is given by $D^* = \frac{R A^{1/2}}{(2 q I_{\text{ph}})}$, where $R$ is the responsivity, $A$ is the area of detector, $q$ is the unit charge, and $I_{\text{dark}}$ is the dark current.$^{[12]}$ Figure 2e shows the calculated $D^*$ of the synthesized MoSe$_2$ and natural MoS$_2$ phototransistors at $\lambda_{\text{ex}} = 405$ nm, which clearly exhibits that the specific detectivity of the MoSe$_2$ is larger than that of MoS$_2$ by one order of magnitude. Linerarity and robust light switching behaviors are also important features required for practical photodetector applications. The main panel in Figure 2f shows the linear response of $I_{\text{ph}}$ to light intensity for our multilayer MoSe$_2$ phototransistor at $\lambda_{\text{ex}} = 405$ and 638 nm in the on state ($V_{\text{gs}} = 40$ V). The linearity at $\lambda_{\text{ex}} = 852$ nm was plotted separately in the inset of Figure 2f considering the photoconductive current in the off state ($V_{\text{gs}} = -40$ V) due to the limited PV effect in the on state (Figure S3b, Supporting Information). The time-resolved photoswitching behavior of the MoSe$_2$ TFT is also presented in Figure S4 (Supporting Information). The photosresponse remains almost identical for multiple cycles of light switching with intervals of 20 s, which demonstrates the robustness and feasibility of our MoSe$_2$ phototransistors for high-performance photodetectors.

In Figure 1d, we could observe interstitial atoms between the basal planes of APCVD-grown MoSe$_2$, however we could not identify the kind of atoms using spectroscopy methods. Here, we identify the kind of interstitial atoms observed in multilayer MoSe$_2$ first, and then discuss the role of such interstitials in phototransistors. Considering our unique growth condition of MoSe$_2$, in which the material is grown on a 100 nm thick Mo-coated silicon (Si) substrates (i.e., Mo-rich condition), it is reasonable to believe that the observed additional atoms in MoSe$_2$ are Mo$_{\text{int}}$, and interstitial Se ($\text{Se}_{\text{int}}$) is very unlikely to be formed due to the deficiency of Se atom. In order to justify our claim, we have calculated defect formation energies using DFT simulations$^{[13]}$ (details of the calculation approach are provided in the Experimental Section). The defects considered include Mo$_{\text{int}}$, Se$_{\text{int}}$, Mo vacancy (Mo$_{\text{vac}}$), and Se vacancy (Se$_{\text{vac}}$). Figure 3a shows the calculated formation energy of the defects. We consider two cases: when the simulation cell is allowed (“free cell”), or not allowed (“fixed cell”), to change shape/volume during the structural relaxation. The “free cell” DFT results indicate that $\text{Se}_{\text{int}}$ is the interstitial with lower formation energy than $\text{Mo}_{\text{int}}$. However, a key observation from the simulations is that the introduction of $\text{Se}_{\text{int}}$ leads to a significant reconstruction of the MoSe$_2$ structure during the atomic relaxation (which seeks to minimize the total energy). With $\text{Mo}_{\text{int}}$, and all other simulated defects except $\text{Se}_{\text{int}}$, the MoSe$_2$ remains hexagonal after relaxation, while with $\text{Se}_{\text{int}}$, there is significant reconstruction resulting in a triclinic lattice. Similar materials, such as MoS$_2$, are known to be susceptible to phase transitions,$^{[14]}$ which can be controllable and reversible.$^{[15]}$
Our XRD analysis, provided in the Supporting Information, confirms the hexagonal structure of the APCVD-grown MoSe$_2$. In light of this observation, we repeated the defect formation energy calculations while preserving the simulation cell shape, in order to conserve the experimentally confirmed hexagonal structure. The “fixed cell” formation energies of our DFT calculations, presented in Figure 3a, in combination with the experimental observations, indicate that Mo$_{\text{int}}$ is the most energetically favorable interstitial atom and the most likely to exist in our APCVD-grown MoSe$_2$ samples. Note that the “fixed cell” calculations are for qualitative comparison purposes, and used to estimate the energetics of Se$_{\text{int}}$ in hexagonal MoSe$_2$. Figure 3b shows the optimized atomic structure of a 3 × 3 × 1 supercell with one interstitial Mo atom (Mo$_{\text{int}}$). The electronic structure of a 4 × 4 × 1 supercell with one Mo$_{\text{int}}$, with contributions from the Mo$_{\text{int}}$ (d-orbitals) depicted by circles, is presented in Figure 3c. We find both Mo$_{\text{int}}$ and Se$_{\text{vac}}$ introduce gap states, however an important distinction is that with Mo$_{\text{int}}$ and Se$_{\text{vac}}$, the gap states are filled and empty, respectively. In the case of Se$_{\text{vac}}$, unoccupied gap states (or equivalently occupied with holes) prevent holes from being trapped by those states, which impedes the photovoltaic effect – a key mechanism observed with the MoSe$_2$ phototransistor. With Mo$_{\text{int}}$, the gap states are filled (empty of holes), and thus can trap holes and contribute significantly to the photovoltaic effect. Therefore, we can conclude that Mo$_{\text{int}}$ is the key element that can most significantly contribute to the photovoltaic effect and the large photoresponsivity in multilayer MoSe$_2$ phototransistors.

Finally, our DFT results suggest that Se$_{\text{vac}}$ is another defect that could potentially exist in MoSe$_2$ (although the Raman spectrum of our APCVD-grown multilayer MoSe$_2$ suggests the absence of Se$_{\text{vac}}$ based on a previous report[16]). Figure 3e presents the electronic structure of a 4 × 4 × 1 MoSe$_2$ supercell with one Se$_{\text{vac}}$. We find both Mo$_{\text{int}}$ and Se$_{\text{vac}}$ introduce gap states, however an important distinction is that with Mo$_{\text{int}}$ and Se$_{\text{vac}}$, the gap states are filled and empty, respectively. In the case of Se$_{\text{vac}}$, unoccupied gap states (or equivalently occupied with holes) prevent holes from being trapped by those states, which impedes the photovoltaic effect – a key mechanism observed with the MoSe$_2$ phototransistor. With Mo$_{\text{int}}$, the gap states are filled (empty of holes), and thus can trap holes and contribute significantly to the photovoltaic effect. Therefore, we can conclude that Mo$_{\text{int}}$ is the key element that can most significantly contribute to the photovoltaic effect and the large photoresponsivity in multilayer MoSe$_2$ phototransistors.

We also confirmed the larger number of gap states in the synthetic MoSe$_2$ compared to natural MoS$_2$ through direct measurements of photoinduced transfer characteristics. Figure 4a,b
Figure 4. Photoinduced spectral response of MoS$_2$ and MoSe$_2$ phototransistors. a, b) Photoinduced $I_{ds}$–$V_{gs}$ curves of the (a) MoS$_2$ and (b) MoSe$_2$ TFTs under monochromatic light radiation with various wavelengths. c) Interband transitions plotted in the simplified energy diagram of MoS$_2$ (left) and MoSe$_2$ (right). $\Gamma_v$ and $|\Gamma - K|$ denote valence band maxima and conduction band minima without spin-orbit coupling (SOC) effects, respectively, and $K_v$ and $K_c$ denote valence band and conduction band edge at $K$ point, respectively. d) Photon energy-dependent areal DOS profiles of MoS$_2$ and MoSe$_2$ TFTs. The profiles reflect the different band-to-band transitions for MoS$_2$ and MoSe$_2$ TFTs, and the areal DOS is significantly larger in MoSe$_2$ than in MoS$_2$.

shows the $I_{ds}$–$V_{gs}$ curves of the MoS$_2$ and MoSe$_2$ TFTs, respectively, under monochromatic light radiation with various wavelengths in the linear regime. Seemingly, there are little changes in threshold voltages and off-state current for both the MoS$_2$ and MoSe$_2$ TFTs. However, a close look on the insets of Figure 4a indicates that the threshold voltage of MoS$_2$ TFT shifts toward
positive values with increasing incident photon energy (i.e., decreasing wavelength). The positive shift of the threshold voltage under illumination of light could be counterintuitive as one would usually expect negative shifts owing to the generation of excess carriers. However, the positive shift in threshold voltage may have resulted from the bias-stress effect induced by the continued photoinduced transfer curve measurements on the device, which in general results in current drop at a fixed gate voltage.\textsuperscript{[17]} Notably, the presence of defects at the interface between the 300 nm thick silicon dioxide (SiO\textsubscript{2}) insulator and the TMD channel in TFTs will be inevitable. In such a case, when the gate bias is continuously applied, some of the charges can be trapped by the defects at the interface, resulting in the positive shift of \( V_{th} \) and the bias-stress effect. In light of this, it may be suggested that the MoS\textsubscript{2} TFT is relatively insensitive to the illumination of light, which cannot fully compensate the bias-stress effects. Unlike the MoS\textsubscript{2} TFTs, the threshold voltages of MoSe\textsubscript{2} TFTs shift toward negative values, as shown in the insets of Figure 4b, in the photon energy range of 1.10–1.35 and 1.50–1.70 eV (see also Figure S7 in the Supporting Information), indicating the remarkable interband charge transitions, as illustrated by the schematic energy diagrams in Figure 4c. Figure 4d shows the areal DOS profiles of both MoS\textsubscript{2} and MoSe\textsubscript{2} TFTs extracted from the \( \Delta V_{th} \) dependent curves by differentiating the excited charge values with the incident photon energy (Figure S7, Supporting Information). The spectral DOS profiles exhibit charge transition peaks with the DOS in the energy range depicted by \( T_1 \) (=1.30 eV) and \( T_3 \) (=1.85 eV) for MoS\textsubscript{2} and \( T_1 \) (=0.85 eV), \( T_2 \) (=1.10 eV), and \( T_3 \) (=1.34 eV) for MoSe\textsubscript{2}, which match well with the previously reported values with only minor deviations.\textsuperscript{[14,18]} A summary of the interband transitions near the bandgap for both bulk MoS\textsubscript{2} and bulk MoSe\textsubscript{2} is presented in Table 1. Note that the assigned energy states in our APCVD-grown multilayer MoSe\textsubscript{2} films have significantly larger areal DOS than the ones in the natural MoS\textsubscript{2} flakes. It is thus inferred that the MoSe\textsubscript{2} has a much larger number of energy states that can act as charge traps, as depicted in the inset of Figure 2e. Some peaks in the spectrum of Figure 4d could not be assigned to any particular state; for example, those arising at \( \approx 0.90 \) and \( \approx 1.65 \) eV for MoS\textsubscript{2}, and at \( \approx 1.55 \) and \( \approx 1.85 \) eV for MoSe\textsubscript{2}. However, given the energy state level, it may be suggested that the peak at \( \approx 0.90 \) eV in MoS\textsubscript{2} is related to the subgap states in the energy bands and the peak at \( \approx 1.65 \) eV corresponds to the interband transition in bilayer MoS\textsubscript{2}, while the peaks at \( \approx 1.55 \) and \( \approx 1.85 \) eV in MoSe\textsubscript{2} are related to the charge transitions in the higher energy states.\textsuperscript{[14,18a]}

In the present work, the fundamental origin of high photoresponsivity in synthetic MoSe\textsubscript{2} phototransistors was sought. Aberration-corrected HRTEM images confirmed the existence of interstitial atoms in synthetic multilayer MoSe\textsubscript{2}, and it was revealed that such interstitials are Mo\textsubscript{int} rather than Se\textsubscript{int} based on DFT calculations. DFT results further exhibited the formation of gap states due to the Mo\textsubscript{int}, and the measurements of photoinduced transfer characteristics also confirmed significantly large subgap states in the synthetic MoSe\textsubscript{2}, unlike typical MoS\textsubscript{2} flakes. The photoresponsive characteristics were analyzed by models, which indicated that Mo\textsubscript{int} induced gap states are the fundamental origin of significant PV effects, leading to large photoresponsivity in synthetic multilayer MoSe\textsubscript{2} phototransistors. The results presented in this work will provide a significant practical advancement in the field of multifunctional 2D electronics for wearable sensor applications.\textsuperscript{[19]}

### Experimental Section

#### Synthesis and Device Fabrication

The single-crystalline MoSe\textsubscript{2} platelets were fabricated through the modified APCVD method based on direct vapor transport of seed materials.\textsuperscript{[20]} First, the polycrystalline MoSe\textsubscript{2} compounds were prepared through solid state reaction,\textsuperscript{[21]} and utilized as precursor (p-MoSe\textsubscript{2}).\textsuperscript{[20a]} To optimize the wettability of the single-crystalline MoSe\textsubscript{2}, a thin layer of molybdenum (Mo) with a thickness of 10 nm was deposited on a silicon (Si) substrate. Then, p-MoSe\textsubscript{2} compounds and Mo-coated Si substrates were placed at the hot and cold zones of the evacuated quartz ampoule, and the reaction temperatures were slowly increased up to 1050 and 1000 °C, respectively.

In order to fabricate phototransistors, multilayer MoSe\textsubscript{2} flakes were mechanically exfoliated from single-crystalline platelets, and transferred onto n-type doped Si substrates covered with a 300 nm thick SiO\textsubscript{2} as the gate insulator. Titanium/gold layers with respective thicknesses of 15/300 nm were deposited by electron beam evaporation. Then, S/D electrodes were patterned through conventional photolithography and etching procedures. To improve the contact resistance, the phototransistor was thermally annealed in a furnace at 200 °C for 2 h under gas flow conditions (100 sccm Ar and 10 sccm H\textsubscript{2}). For quantitative comparisons, multilayer MoS\textsubscript{2} phototransistors were also fabricated based on the above procedure using mechanically exfoliated flakes from bulk crystals (SPI supplies, USA). Details of synthesis and device fabrication were reported earlier.\textsuperscript{[4b,5,20a]}

#### Characterization

Morophologies of the APCVD-grown MoSe\textsubscript{2} layers were characterized by STEM (JEM-ARM200F, jeol) and HRTEM (FEI Titan Cubed G\textsubscript{i} 60-300).

The electrical properties of APCVD-grown MoSe\textsubscript{2} phototransistors were investigated using a Keithley 4200-SCS semiconductor characterization system equipped with a probe station at room temperature under ambient conditions. Radiations with various wavelengths were generated with a Multichannel Fiber-Coupled Laser Source (MCL51, Thorlabs), and guided in a direction perpendicular to the active channel of the phototransistors via Single Mode Fiber Optic Patch Cables (S405-HP for 405 nm, SM600 for 638 nm, and SM800 for 852 nm, Thorlabs). Power densities of the incident light were measured using a Standard Photodiode Power Sensor (S120VC, Thorlabs), connected to an Analog Handheld Laser Power Meter Console (PM100A, Thorlabs).

In order to measure the photoinduced transfer curves of the TFTs, the electrical measurements were performed under an intense monochromatic light (photon flux of at least \( \approx 10^{15} \) cm\textsuperscript{-2} s\textsuperscript{-1} as estimated from the optical power density, \( \approx 0.1 \) mW cm\textsuperscript{-2}). The optical spectroscopic system is equipped with a light source of 500 W Hg(Xe) arc lamp, a grating monochromator covering a spectral range of 300–1000 nm and an optical fiber (core diameter of 200 µm) as an optical probe that guides photons to the channel area of the testing device, which is connected to an electrical measurement unit (4155C Semiconductor Parameter Analyzer, Agilent Technologies).

### Table 1. Band-to-band transitions near the gap in bulk MoSe\textsubscript{2} and bulk MoS\textsubscript{2}

<table>
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<th>Label</th>
<th>Transition</th>
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<th>MoS\textsubscript{2}</th>
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<td>1.85</td>
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</table>

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Model: To calculate the conductivity increase due to illumination, a modified Hornbeck–Haynes model is used as Δσ = q(μ⊥ + μ∥)Δp + qαα‖, where μ⊥ and μ∥ are the electron and hole mobilities, respectively. Δp is the excess hole density in the valence band, and p∥ is the trapped hole density.[10] The mobilities of 97.4 and 16.6 cm² V⁻¹ s⁻¹ are extracted from the experiments and used for MoSe₂ and MoS₂ TFFs, respectively, and Δp is obtained by Δp = gτ, where g = (πηPabs/ν) is the generation rate of photons and τ is the carrier recombination lifetime (fitted). η and ν are the internal quantum efficiency and the single photon energy, respectively. The internal quantum efficiency is chosen as η = 0.3, 0.5, 0.07 for MoSe₂, 405, 638, 852 nm, respectively. Pabs is the absorbed power density, given by Pabs = 1 − e⁻ⁿa d P r e⁻ⁿd τ, where n is the absorption coefficient in the vertical (n² = 28.3 × 10⁻²⁶ cm⁻² at λ = 405 nm, 1.22 × 10⁻²⁶ cm⁻² at 638 nm, 4.88 × 10⁻²⁶ cm⁻² at 852 nm for MoSe₂; 26.6 × 10⁻²⁶ cm⁻² at 405 nm for MoS₂)[24] and lateral direction (n² = 103.4 × 10⁻²⁶ cm⁻² at λ = 405 nm, 10.3 × 10⁻²⁶ cm⁻² at 638 nm, 1.37 × 10⁻²⁶ cm⁻² at 852 nm for MoSe₂; 87.1 × 10⁻²⁶ cm⁻² at 405 nm for MoS₂)[24], respectively, and d is the thickness of channel material (d = 60 nm for MoSe₂; 40 nm for MoS₂). The trapped hole density is calculated by p∥ = (P∥τ∥/gτ∥ + Pr/(τr/τ∥)), where Pr is the trap density, and τ∥ and τr are the trapping and escaping times of holes into and from the trap states, respectively.[10] Photocurrent density (Ip,pc) is obtained in the off state (Vgs = −40 V) from the measurement data (Figure 2a,b and Figure S3 (Supporting Information)) and fitted with Ip,PC = W T √ Vgs DAσ in Figure 2d, resulting in the following fitting parameters: P∥ = 5 × 10⁻¹⁰ cm⁻², τ∥ = 150 ps, and τr/τ∥ = 1/1000 for MoSe₂; P∥ = 3 × 10⁻¹⁰ cm⁻², τ∥ = 8 ns, and τr/τ∥ = 1/100 for MoS₂. To evaluate the PV effect below, τ∥ and τr are assumed for MoSe₂ and MoS₂, respectively. W/L is 8.3 μm/13.1 μm for MoSe₂; 63 μm/15.1 μm for MoS₂.

On the other hand, the PV effect is modeled with the threshold voltage shift (ΔVth) due to potential barrier lowering (Δα∥). Considering that ΔVth is proportional to Δα∥.[11] When positive charges are locally accumulated inside the device, potential barriers for electrons can be lowered, in which the potential energy varies linearly while the amount of charges changes exponentially.[12] Therefore, the barrier lowering can be modeled as Δα∥ = n kBT q ln(β effτp d), where kBT, q, T, q, τp, and n are the Boltzmann constant, the temperature, the effective lifetime, and a constant accounting for the saturation effect, respectively.[12] The number of holes (p) can be expressed as p = P √ T √ g √ v √ hν τ p d τ g, where P, τp, τg, v, and v correspond to the background charge (in dark), the excess carriers in the valence band due to the illumination, and the trapped charges in subgap states, respectively. Considering hole accumulation, barrier lowering, and threshold voltage shift all together, the photovoltaic current can be determined by Ip, PV = βmσDV th = XβmσDV th = kBT q ln(1 + Pαα∥ √ g √ d τ p d τ g/µ∥) − XβmσDV th = kBT q ln(1 + Pαα∥ √ g √ d τ p d τ g/µ∥), where Xβ is the barrier-lowering efficiency, the only fitting parameter for the PV effect, which is directly related to the trapped density and also to the wavelength of incident light. Xβ = 25, 19.5, 9 are used for MoSe₂, 405, 638, 852 nm, respectively, and g∥ = 4.55 × 10⁻⁷ S for MoSe₂; Xβ = 2.5 at λ = 405 nm and g∥ = 6.64 × 10⁻⁷ S for MoS₂. The fitted values of Xβ suggest that the trap density in MoSe₂ is significantly larger than that of MoS₂, which is consistent with P∥ values determined for the PC effect above and also with DFT simulation results and the measurement of photoinduced transfer characteristics. For n-type transistors considered in this study, it is assumed that μ∥ is less than the dark electron current density (jD) by three orders of magnitude.

DFT Simulations: The DFT calculations were performed using the Vienna ab initio simulation package (VASP).[24] A plane-wave expansion cutoff energy of 450 eV for the wave function, the projector augmented wave method for the treatment of the core potential, and the local density approximation (LDA) for exchange-correlation potential were used.[23] LDA is known to underestimate bandgap and lattice constant values, however the qualitative results and conclusions from the DFT calculations should hold true. Spin–orbit coupling (SOC) was not included in the presented results, however a test with spin–orbit interaction activated showed no qualitative differences. For pure bulk MoSe₂, a Monkhorst–Pack G-centered k-grid of 8 × 8 × 2 was used. The optimized lattice constants of the hexagonal structure are a = 3.25 Å and c = 12.73 Å, obtained using a total energy convergence of 10⁻⁶ eV and with forces acting on each atom less than 0.01 eV Å⁻¹. van der Waals interaction was omitted, but is not expected to alter the conclusions since the optimized lattice constants of pristine MoSe₂ are within 2% of the experimental values[26] and that the interstitial defects form strong bonds with the neighboring MoSe₂ layers.

The defect calculations are performed by (i) introducing each defect into a 4 × 4 × 1 supercell of MoSe₂ (96 atoms without the defects), (ii) relaxing the atomic structure using the same criteria described above, and (iii) performing a self-consistent calculation to extract the total energy. The defect formation energies are calculated using Eₖ = Eₖ + E₀ - Eₙ, where Eₖ is the formation energy, E₀ is the total energy of the supercell without the defect, Eₙ is the chemical potential of element i (+ is used if element i is added to the pristine supercell to form the defect, and − is used if element i is removed from the pristine supercell to form the defect).[11] The chemical potentials, µ, are obtained from E₀MoSe₂ = µMo + 2µSe, where E₀MoSe₂ is the total energy of the pristine material per unit formula MoSe₂; µMo and µSe are determined by µMo = E₀Mo and µSe = (E₀MoSe₂ − µMo)/2, where E₀Mo is the total energy per atom of a body-centered cubic (BCC) crystal of Mo (the stable/common bulk form of Mo), considering Mo-rich condition. For the 4 × 4 × 1 supercell calculations with a defect, a Monkhorst–Pack G-centered k-grid of 2 × 2 × 2 was used. The optimized lattice constants of the supercell with 1% Mo int are a = 3.25 Å and c = 12.99 Å, obtained using the same convergence criteria as with the primitive cell. At the start of the atomic relaxation, the interstitial Mo atom was randomly displaced slightly away from the high-symmetry location where it finally settled at a high-symmetry point that is equidistant to the six Se nearest neighbors with a bond distance of 2.50 Å.

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.
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