Ultra-Broadband Photodetectors



High-Performance, Room Temperature, Ultra-Broadband Photodetectors Based on Air-Stable PdSe₂

Qijie Liang, Qixing Wang, Qian Zhang, Jingxuan Wei, Sharon Xiaodai Lim, Rui Zhu, Junxiong Hu, Wei Wei, Chengkuo Lee, ChorngHaur Sow, Wenjing Zhang,* and Andrew Thye Shen Wee*

Photodetection over a broad spectral range is crucial for optoelectronic applications such as sensing, imaging, and communication. Herein, a high-performance ultra-broadband photodetector based on PdSe₂ with unique pentagonal atomic structure is reported. The photodetector responds from visible to mid-infrared range (up to ≈4.05 μ m), and operates stably in ambient and at room temperature. It promises improved applications compared to conventional mid-infrared photodetectors. The highest responsivity and external quantum efficiency achieved are 708 A W⁻¹ and 82 700%, respectively, at the wavelength of 1064 nm. Efficient optical absorption beyond 8 μ m is observed, indicating that the photodetection range can extend to longer than 4.05 μ m. Owing to the low crystalline symmetry of layered PdSe₂, anisotropic properties of the photodetectors are observed. This emerging material shows potential for future infrared optoelectronics and novel devices in which anisotropic properties are desirable.

Dr. Q. Liang, Prof. W. Zhang SZU-NUS Collaborative Innovation Center for Optoelectronic Science and Technology International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education College of Optoelectronic Engineering Shenzhen University Shenzhen 518060, P. R. China E-mail: wjzhang@szu.edu.cn Dr. Q. Liang, Q. Wang, Dr. S. X. Lim, R. Zhu, J. Hu, Prof. C. H. Sow, Prof. A. T. S. Wee Department of Physics National University of Singapore 2 Science Drive 3, Singapore 117551, Singapore E-mail: phyweets@nus.edu.sg Dr. Q. Zhang Department of Materials Science and Engineering National University of Singapore Singapore 117574, Singapore J. Wei, W. Wei, Prof. C. Lee Department of Electrical and Computer Engineering National University of Singapore 117583, Singapore Prof. C. H. Sow, Prof. A. T. S. Wee Centre for Advanced 2D Materials

National University of Singapore Block S14, 6 Science Drive 2, Singapore 117546, Singapore

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201807609.

DOI: 10.1002/adma.201807609

The ability to realize photodetection over a broad spectral range, particularly in the mid-infrared (mid-IR) region, is invaluable for sensing, imaging, spectroscopy, and optical communication. Commercially available photodetectors used for sensing different wavelength regions are usually carried out by separate photoactive semiconductors, for example, GaN (<400 nm), silicon (400–1100 nm), InGaAs (800-1600 nm), and HgCdTe (2-5.5 µm) alloys, which exhibit excellent performance but require high temperature growth, complicated fabrication procedures, or a cryogenic environment with expensive facilities. Some materials including hybrid perovskites,^[1,2] bimolecular crystals,^[3] and colloidal quantum dot^[4] have shown their potential in broadband photodetection. Another promising

material system for high-performance photodetection is 2D materials including graphene^[5-7] and transition metal dichalcogenides (TMDs).^[8-11] Their naturally terminated surfaces make them free of dangling bonds and this will endow them with protection from surface-induced performance degradation.^[12,13] Graphene has been demonstrated to be a promising material for broadband photodetectors due to its gapless bandstructure that enables broadband absorption from the ultraviolet to far-infrared. However, the low optical absorption of graphene limits the responsivity of graphene-based photodetectors to the mA W⁻¹ scale.^[14] Recently, a narrow-bandgap oxide was coupled with graphene to enhance the performance of graphene-based photodetector.^[15] Black phosphorus (BP) has the ability to detect light in both visible and infrared band due to its tunable bandgap from 0.3 to 1.5 eV, but its environmental instability is a disadvantage.^[16-19] Photodetectors based on BP and other 2D materials such as tellurium (Te) have detection ranges limited to the mid-infrared due to the intrinsic minimum bandgap of above 0.3 eV.^[20,21] As a well-explored 2D material system, TMDs have shown excellent performance for optoelectronic applications owing to their direct bandgap structure and strong optical absorption.[22-26] Nevertheless, most TMD materials are only suitable for applications in the visible range. Therefore, a high-performance, air-stable photodetector capable of photodetection in the visible, near-infrared (near-IR), and mid-infrared band is highly desirable for future optical and optoelectronic applications.

Recently, a noble transition metal dichalcogenide, $PdSe_2$, was reported to be air stable and has been predicted to have high mobility of up to 40 000 cm⁻² V⁻¹ s⁻¹, one order higher than that of BP.^[27,28] The bandgap of PdSe₂, with its unique pentagonal atomic structure,^[29–31] is thickness dependent, and can be narrowed from 1.3 eV for the monolayer to 0 eV for bulk.^[32,33] This exceptional characteristic endows devices based on PdSe₂ with the possibility of extending detection from the visible to near-infrared and mid-infrared regions.

In this work, we demonstrate a high-performance broadband photodetector based on $PdSe_2$ with pentagonal structure. In the visible, near-infrared, and mid-infrared range (up to 4.05 µm), the $PdSe_2$ -based devices delivered high responsivity. The maximum responsivity and photogain (*G*) is 708 A W⁻¹ and 82 700% under 1064 nm laser illumination, respectively. Efficient optical absorption beyond 8 µm is observed, indicating that the photodetection range can extend to wavelengths longer than 4.05 µm. In addition, the photoresponsivity and photogain can be modulated by a simple gate bias. The device shows polarization-dependent photoresponsivity due to its low crystal symmetry, which adds another degree of freedom to photodetection. This work demonstrates that $PdSe_2$ can be a potential interesting candidate material for future novel optical and optoelectronic applications.

Unlike most well-studied TMDs with hexagonal structure, PdSe₂ was theoretically predicted to possess a unique pentagonal structure in 2D layers, which may endow it with some fascinating optical, electrical, and thermoelectric properties.^[27] As depicted in the top view and side view of a 2D PdSe₂ monolayer (Figure 1a,b), it is entirely composed of pentagonal rings and every Pd atom combines with four Se atoms in the same layer while a covalent Se-Se bond is formed between two neighboring Se atoms. Figure 1c displays the Raman spectra of the few-layered exfoliated PdSe2. The Raman spectrum gives vibrational modes at 151, 213, and 264 cm⁻¹ corresponding to the A_{α} peaks and 229 cm⁻¹ that can be assigned to the contribution of B_{1g} modes, consistent with previous reports.^[28] Figure 1d presents an optical image of a typical few-layer PdSe₂-based device and the topography of the device is investigated by atomic force microscopy (AFM). As shown in Figure 1e, the measured thickness of the thin flake is 2.4 nm, corresponding to four layers of PdSe₂.

To investigate the electrical performance of the $PdSe_2$ flake, a back-gated field effect transistor (FET) was fabricated on Si



Figure 1. Characterization of few-layered PdSe₂ flake. a) Top view and b) side view of the crystal structure of $PdSe_2$ with pentagonal atomic structure. c) Raman spectrum of the few-layered PdSe₂. d) Optical microscope image of the fabricated device; scale bar is 10 μ m. e) AFM image of the device and the corresponding height profile.







Figure 2. Basic electrical performance characteristics of the PdSe₂-based transistor. a) Schematic diagram of the PdSe₂-based photodetector. b) $I_{ds}-V_{ds}$ characteristics of the PdSe₂-based FET as a function of different gate voltages from -20 to 60 V. c) Back-gated $I_{ds}-V_g$ characteristics of a few-layered PdSe₂ nanoflake measured at room temperature. d) Logarithmic plot of the transfer curve in (c), showing ambipolar characteristics.

with 285 nm SiO₂ overlayer by patterning Ti/Au (5/50 nm) on the PdSe₂ nanoflake, as depicted in **Figure 2a**. The output characteristics of the prepared PdSe₂-based FET with gate voltage from -20 to 60 V are displayed in Figure 2b. A good linear relationship between source–drain current (I_{ds}) and source–drain voltage (V_{ds}) confirms the ohmic contact between the electrodes and PdSe₂ flake. Figure 2c,d shows the transfer curves both in linear and logarithmic scale obtained by sweeping the gate bias from -50 to 50 V. The drain current first decreases and then goes up with increasing gate voltage, indicating an ambipolar transport behavior. The I_{on}/I_{off} ratio of the few-layered PdSe₂based FET is up to 10⁴. The electron mobility can be estimated from the linear region in the transfer curve with the following equation

$$\mu = \frac{1}{C_{\rm g}} \frac{L}{W} \frac{1}{V_{\rm ds}} \frac{\mathrm{d}I_{\rm ds}}{\mathrm{d}V_{\rm g}} \tag{1}$$

where dI_{ds}/dV_g is the maximum slope of the linear region of the transfer curve, *L* and *W* are the length and width of the channel, V_{ds} is the source–drain voltage, and C_g is the capacitance of the dielectric. $C_g = \varepsilon_0 \varepsilon_r/d$, ε_0 and ε_r denote the vacuum permittivity and relative permittivity of SiO₂, and *d* is the thickness of the SiO₂ (285 nm). The electron mobility is calculated to be 4 cm² V⁻¹ s⁻¹, which is comparable with the well-studied 2D MoS₂.

To further investigate the photoresponse of the fabricated PdSe₂-based FET, we mechanically modulated the intensity of the incoming light and recorded the current by sweeping the gate bias from 0 to 60 V at $V_{ds} = 1$ V. The $I_{ds}-V_g$ characteristics of the device in the dark and under illumination with

a 532 nm laser are displayed in Figure 3a. The photocurrent $(I_{\rm ph} = I_{\rm light} - I_{\rm dark})$ generated increases with the incident power and gate bias. With the power density varying from 0.475 to 50 $\mu W~\mu m^{-2},$ the photocurrent increases from 1.42×10^{-6} to 3.72×10^{-6} A (Figure 3b). Unlike some traditional thin film photodetectors with a wide linear dynamic range (LDR), the photocurrent presents a linear relation with the incident light power before saturated absorption. The dependence of the photocurrent on the light power can be described with a simple power law dependence $I_{\rm ph} \propto P^{\alpha}$. The power exponent α of some photodetectors with large LDR can be very close to 1 in practice.^[34] However, in low-dimensional photodetectors, [35,36] the nonunity exponents of $0 < \alpha < 1$ are usually demonstrated. For our PdSe2 phototransistor, the nonlinear power law dependence of photocurrent is also displayed. The power exponent α is extracted to be 0.22, which deviates from the ideal slope of α = 1. The deviation from a linear photoresponse can be attributed to the photogating dominated gain mechanism involving complex process of carrier generation, trapping, and recombination within PdSe₂.^[37] The photoresponsivity, quantum efficiency, and photoresponse spectral range are important parameters in photodetectors. The dependence of the photoresponsivity on the incident power density of the 532 nm laser is plotted in Figure 3c. The maximum photoresponsivity reaches 3.35 A W⁻¹ at the power density of 0.475 $\mu W \ \mu m^{-2},$ which is comparable with other TMD-based photodetectors.^[58]

We also investigated the photoresponsivity dependence on the gate bias. As shown in Figure 3d, the photoresponsivity increases with the gate voltage and decreases with input light power density. With the gate voltage increasing from 0 to 60 V,







Figure 3. Photoresponse properties in the visible region. a) $I_{ds}-V_g$ characteristics of the PdSe₂-based FET under dark and illumination of 532 nm laser. b) The power-dependence of the photocurrent of the device. c) The photoresponsivity as a function of excitation power. d) Gate-tunable photoresponsivity of the PdSe₂-based device. V_{ds} is 1 V.

the photoresponsivity changes from 0.65 to 3.35 A W^{-1} at light power density of 0.475 $\mu W \mu m^{-2}$. The photogain is defined as^[60]

$$G = \frac{hcR}{e\lambda\eta}$$
(2)

where *h* is Planck's constant, *c* is the light velocity, *e* is the electron charge, λ is the wavelength of the incident light, *R* is the photoresponsivity, and η is external quantum efficiency (assuming 100%). The calculated photogain increases from 151% at $V_{\rm g} = 0$ V to 780% at $V_{\rm g} = 60$ V under 532 nm light excitation at the power density of 0.475 μ W μ m⁻². Our study shows that the ability to modulate the photoresponsivity and photogain by an external gate bias enables the photodetector to manipulate the photocarrier generation, separation, and recombination processes.

In addition to the photoresponse of the PdSe₂-based FET at 532 nm wavelength, we also investigated its photoresponse to red light of 633 nm wavelength (Figure S1a, Supporting Information). Similarly, the photocurrent of the device increases with the power density of the 633 nm laser. The dependence of the photocurrent and photoresponsivity on the light power follows a similar trend with that of 532 nm light (Figure S1b,c, Supporting Information). We determine α to be 0.28, revealing similar recombination kinetics. The photoresponsivity of the PdSe₂-based FET to 633 nm light at power density of 0.47 μ W μ m⁻² is 0.37 A W⁻¹, lower than that of 532 nm light. This may be due to an increase in the optical absorption of the PdSe₂ flake at higher photon energy.

The time-dependent photoresponse of the PdSe₂-based FET was also investigated. Here, we use a focused laser beam (532 and 633 nm) as the illumination source. The photocurrent versus time plots of the device under illumination of the 532 and 633 nm light with power density of 3 μ W μ m⁻² are shown in Figure S2 in the Supporting Information. V_{ds} was kept constant at 1 V and no gate bias was applied. With the irradiation source periodically switched on and off at 20 s intervals, the device exhibited a response time of 220 ms, which is still slower than conventional photodetectors.

In addition to the visible spectrum, the PdSe₂-based device also exhibits excellent photoresponse in the near-infrared band. We use a 1064 nm laser to investigate the photoresponse of the PdSe₂-based device in the near-infrared which is important for imaging and optical communications.[38-42] According to previous reports, the bandgap of PdSe₂ is thickness dependent.^[28] A PdSe₂ flake with thickness of 6 nm was used to fabricate the phototransistor. The laser power density dependence of the source-drain current was investigated by sweeping the gate bias from 0 to 30 V at $V_{ds} = 1$ V. As the power density increases from 0.18 to 1.56 mW mm $^{-2}$, $\it I_{\rm ds}$ varies from 3.8 \times 10^{-7} to 1.5×10^{-6} A (Figure 4a). Fitting with a simple power law relation $I_{\rm ph} = P^{\alpha}$, we extract α to be 0.51, indicating that there are lower trap states in the near-infrared region than that in visible region.^[37] Figure 4b plots the dependence of photoresponsivity on the power density of the 1064 nm laser. The device delivered an high photoresponsivity of 708 A W⁻¹ at 0.18 mW mm⁻² which is five orders of magnitude higher than that of the near-IR photodetector based on BP,^[16] and two orders of magnitude higher than that of commercial infrared photodetectors

www.advancedsciencenews.com





Figure 4. Photoresponse properties in the near-infrared and mid-infrared regions. a) The power-dependence of the photocurrent of the device on 1064 nm laser. b) The power-dependence of the photoresponsivity of the device. c) The photoresponsivity to 1064 nm light as a function of gate bias. V_{ds} is 1 V. d) The $I_{ds}-V_{ds}$ characteristics in dark and under illumination of 4.05 μ m laser. e) The photoresponsivity on 4.05 μ m light as a function of gate bias. V_{ds} is 0.2 V. f) Absorption spectra of the PdSe₂ nanoflake, showing the strong absorption of mid-IR spectrum.

based on Si, Ge, or InGaAs (less than 1 A $W^{\!-1}\!).^{[43,44]}$ As summarized in Table 1, the photoresponsivity surpasses other photodetectors based on 2D materials including graphene, BP, Te, and so forth. The maximum photogain was calculated to be 82 700% which is high for photodetectors working in the near-infrared band. The high photoresponsivity and photogain can be attributed to photogating effect, which was also observed in other 2D material-based photodetectors.[45,46] To clearly demonstrate that the photogating effect exists in PdSe₂based phototransistors, we investigate the influence of light on the transport behavior of PdSe2-based FET. As displayed in Figure S3 in the Supporting Information, when we applied light of 532 nm to the PdSe2-based FET, the charge neutral point shifted from -44 V to lower than -60 V. The PdSe₂-based FET turned from ambipolar to n-type, which clearly showed the photodoping effect in the PdSe₂-based FET. From the result of the electron doping effect in the FET, we can conclude that some of the generated holes are trapped by trap states, and this will cause the extended lifetime of electrons which will be recirculated between source and drain. According to the equation: $G_{\rm ph} = \tau_{\rm tr} / \tau_{\rm transit}$, $\tau_{\rm tr}$ is the lifetime of carriers, and $\tau_{\rm transit}$ is the drift transit time of charge carriers from source to drain which is governed by the applied field. τ_{tr} will greatly increase due to the trapped carriers by trap states and a high photogain can be achieved.^[37,47,48] With increasing power density, the device shows decreased photoresponsivities, similar to that reported for other photodetectors.^[49,50] The decreased photoresponsivity with increasing power is commonly observed in low-dimensional photodetectors. This phenomenon is a result of the complex process of carrier generation, trapping, and recombination within low-dimensional materials. For photodetectors using with photogating effect, the decreased photoresponsivity is caused by gradually filled trap states. When all the trap states are completely filled at a certain intensity of light power, more free carriers which cannot be trapped will be generated. This will result in a decreased average carrier lifetime. According to the equation: $G_{\rm ph}=\,\tau_{\rm tr}/\tau_{\rm transit}$, the photoresponsivity and photogain will decrease. The influence

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

Materials	Wavelength [µm]	<i>V</i> _{ds} [V]	<i>V</i> _g [V]	Responsivity [A W ⁻¹]	Gain [%]	Detectivity [Jones]	Ref.
Graphene	1.3	1.5	-80	0.0005			[5]
Graphene	1.55	0.05	-15	0.006	-	_	[14]
Graphene	1.47	0.02	0	0.2	-	_	[56]
MoTe ₂	1.06	10	10	0.02	-	$1.3 imes 10^9$	[57]
MoS ₂	1.07	0.8	0	5.2	$1.4 imes 10^7$		[58]
BP	3.39	0.5	3	82	-	-	[59]
BP	0.94	0.2	0	0.005	-	_	[16]
b-AsP	3.66	0	0	0.03	6.1	$4.9 imes 10^9$	[60]
Те	1.4	5	25	13	-	2.9×10^9	[21]
PdSea	1.06	1	30	708	82 700	1.31×10^{9}	This work

Table 1. Comparison with some reported 2D-based materials infrared photodetectors.

of the gate voltage on the photoresponse properties at 1064 nm wavelength was studied. As presented in Figure 4c, the photoresponsivity displays a continuous increase with gate bias from 0 to 30 V. The photogain can also be modulated by the gate bias. As the gate voltage varies from 0 to 30 V, the gain increases from 47 900% to 82 700%. The detectivity D^* of the device under 1064 nm laser illumination is calculated by the following equation

$$NEP = \frac{i_n}{R_{res}}$$
(3)

$$D^* = \frac{\sqrt{A\Delta f}}{\text{NEP}} \tag{4}$$

where NEP is noise equivalent power, i_n is noise current, $R_{\rm res}$ is photoresponsivity, A is active area, and Δf is electrical bandwidth. The detectivity (D^*) is assessed using standard methodology for phototransistor photodetector noise by direct measurement of the actual noise spectral density.^[51,52] The measured noise is dominated by 1/f noise (Figure S4, Supporting Information). At low frequency, the current noise is more than one order of magnitude than the calculated shot noise derived from dark current. The detectivity is calculated to be 1.31×10^9 Jones, which is comparable to other hexagonal 2D TMDs, as shown in Table 1.

We also successfully demonstrated the operation of $PdSe_2$ based photodetectors in the mid-IR region, which has broad applications in spectroscopy, materials processing, and chemical and biomolecular sensing. Here, at room temperature and in ambient air, mid-IR light with wavelength of 4.05 μ m was used to illuminate the PdSe₂-based device with flake thickness of about 50 nm. As shown in Figure 4d, the source–drain current increases with the power density of the 4.05 μ m laser. The maximum photoresponsivity at 4.05 μ m wavelength is calculated to be 1.9 mA W⁻¹. The photoresponsivity in mid-IR region is lower than that in visible region. The reason may be the energy of the optical photon in the visible is much higher than that in the mid-IR range. The influence of the gate bias on the photoresponse properties at 4.05 μ m wavelength was also studied. As presented in Figure 4e, the photoresponsivity

displays a continuous increase with gate voltage from 0 to 30 V. The time-dependent photoresponse to 4.05 µm wavelength was also investigated. As shown in Figure S5 in the Supporting Information, when the light is applied onto the device, an obvious photocurrent will be generated. This demonstrates that PdSe₂ is capable of photodetection in the mid-IR region. The response time is in the millisecond range. This can be explained by the photogating effect. As discussed above, the photogenerated holes are trapped in trap states in PdSe₂, which will extend the lifetime of photogenerated electrons in PdSe₂. The trapped holes in PdSe₂ cannot recombine with the photogenerated electrons in a timely manner, and this leads to the slow response. As the photoresponsivity in mid-IR region is lower than that in near-IR region, the detectivity in mid-IR will be lower than that in near-IR, which makes it much lower than the theoretical background limited infrared photodetection. However, in future optimization, the small specific detectivity in the junctionless PdSe₂ caused by high dark noise can be further improved by forming a junction with other 2D materials to suppress the dark current noise.^[53] To demonstrate that thicker PdSe₂ flakes can realize photodetection in the mid-infrared and even far-infrared region, we performed Fourier transform infrared spectroscopy (FTIR) on 250 and 370 nm thick PdSe₂ flakes. Optical absorption was calculated by using the transmission and reflection spectra shown in Figure S6 in the Supporting Information. From the absorption spectra (Figure 4f), we observe that thick PdSe₂ exhibits more than 10% absorption even for the wavelengths beyond 8 µm. This is a significant intrinsic advantage over many other 2D materials whose bandgap cannot be reduced to 0 eV, for example, BP, Te, and other TMDs.

The symmetry of $PdSe_2$ is orthorhombic, which is similar to black phosphorus.^[30,33] This endows $PdSe_2$ with a unique anisotropy on account of its in-plane low symmetry. The structure anisotropy in $PdSe_2$ enables us to investigate its properties as a polarization sensitive photodetector.^[54,55] We also performed angle-resolved polarized Raman spectroscopy to investigate the vibrational anisotropy of $PdSe_2$. The polarized Raman spectra were collected using a 532 nm laser in a backscattering geometry. **Figure 5a** displays the angle-dependent Raman peak intensity of the A_g mode at 151 cm⁻¹. As the rotation angle increases in steps of 15°, the Raman peak intensity exhibits







Figure 5. Anisotropic photoresponse of the $PdSe_2$ -based phototransistor. a) Polar plots of the peak intensities of A_g mode as a function of polarization angle under parallel configurations. b) Polar plot showing the photocurrent of the device with gate bias of 50 V at wavelength of 532 nm as a function of polarization.

clear periodical variation with increasing angle from 0° to 360°. The maximum peak intensities occur at 0°, 90°, 180°, and 360° while the minimum at 45°, 135°, 225°, and 315°. Finally, the linear polarization dependence of the photoresponse properties of the PdSe₂-based photodetector was investigated by mechanically modulating the linear polarization angle of the excitation laser. Figure 5b displays the dependence of the photoresponsivity of the device as a function of the polarization angle of the linear polarizer. With the polarization angle varying from 0° to 180°, the photocurrent changes periodically and achieves maximum value at 45° and 135° and minimum at 90° and 180°. Our results indicate that PdSe₂ has the potential to serve as a linear dichroism media, which has important application in structural study and characterization in inorganic chemistry, polymer chemistry, material science, and biochemistry.

The noble transition metal dichalcogenides including PtSe₂ and PdSe₂ have been demonstrated as promising candidates due to their suitable bandgaps for broadband photonic and optoelectronic applications with high environmental stability. A recent work has also demonstrated a high-performance broadband mid-infrared photodetector based on PtSe2.^[61] We discuss several reasons why this work on PdSe₂ phototransistors is superior or different from the PtSe₂ photodetector. First, PdSe₂ possesses a unique pentagonal structure^[28-31] in 2D layers while PtSe₂ has a hexagonal structure.^[62-64] The properties of 2D materials are closely related to their structures. For example, PtSe₂ lacks anisotropic property due to its symmetrical hexagonal structure while PdSe₂ is anisotropic. This unique pentagonal structure of PdSe₂ may endow it with fascinating optical, electrical, and thermoelectric properties. Second, our highest photoresponsivity is 708 A W⁻¹ which is two orders of magnitude higher than that (6.25 A W^{-1}) of the PtSe₂-based photodetector. Photogating contributes to the high photoresponsivity and high gain. Due to the photogating effect, one type of photo carrier (electron/hole) is trapped by localized states, which will effectively increase the recombination lifetime of the other type, and thus a high photogain can be achieved. Third, we show evidence for the photogating effect. As displayed in Figure S3 in the Supporting Information, an obvious shift of the charge

neutral point of the PdSe₂-based FET was observed when illuminated by light. The PdSe₂-based FET turned from ambipolar to n-type after the light was applied, which clearly showed the photodoping effect in the PdSe₂-based FET. Fourth, we confirm the anisotropic property of PdSe₂. We demonstrated that the photoresponse of the PdSe₂-based photodetector can vary with the polarization angle of the applied light, while PtSe₂based photodetector has no anisotropic photoresponse because the PtSe₂ has a symmetrical hexagonal structure. This character may endow the PdSe₂-based photodetector with the potential to serve as a linear dichroism media, which has important applications in structural studies. Finally, this work presents the gatetunable photoresponsivity while the previous work did not.^[61] The gate-tunable photoresponsivity may endow us with more freedom of controlling the performance of phototransistor.

In summary, a high-performance broadband PdSe2-based photodetector has been demonstrated. The PdSe2-gated photodetectors exhibit high photoresponsivity in the visible, near-infrared, and mid-infrared regions. When illuminated by a 1064 nm laser with power density of 0.18 mW mm⁻², the photoresponsivity and photogain of the device reach 708 A W⁻¹ and 82 700%, respectively. Photodetection at mid-IR (up to 4.05 μ m) is also realized and FTIR spectroscopy demonstrates optical absorption by PdSe₂ beyond 8 µm. In addition, the anisotropy of the PdSe₂ flake is demonstrated by angle-resolved polarized Raman spectroscopy and a polarization-sensitive photocurrent is presented. Our study suggests that PdSe₂ is a potential candidate material for high-performance broadband photodetectors and other optoelectronics applications. Finally, considering its ability to narrow the bandgap to 0 eV, this material has the potential for realizing photodetection in the midinfrared or even far-infrared band.

Experimental Section

Device Fabrication: Thin $PdSe_2$ flakes were prepared by micromechanically exfoliating $PdSe_2$ from a bulk crystal (2D semiconductor) onto a polydimethylsiloxane stamp. Target flakes were then identified with optical microscopy and transferred onto a





www.advmat.de

 $\rm SiO_2/Si$ substrate with a micromanipulator. The electrode contacts were patterned by the Laser Writer (Microtech LW405B). After that, Ti/Au (5/70 nm) was deposited in a thermal evaporator and liftoff was performed by using PG remover.

Characterization Methods: AFM measurements under tapping mode were conducted with an AFM (Bruker) under ambient environment. Raman spectra were collected using a commercial WITec Raman system with 532 nm laser. A polarizer was placed between the edge filter and detector to obtain a parallel polarization configuration. Samples for absorption measurements were transferred onto an intrinsic silicon and FTIR was performed using Fourier transform infrared spectrophotometer (Agilent Technology, Cary 600 series FTIR spectrometer). Electrical measurements were carried out in a probe station. Lasers of 532, 633, 1064 nm, and 4.05 µm source wavelengths were used to investigate the photoresponse of the PdSe2-based FET. Light power dependence of the photoresponse was conducted by varying the light power while maintaining the light polarization unchanged. The influence of the polarization on the photoresponse of the PdSe2-based FET was realized by rotating the polarization of the light using a half-wave plate and a polarizer. The noise spectral density was acquired with a low-noise current preamplifier (SR570), a dynamic signal analyzer (Hewlett-Packard, 35670A), and a parameter analyzer (Agilent 4156B).

Supporting Information

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

Acknowledgements

The authors thank Dr. Wang Lin from the Electrical & Computer Engineering for the fruitful discussions. This work was financially supported by the National Natural Science Foundation of China (Grant No. 51472164), the 1000 Talents Program for Young Scientists of China, Shenzhen Peacock Plan (Grant No. KQTD2016053112042971), the Educational Commission of Guangdong Province (Grant Nos. 2015KGJHZ006 and 2016KCXTD006), and the Science and Technology Planning Project of Guangdong Province (Grant No. 2016B050501005). A.T.S.W. acknowledges funding support from MOE Tier 2 (Grant No. 1527300025), and facility support from the NUS Centre for Advanced 2D Materials (CA2DM).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

anisotropic, near-infrared and mid-infrared, photogating, room temperature, ultra-broadband photodetectors

Received: November 24, 2018 Revised: March 31, 2019

Published online: April 26, 2019

- M. I. Saidaminov, M. A. Haque, M. Savoie, A. L. Abdelhady, N. Cho, I. Dursun, U. Buttner, E. Alarousu, T. Wu, O. M. Bakr, *Adv. Mater.* 2016, *28*, 8144.
- [2] N. Alwadai, M. A. Haque, S. Mitra, T. Flemban, Y. Pak, T. Wu, I. Roqan, ACS Appl. Mater. Interfaces 2017, 9, 37832.

- [3] Z. Tang, Z. Ma, A. Sánchez-Díaz, S. Ullbrich, Y. Liu, B. Siegmund, A. Mischok, K. Leo, M. Campoy-Quiles, W. Li, K. Vandewal, Adv. Mater. 2017, 29, 1702184.
- [4] M. M. Ackerman, X. Tang, P. Guyot-Sionnest, ACS Nano 2018, 12, 7264.
- [5] F. Xia, T. Mueller, Y. M. Lin, A. Valdes-Garcia, P. Avouris, Nat. Nanotechnol. 2009, 4, 839.
- [6] C. H. Liu, Y. C. Chang, T. B. Norris, Z. Zhong, Nat. Nanotechnol. 2014, 9, 273.
- [7] J. D. Mehew, S. Unal, E. Torres Alonso, G. F. Jones, S. Fadhil Ramadhan, M. F. Craciun, S. Russo, Adv. Mater. 2017, 29, 1700222.
- [8] Y.-H. Chang, W. Zhang, Y. Zhu, Y. Han, J. Pu, J.-K. Chang, W.-T. Hsu, J.-K. Huang, C.-L. Hsu, M.-H. Chiu, T. Takenobu, H. Li, C.-I. Wu, W.-H. Chang, A. T. S. Wee, L.-J. Li, ACS Nano 2014, 8, 8582.
- [9] R. Cheng, D. Li, H. Zhou, C. Wang, A. Yin, S. Jiang, Y. Liu, Y. Chen, Y. Huang, X. Duan, *Nano Lett.* **2014**, *14*, 5590.
- [10] Y. Huang, F. Zhuge, J. Hou, L. Lv, P. Luo, N. Zhou, L. Gan, T. Zhai, ACS Nano 2018, 12, 4062.
- [11] Y. Yu, G. Wang, Y. Tan, N. Wu, X. A. Zhang, S. Qin, Nano Lett. 2018, 18, 675.
- [12] M. Chhowalla, H. S. Shin, G. Eda, L. J. Li, K. P. Loh, H. Zhang, Nat. Chem. 2013, 5, 263.
- [13] J. Kang, W. Liu, D. Sarkar, D. Jena, K. Banerjee, Phys. Rev. X 2014, 4, 031005.
- [14] T. Mueller, F. Xia, P. Avouris, Nat. Photonics 2010, 4, 297.
- [15] X. Yu, Y. Li, X. Hu, D. Zhang, Y. Tao, Z. Liu, Y. He, M. A. Haque, Z. Liu, T. Wu, Q. J. Wang, *Nat. Commun.* **2018**, *9*, 4299.
- [16] M. Buscema, D. J. Groenendijk, S. I. Blanter, G. A. Steele, H. S. J. van der Zant, A. Castellanos-Gomez, *Nano Lett.* 2014, 14, 3347.
- [17] S. B. Lu, L. L. Miao, Z. N. Guo, X. Qi, C. J. Zhao, H. Zhang, S. C. Wen, D. Y. Tang, D. Y. Fan, *Opt. Express* **2015**, *23*, 11183.
- [18] D. Xiang, C. Han, J. Wu, S. Zhong, Y. Liu, J. Lin, X.-A. Zhang, W. Ping Hu, B. Özyilmaz, A. H. C. Neto, A. T. S. Wee, W. Chen, *Nat. Commun.* **2015**, *6*, 6485.
- [19] V. Tran, R. Soklaski, Y. Liang, L. Yang, Phys. Rev. B 2014, 89, 235319.
- [20] H. Yuan, X. Liu, F. Afshinmanesh, W. Li, G. Xu, J. Sun, B. Lian, A. G. Curto, G. Ye, Y. Hikita, Z. Shen, S.-C. Zhang, X. Chen, M. Brongersma, H. Y. Hwang, Y. Cui, *Nat. Nanotechnol.* **2015**, *10*, 707.
- [21] M. Amani, C. Tan, G. Zhang, C. Zhao, J. Bullock, X. Song, H. Kim, V. R. Shrestha, Y. Gao, K. B. Crozier, M. Scott, A. Javey, ACS Nano 2018, 12, 7253.
- [22] S. Kim, J. Maassen, J. Lee, S. M. Kim, G. Han, J. Kwon, S. Hong, J. Park, N. Liu, Y. C. Park, I. Omkaram, J.-S. Rhyee, Y. K. Hong, Y. Yoon, *Adv. Mater.* **2018**, *30*, 1705542.
- [23] F. Liu, H. Shimotani, H. Shang, T. Kanagasekaran, V. Zólyomi, N. Drummond, V. I. Fal'ko, K. Tanigaki, ACS Nano 2014, 8, 752.
- [24] D. Kufer, G. Konstantatos, Nano Lett. 2015, 15, 7307.
- [25] Q. Wang, J. Guo, Z. Ding, D. Qi, J. Jiang, Z. Wang, W. Chen, Y. Xiang, W. Zhang, A. T. S. Wee, *Nano Lett.* **2017**, *17*, 7593.
- [26] Y. Xie, B. Zhang, S. Wang, D. Wang, A. Wang, Z. Wang, H. Yu, H. Zhang, Y. Chen, M. Zhao, B. Huang, L. Mei, J. Wang, *Adv. Mater.* 2017, *29*, 1605972.
- [27] J. Sun, H. Shi, T. Siegrist, D. J. Singh, Appl. Phys. Lett. 2015, 107, 153902.
- [28] W. L. Chow, P. Yu, F. Liu, J. Hong, X. Wang, Q. Zeng, C.-H. Hsu, C. Zhu, J. Zhou, X. Wang, J. Xia, J. Yan, Y. Chen, D. Wu, T. Yu, Z. Shen, H. Lin, C. Jin, B. K. Tay, Z. Liu, *Adv. Mater.* **2017**, *29*, 1602969.
- [29] J. Lin, S. Zuluaga, P. Yu, Z. Liu, S. T. Pantelides, K. Suenaga, Phys. Rev. Lett. 2017, 119, 016101.
- [30] C. Soulard, X. Rocquefelte, P. E. Petit, M. Evain, S. Jobic, J. P. Itié, P. Munsch, H. J. Koo, M. H. Whangbo, *Inorg. Chem.* 2004, 43, 1943.
- [31] E. Li, D. Wang, P. Fan, R. Zhang, Y.-Y. Zhang, G. Li, J. Mao, Y. Wang, X. Lin, S. Du, H.-J. Gao, *Nano Res.* 2018, *11*, 5858.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com



www.advmat.de

- [32] H. Fang, W. Hu, Adv. Sci. 2017, 4, 1700323.
- [33] A. D. Oyedele, S. Yang, L. Liang, A. A. Puretzky, K. Wang, J. Zhang, P. Yu, P. R. Pudasaini, A. W. Ghosh, Z. Liu, C. M. Rouleau, B. G. Sumpter, M. F. Chisholm, W. Zhou, P. D. Rack, D. B. Geohegan, K. Xiao, J. Am. Chem. Soc. 2017, 139, 14090.
- [34] A. De Sanctis, G. F. Jones, D. J. Wehenkel, F. Bezares, F. H. L. Koppens, M. F. Craciun, S. Russo, *Sci. Adv.* 2017, *3*, e1602617.
- [35] S. Du, W. Lu, A. Ali, P. Zhao, K. Shehzad, H. Guo, L. Ma, X. Liu, X. Pi, P. Wang, H. Fang, Z. Xu, C. Gao, Y. Dan, P. Tan, H. Wang, C.-T. Lin, J. Yang, S. Dong, Z. Cheng, E. Li, W. Yin, J. Luo, B. Yu, T. Hasan, Y. Xu, W. Hu, X. Duan, *Adv. Mater.* **2017**, *29*, 1700463.
- [36] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. de Arquer, F. Gatti, F. H. L. Koppens, *Nat. Nanotechnol.* 2012, 7, 363.
- [37] F. H. L. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, M. Polini, Nat. Nanotechnol. 2014, 9, 780.
- [38] S. Goossens, G. Navickaite, C. Monasterio, S. Gupta, J. J. Piqueras, R. Pérez, G. Burwell, I. Nikitskiy, T. Lasanta, T. Galán, E. Puma, A. Centeno, A. Pesquera, A. Zurutuza, G. Konstantatos, F. Koppens, *Nat. Photonics* 2017, *11*, 366.
- [39] J. Yao, Z. Deng, Z. Zheng, G. Yang, ACS Appl. Mater. Interfaces 2016, 8, 20872.
- [40] H. Wook Shin, S. Jun Lee, D. Gun Kim, M.-H. Bae, J. Heo, K. Jin Choi, W. Jun Choi, J.-W. Choe, J. Cheol Shin, *Sci. Rep.* 2015, 5, 10764.
- [41] Q. Lin, Z. Wang, M. Young, J. B. Patel, R. L. Milot, L. Martinez Maestro, R. R. Lunt, H. J. Snaith, M. B. Johnston, L. M. Herz, Adv. Funct. Mater. 2017, 27, 1702485.
- [42] W. Guangjian, W. Xudong, W. Peng, H. Hai, C. Yan, S. Shuo, S. Hong, L. Tie, W. Jianlu, Z. Shangtao, B. Lifeng, S. Jinglan, M. Xiangjian, C. Junhao, *Nanotechnology* **2016**, *27*, 364002.
- [43] A. I. Yakimov, V. V. Kirienko, A. A. Bloshkin, V. A. Armbrister, A. V. Dvurechenskii, J. M. Hartmann, Opt. Express 2017, 25, 25602.
- [44] M. Casalino, G. Coppola, M. Iodice, I. Rendina, L. Sirleto, Sensors 2010, 10, 10571.
- [45] X. Chen, X. Lu, B. Deng, O. Sinai, Y. Shao, C. Li, S. Yuan, V. Tran, K. Watanabe, T. Taniguchi, D. Naveh, L. Yang, F. Xia, *Nat. Commun.* 2017, *8*, 1672.
- [46] L. Qian, Y. Sun, M. Wu, D. Xie, L. Ding, G. Shi, Adv. Mater. 2017, 29, 1606175.
- [47] J. O. Island, S. I. Blanter, M. Buscema, H. S. J. van der Zant, A. Castellanos-Gomez, Nano Lett. 2015, 15, 7853.

- [48] L. Li, W. Wang, Y. Chai, H. Li, M. Tian, T. Zhai, Adv. Funct. Mater. 2017, 27, 1701011.
- [49] C. Tan, X. Cao, X. J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G. H. Nam, M. Sindoro, H. Zhang, *Chem. Rev.* **2017**, *117*, 6225.
- [50] F. Xia, H. Wang, Y. Jia, Nat. Commun. 2014, 5, 4458.
- [51] Y. Fang, A. Armin, P. Meredith, J. Huang, Nat. Photonics 2019, 13, 1.
- [52] Z. Wu, Y. Zhai, H. Kim, J. D. Azoulay, T. N. Ng, Acc. Chem. Res. 2018, 51, 3144.
- [53] M. Long, A. Gao, P. Wang, H. Xia, C. Ott, C. Pan, Y. Fu, E. Liu, X. Chen, W. Lu, T. Nilges, J. Xu, X. Wang, W. Hu, F. Miao, *Sci. Adv.* 2017, *3*, e1700589.
- [54] E. Zhang, P. Wang, Z. Li, H. Wang, C. Song, C. Huang, Z.-G. Chen, L. Yang, K. Zhang, S. Lu, W. Wang, S. Liu, H. Fang, X. Zhou, H. Yan, J. Zou, X. Wan, P. Zhou, W. Hu, F. Xiu, ACS Nano 2016, 10, 8067.
- [55] Y. Yang, S.-C. Liu, W. Yang, Z. Li, Y. Wang, X. Wang, S. Zhang, Y. Zhang, M. Long, G. Zhang, D.-J. Xue, J.-S. Hu, L.-J. Wan, *J. Am. Chem. Soc.* **2018**, *140*, 4150.
- [56] B. Y. Zhang, T. Liu, B. Meng, X. Li, G. Liang, X. Hu, Q. J. Wang, Nat. Commun. 2013, 4, 1811.
- [57] H. Hai, W. Jianlu, H. Weida, L. Lei, W. Peng, W. Xudong, G. Fan, C. Yan, W. Guangjian, L. Wenjin, S. Hong, L. Tie, S. Jinglan, M. Xiangjian, C. Xiaoshuang, C. Junhao, *Nanotechnology* **2016**, *27*, 445201.
- [58] W. Wang, A. Klots, D. Prasai, Y. Yang, K. I. Bolotin, J. Valentine, Nano Lett. 2015, 15, 7440.
- [59] Q. Guo, A. Pospischil, M. Bhuiyan, H. Jiang, H. Tian, D. Farmer, B. Deng, C. Li, S.-J. Han, H. Wang, Q. Xia, T.-P. Ma, T. Mueller, F. Xia, Nano Lett. 2016, 16, 4648.
- [60] K. Xu, Z. Wang, F. Wang, Y. Huang, F. Wang, L. Yin, C. Jiang, J. He, Adv. Mater. 2015, 27, 7881.
- [61] X. Yu, P. Yu, D. Wu, B. Singh, Q. Zeng, H. Lin, W. Zhou, J. Lin, K. Suenaga, Z. Liu, Q. J. Wang, *Nat. Commun.* **2018**, *9*, 1545.
- [62] Y. Wang, L. Li, W. Yao, S. Song, J. T. Sun, J. Pan, X. Ren, C. Li, E. Okunishi, Y.-Q. Wang, E. Wang, Y. Shao, Y. Y. Zhang, H.-T. Yang, E. F. Schwier, H. Iwasawa, K. Shimada, M. Taniguchi, Z. Cheng, S. Zhou, S. Du, S. J. Pennycook, S. T. Pantelides, H.-J. Gao, *Nano Lett.* **2015**, *15*, 4013.
- [63] Z. Wang, Q. Li, F. Besenbacher, M. Dong, *Adv. Mater.* 2016, 28, 10224.
- [64] K. Zhang, M. Yan, H. Zhang, H. Huang, M. Arita, Z. Sun, W. Duan, Y. Wu, S. Zhou, *Phys. Rev. B* 2017, 96, 125102.