Palladium Diselenide Long-Wavelength Infrared Photodetector with High Sensitivity and Stability

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1. Performance of LWIR detectors based on 2D and conventional materials

The performance characteristics of previously reported LWIR photodetectors based on 2D materials, such as graphene, black phosphorus, black arsenic phosphorus, and MoS$_2$, and conventional materials such as those in groups III-V and II-VI and HgCdTe are summarized in Table 1. The advantage of 2D materials is that they can operate at room temperature with high photoresponsivity. Conventional LWIR materials can operate at very high speed and with high sensitivity but only at cryogenic temperatures.

Table 1

| Material        | Wavelength (μm) | R (mA/W) | $D^*$ (Jones) | Temperature (K) | Time   | NEP (pW Hz$^{-1/2}$) | $V_{ds}$ (V) | Ref. |
|-----------------|----------------|----------|---------------|----------------|--------|----------------------|-------------|------|
| b-As            | 8.05           | 10.2     | ~10$^4$       | 300            | 0.54, 0.52 ms | 0        | 1            |
| b-P             | 7.7            | 2.2      | -             | 300            | -      | 672                  | 1.2         | 2    |
| MoS$_2$         | 9.5            | 11       | -             | 300            | -      | -                    | -           | 3    |
| PtSe$_2$        | 10.0           | 4500     | 7×10$^8$      | 300            | 1.1, 1.2 ms | 0.1      | 4            |
| Graphene        | 10.31          | 400      | -             | 300            | 100 s  | -                    | 0.02        | 5    |
| GNR             | 10.6           | 7.5×10$^{-3}$ | -         | 300            | -      | -                    | -           | 6    |
| Graphene-Ti$_2$O$_3$ | 10.48            | 300,000  | 7×10$^8$      | 300            | 1.2, 2.6 ms | -        | 0.1         | 7    |
| PdSe$_2$        | 10.6           | 42100    | 8.2×10$^9$    | 300            | 74.5, 93.1 ms | 0.28     | 1            |
| HgCdTe          | 10.6           | 2×10$^8$ | 300           | 1 ns           |        |                      | -           | 8    |
| VO$_x$ Bolometer | 8-12           | 1.89×10$^8$ | 296       | 11 ms          | 16.7   |         | -           | 9    |
| Bolometer       | 16             | 42 kV/W  | 3×10$^8$ (peak) | 300        | 263 μs |         | -           | 10   |
| PbSe (PC)       | 4.4            | 600 v/W  | 3.1×10$^9$ (peak) | 295       | <2 μs  |         | -           | 11   |
| PbSe (PC)       | 5.5            | 158 kV/W | 4×10$^{10}$ (peak) | 195       | <2 μs  |         | -           | 12   |
| InSb (PC)       | 5.6            | 40kV/W   | 1×10$^{11}$ (peak) | 77        |         |         | -           | 13   |
| HgCdTe (PV)     | 12             | ~3.2×10$^{10}$ (peak) | 77        | 0.4 μs  |         |         | -           | 14   |
PEM: photoelectromagnetic detector, PC: photoconductive detector, PV: photovoltaic detector.

2. First-principles calculated band structure of few-layer PdSe$_2$

The band structures of monolayer and bilayer PdSe$_2$ flakes are both indirect with band gaps of $\sim$1.23 eV, which is quite close to the direct bandgap of $\sim$1.43 eV marked by red arrows in Fig. S1a. With increasing layer thickness, both the direct and indirect bandgaps decrease. For the bilayer PdSe$_2$, the indirect and direct bandgaps decrease to 0.85 and 1.11 eV, respectively, as shown in Fig. S1b. For the trilayer PdSe$_2$, the indirect bandgap decreases to 0.64 eV and the direct bandgaps decreases to 0.93 eV as presented in Fig.S1c. The valence band maximum (VBM) is located at the high-symmetry direction between the $\Gamma$ (0, 0, 0) point and X (0.5, 0, 0). As the layer thickness increases, the VBM is pushed closer to the $\Gamma$ point from the X point. For the bulk form of PdSe$_2$, the indirect bandgap is $\sim$0.054 eV.

Fig. S1. Calculated electronic band structure of monolayer PdSe$_2$. (a) Monolayer PdSe$_2$, (b) Bilayer PdSe$_2$, (c) Trilayer PdSe$_2$ and (d) bulk PdSe$_2$. The red arrows indicate the indirect band transition from the valence band maximum (VBM) to the conduction band minimum (CBM). The black arrows indicate the direct band transition.
3. EDX results of PdSe₂ single-crystal flakes

PdSe₂ single-crystal flakes are obtained by the self-flux method as shown in Fig. S2a. To determine the elemental composition of PdSe₂, energy dispersive X-ray spectroscopy (EDX) measurements were performed. We exfoliated the bulk PdSe₂ crystal onto silicon wafers (coated with 300 nm SiO₂) and then transferred several flakes to a TEM holder for the measurement. The EDX spectrum is shown in Fig. S2b. The copper peaks and carbon peaks originated from the carbon-film-covered copper net TEM sample holder. The atomic ratio of Pd to Se is 33.05: 66.95, which is close to 1:2. A low-magnification TEM image of PdSe₂ is shown in Fig. S2c.

Fig. S2. Energy dispersive X-ray spectroscopy (EDX) measurement of PdSe₂. (a) Optical image of single-crystal PdSe₂ obtained using the self-flux method. (b) Energy dispersive X-ray spectroscopy (EDX) of PdSe₂. (c) Low-magnification TEM image of the PdSe₂.
4. Mid-IR photoresponse and light absorption spectrum

Transfer curves of the PdSe$_2$ FETs with and without illumination are shown in Fig. S3a. A p-type conduction property is observed. The optical absorption spectra of two PdSe$_2$ flakes are shown in Fig. S3b. The blue line shows the absorption of the 30 nm thick sample. The absorption edge is located at ~650 cm$^{-1}$, marked by the crossing of the two dashed cyan lines, indicating that the sample can absorb LWIR up to 15.4 μm and corresponds to a ~0.081 eV bandgap.

![Graph showing Tl/Au contact and light and dark transfer curves](image)

**Fig. S3. Infrared absorption and photoresponse.** (a) Transfer curves of a typical PdSe$_2$ FET device with and without 10.6 μm illumination at 0.1 V bias. (b) Infrared absorption spectra of the few-layer PdSe$_2$ sample. The absorption edge is approximately at 650 cm$^{-1}$, corresponding to a ~0.081 eV bandgap. Inset: AFM image of a measured sample with a thickness of 30 nm. (c) AFM image of a measured PdSe$_2$ sample (red line in Fig. S3b), scale bar 2 μm. (d) The reflectance spectra of PdSe$_2$-MoS$_2$ (black) and MoS$_2$ (blue) on SiO$_2$/Si substrate.
5. Photoresponse of PdSe$_2$ FET devices

**Fig. S4.** Time-resolved photoresponse under various wavelengths. (a-d) Time-resolved photoresponse at 1 V bias under illumination wavelengths of 450 nm, 520 nm, 637 nm, and 940 nm.
6. Noise current measurements and calculation of specific detectivity $D^*$

The noise power spectra $S_n(f)$ of PdSe$_2$ phototransistor and PdSe$_2$-MoS$_2$ heterostructure devices were analyzed by using a low-noise current preamplifier and a dynamic signal analyzer (SR770) in ambient conditions. The devices were encapsulated in a metal box to shield them from environmental noise. The specific detectivity $D^*$ can be calculated from the following equation:

$$D^* = \frac{\sqrt{AB}}{\sqrt{\langle i_n \rangle^2}} B$$

where $\langle i_n \rangle^2 = \int_0^B S_n(f) df$ is the mean square noise current, $A$ is the device area, and $B$ is the electric bandwidth. Thus, $\langle i_n \rangle^2$ can be determined by integrating the noise power density for a given bandwidth. For the PdSe$_2$ phototransistor, the mean square noise current $\langle i_n \rangle^2$ was obtained as $\sim 5.8 \times 10^{-23}$ A$^2$ Hz$^{-1}$. The root mean square noise current $\overline{i_n}^{1/2}$ was thus calculated to be $\sim 0.76 \times 10^{-11}$ A Hz$^{-1/2}$, and $A = 9$ $\mu$m$^2$, which was used to calculate $D^*$. For the PdSe$_2$-MoS$_2$ heterostructure device, the mean square noise current $\langle i_n \rangle^2$ was obtained as $\sim 3.28 \times 10^{-25}$ A$^2$ Hz$^{-1}$. The root mean square noise current $\overline{i_n}^{1/2}$ was thus calculated to be $\sim 5.7 \times 10^{-13}$ A Hz$^{-1/2}$, and $A = 35$ $\mu$m$^2$. 

Fig. S5. Photoresponse over the visible-to-LWIR range for the PdSe$_2$ FET device.

(a) and (b) The rise time is $\tau_{\text{rise}} = 74.5$ ms, and the fall time is $\tau_{\text{fall}} = 93.1$ ms for LWIR 10.6 $\mu$m, whereas $\tau_{\text{rise}} = 51.3$ $\mu$s, and $\tau_{\text{fall}} = 53.7$ $\mu$s for 637 nm laser illumination. Response time of the PdSe$_2$ FET device at $V_{ds} = 1$ V. The rise/fall time is defined as the time required to transition from 10/90% to 90/10% of a stable photocurrent after turning the light on/off. (c) Output curves with and without illumination. The wavelength of the incident laser illumination is 637 nm. (d) Power-dependent photoresponsivity of the PdSe$_2$ phototransistor under laser illumination wavelengths of 2.7 $\mu$m, 3.0 $\mu$m, 4.012 $\mu$m and 10.6 $\mu$m at $V_{ds} = 1$ V. (e) Transfer curves of the PdSe$_2$ FET device in the dark and under various incident light power levels at $V_{ds} = 0.1$ V. As the light power increases, the horizontal shift of $I_{ds}$-$V_{g}$ indicates that $\Delta V_{g}$ has increased. (f) Measured current noise spectra density at 1 V bias of the PdSe$_2$ FET device (blue line) and the PdSe$_2$-MoS$_2$ heterojunction device (red line).
7. Photoresponse of PdSe$_2$-MoS$_2$ heterostructures

Fig. S6. Photoresponse of the PdSe$_2$-MoS$_2$ heterostructure device in the visible and near-infrared ranges. (a) Photovoltaic response under 940 nm illumination. (b) $I$-$V$ curves of a typical PdSe$_2$ phototransistor with (laser wavelength of 940 nm) and without illumination. Inset shows the zoom in of the $I$-$V$ curves. The short circuit current is $\sim$45 nA and the open circuit voltage is $\sim$0.09 V. (c) Power-dependent photovoltaic response and EQE under 940 nm illumination. (d) Photoresponsivity as a function of the illumination power for the PdSe$_2$-MoS$_2$ heterostructure in the visible (637 nm) and near-infrared (940 nm) range at $V_{ds} = 1$ V.
The high photoresponsivity around ~4.012 μm could be attributed to the following reasons. At first, we have performed a further experiment of the reflection spectrum for MoS$_2$-PdSe$_2$ heterostructure placed on a Si/SiO$_2$ substrate. We found that there is a reflect dip at ~4.5 μm. The reflection dip (Fig. S3d) indicates the light absorption at this range is comparatively fairly high which may originate from the interlayer absorption. Besides, the photogating effect is the major contribution to the photoresponse for this MoS$_2$-PdSe$_2$ heterostructure device. The photoconductive gain of photogating effect is much higher at the weak light condition.$^{15}$ The photoresponsivity peak around ~4 μm is obtained at low incident light power condition due to the combination of comparatively high light absorption and much higher photo gain at low light density condition.

Fig. S7. Photoresponse of the PdSe$_2$-MoS$_2$ heterostructure device over the mid-wave infrared range. (a) Wavelength-dependent photoresponsivity of a typical PdSe$_2$-MoS$_2$ heterostructure device, $V_{ds} = 1$ V. Inset: optical image of the measured device,
scale bar 2 μm. (b) Photoresponsivity as a function of the illumination power for various wavelengths from MWIR to LWIR with 1 V bias. (c) Type-I band alignment diagram of the MoS\(_2\)-PdSe\(_2\) heterostructure. The intralayer excitons generated from \(h\nu_1\) and \(h\nu_2\) photons absorbed by MoS\(_2\) and PdSe\(_2\), respectively, are shown by red arrows. The interlayer excitons generated from absorbed \(h\nu_3\) and \(h\nu_4\) photons are shown by blue arrows. (d) Response time of the PdSe\(_2\)-MoS\(_2\) heterostructure device under 637 nm illumination.

8. Stability of PdSe\(_2\) samples

The PdSe\(_2\) samples are very stable in ambient air. The photograph shown in Fig. S8a was taken on July 10, 2018, and the photograph shown in Fig. S8b was taken on October 18, 2018. Thus, this PdSe\(_2\) phototransistor had been exposed to ambient air for more than three months. Hardly any degradation of the sample can be detected in the optical images. We also checked the photoresponse of this device. Figures S8c and S8d show the measured photocurrents under the same incident light power. The photoresponse does not show any decrease over that exposure duration. The PdSe\(_2\)-MoS\(_2\) heterostructure device was placed in a dry box in air, where it remained for nearly one year. The test device and its photoresponse under 10.6 μm illumination are the same as that of a newly fabricated device as shown in Fig. S8e to Fig. S8h. All the optoelectric measurements were carried out in ambient air. We also measured the Raman spectrum of PdSe\(_2\) and the Raman and PL spectrum of MoS\(_2\) using a typical PdSe\(_2\)-MoS\(_2\) heterostructure device which was fabricated 6 months ago (from April 2, 2018 to October 18, 2018) as shown in Fig. S9a. The high quality of the Raman spectrum presented in Fig. S9b further confirms the stability of the PdSe\(_2\) sample. The Raman and PL spectrum of MoS\(_2\) are presented in Fig. S9c and S9d. The indirect PL peak of MoS\(_2\) is located at \(~682\) cm\(^{-1}\), which corresponds to 1.8 eV. The separation between the in-plane \(E_{2g}^1\) (383.6 cm\(^{-1}\)) and out-of-plane \(A_{1g}\) (407.5 cm\(^{-1}\)) vibration modes is 23.9 cm\(^{-1}\), which corresponds to the multi-layer configuration of the MoS\(_2\) sample.\(^{16,17}\)
Fig. S8. Optical images and temporal photoresponse of a typical PdSe$_2$ phototransistor and PdSe$_2$-MoS$_2$ heterostructure device. Optical image of a typical PdSe$_2$ phototransistor (a) as fabricated and (b) after three months exposure to air. (c) and (d) Temporal photoresponse of a typical newly fabricated PdSe$_2$ phototransistor and one exposed to air for three months, respectively. (e) Optical photograph of a typical newly fabricated PdSe$_2$-MoS$_2$ heterostructure device and (f) the device after having been exposed to air for nearly one year. (g) and (h) Temporal photoresponse of a typical PdSe$_2$-MoS$_2$ heterostructure device as fabricated and after exposure to air for nearly one year, respectively.
Fig. S9. Raman and PL spectra of a typical PdSe$_2$-MoS$_2$ heterostructure device.
(a) Optical image of a typical PdSe$_2$-MoS$_2$ heterostructure device after being exposed in air more than 6 months, scale bar 5 µm. (b) Raman spectrum of PdSe$_2$ after the device was exposed to air for more than 6 months. The illuminating laser beam was located at point 1 in the optical image. (c) Raman spectrum of MoS$_2$ when the laser beam was located at point 2. (d) PL spectrum of MoS$_2$; the two peaks labeled as $A_1$ and $B_1$ correspond to indirect and direct excitonic emission, respectively.
Fig. S10. Output curves of PdSe$_2$ FET devices using different metals as contacts in the dark condition. By using Ti/Au (5 nm Pd and 50 nm Au) as contacts, good Ohmic contacts are obtained. When Pd/Au (5 nm Pd and 50 nm Au) and Cr/Au (5 nm Cr and 50 nm Au) are used as contacts, non-linear $I$-$V$ curves indicate the formation of the Schottky barriers.

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