

PdSe₂: Pentagonal Two-Dimensional Layers with High Air Stability for Electronics

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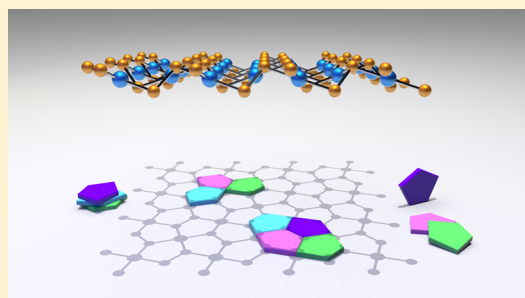
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Supporting Information

ABSTRACT: Most studied two-dimensional (2D) materials exhibit isotropic behavior due to high lattice symmetry; however, lower-symmetry 2D materials such as phosphorene and other elemental 2D materials exhibit very interesting anisotropic properties. In this work, we report the atomic structure, electronic properties, and vibrational modes of few-layered PdSe₂, exfoliated from bulk crystals, a pentagonal 2D layered noble transition metal dichalcogenide with a puckered morphology that is air-stable. Micro-absorption optical spectroscopy and first-principles calculations reveal a wide band gap variation in this material from 0 (bulk) to 1.3 eV (monolayer). The Raman-active vibrational modes of PdSe₂ were identified using polarized Raman spectroscopy, and a strong interlayer interaction was revealed from large, thickness-dependent Raman peak shifts, agreeing with first-principles Raman simulations. Field-effect transistors made from the few-layer PdSe₂ display tunable ambipolar charge carrier conduction with a high electron field-effect mobility of $\sim 158 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, indicating the promise of this anisotropic, air-stable, pentagonal 2D material for 2D electronics.



INTRODUCTION

The emergence of two-dimensional (2D) crystals with unique structures and extraordinary electronic properties provides exciting opportunities for applications in nanoscale electronics.¹ For example, graphene has gained attention due to its high carrier mobility resulting from an effectively massless state of charge carriers,² but its inherent lack of a band gap, and the inability so far to induce a sizable one, limits its application in electronics. It would thus be desirable to realize a 2D system with a widely tunable band gap when targeting applications in nanoscale devices. This has led to the exploration of transition metal dichalcogenides (TMDs) and other 2D materials beyond graphene.³ In this regard, MoS₂ has attracted the most attention because of its moderate mobility and high current on/off ratio in transistors; however, MoS₂ possesses a limited band gap variation between ~ 1.2 and 1.9 eV .^{4,5} Similarly, the relatively new 2D Bi₂O₂Se system shows high electron mobility and high on/off ratio but possesses a small band gap of $\sim 0.8 \text{ eV}$.^{6,7} For

electronic and photonic applications, a material that is air-stable and has high carrier mobility, high on/off ratio, as well as a more widely tunable band gap is far more desirable.

Until the recent introduction of black phosphorus (BP), with a band gap variation from 0.3 to 1.5 eV, materials with such a widely tunable band gap were difficult to find.⁸ BP has a honeycomb network similar to graphene but is strongly puckered (that is, not ideally planar, but oscillating out-of-plane in a regular corrugated manner), rendering exotic properties of the in-plane anisotropic response to external stimulations, such as polarized light, electric field, and applied strain.^{9–11} These anisotropies have their origins rooted in the puckering of the hexagonal lattice structure, which provides a new degree of freedom to explore in 2D materials. Recently, other buckled or puckered 2D materials with hexagonal

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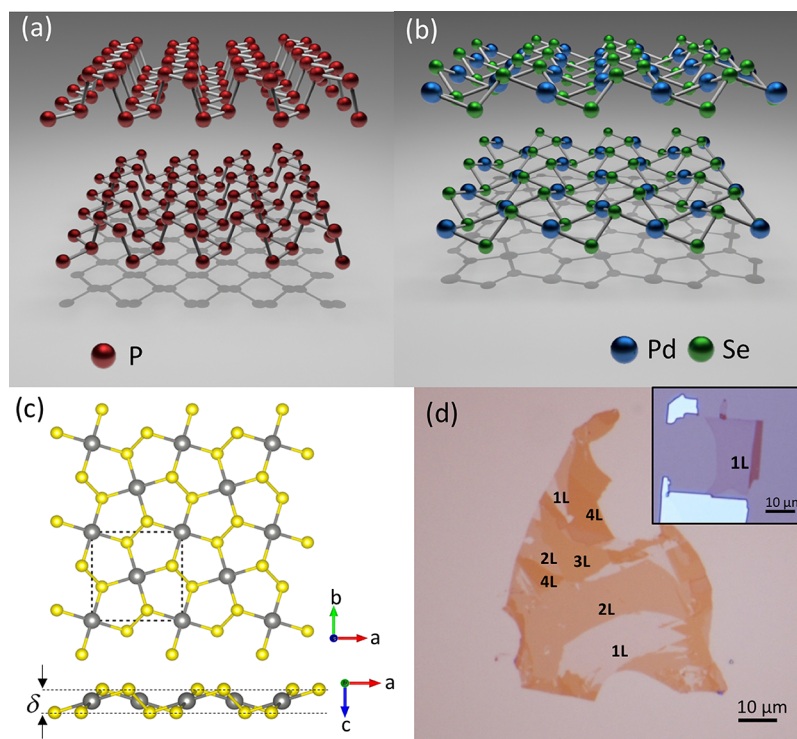


Figure 1. Crystallographic structure of 2D puckered (a) hexagonal black phosphorus and (b) pentagonal PdSe₂. (c) Top and side view of the crystal structure of monolayer PdSe₂ showing a puckered pentagonal configuration. The gray spheres represent the Pd atoms, while the yellow spheres represent the Se atoms. Dashed line indicates the unit cell. The vertical puckering distance, δ , is ~ 1.6 Å. (d) Optical image (OM) of exfoliated monolayer and few-layer PdSe₂ flakes on silicon substrate with 300 nm SiO₂ layer. The layer numbers were estimated from associated AFM measurements. Inset shows a large monolayer PdSe₂ flakes.

structure have been theoretically and experimentally reported in elemental 2D materials (also called Xenes) such as silicene, germanene, and stanene.^{12,13} In contrast with an isotropic planar hexagonal structure, the buckling breaks the sublattice symmetry, enhances spin–orbit coupling, and allows tuning of a topological quantum phase transition.¹⁴ However, despite their potential importance for device applications, the realization of stable 2D buckled or puckered hexagonal structures of 2D elemental materials including BP, silicene, germanene, and stanene is still a great challenge for practical electronics. Furthermore, 2D materials with buckled or puckered *pentagonal* structure are another class of highly desirable 2D materials due to the low-symmetry lattice structure. They have recently been theoretically predicted but have remained unexplored experimentally.^{15–17} The pentagons are usually considered as topological defects or geometrical frustrations, as stated in the well-known “isolated pentagon rule” (IPR),¹⁸ but are rarely found as basic building blocks in 2D materials. Unlike the hexagonal structure as the dominant motifs in 2D materials, most of the predicted pentagonal 2D materials, including penta-graphene and penta-SnS₂, are buckled or puckered in a regular corrugated manner to maintain symmetry. For example, pentagonal graphene presents a hybrid bond structure consisting of both sp³ and sp² carbons in a repeating pentagon arrangement. This unique atomic configuration coupled with the buckled structure results in a large band gap and exotic mechanical properties with an unusual negative Poisson’s ratio and ultrahigh mechanical strength,¹⁵ which are interesting for flexible device applications. Also, penta-SnS₂ has been theoretically predicted to be a room-temperature 2D quantum spin Hall (QSH) insulator with

sizable and nontrivial band gaps.¹⁶ Therefore, 2D buckled pentagonal materials with low symmetry could open the possibility for future optoelectronic, piezoelectric, spintronic, and valleytronic applications. To the best of our knowledge, 2D materials composed of pentagonal structure have never been demonstrated experimentally.

Here, we demonstrate the isolation and characteristics of atomically thin palladium diselenide crystals with a novel puckered pentagonal structure, experimentally revealed by atomic-resolution scanning transmission electron microscopy (AR-STEM). The puckered 2D PdSe₂ flakes exhibit a widely tunable band gap that varies from metallic (bulk) to ~ 1.3 eV (monolayer). Raman-active modes in PdSe₂ were identified by polarized Raman spectroscopy and first-principles calculations, with a strong interlayer interaction in PdSe₂ revealed by the large, layer-dependent Raman peak shifts. Field-effect transistors made from the few-layer PdSe₂ display ambipolar charge carrier conduction with high electron field-effect mobility of ~ 158 cm² V⁻¹ s⁻¹. In addition, few-layer PdSe₂ systems exhibit a metal–insulator transition (MIT), which is absent in bulk PdSe₂. Unlike BP, PdSe₂ is air-stable and can be synthesized potentially via chemical vapor deposition, which makes it an excellent candidate for practical electronics. Overall, our results indicate that 2D pentagonal materials should be useful in designing novel electronic devices that combine the charge, spin, and other degrees of freedom resulting from the low symmetry to achieve better performance and unprecedented functionalities.

■ EXPERIMENTAL DETAILS

Synthesis of Bulk PdSe₂ Crystals and Exfoliation. Bulk PdSe₂ single crystals were grown by a self-flux method through melting stoichiometric amounts of Pd powder (99.98%, Alfa Aesar) and Se powder (99.94%, Alfa Aesar). The Pd and Se powders in an atomic ratio of Pd:Se = 1:6 were thoroughly mixed together and sealed in an evacuated quartz ampule under a vacuum condition of 10⁻⁶ Torr and then placed in a single-zone thermal furnace. The furnace was slowly heated up to 850 °C, held for 50 h, and then allowed to cool to 450 °C at a rate of 3 °C/h, followed by cooling down to room temperature. Shiny single crystals of PdSe₂ were obtained by cleaving the ingot product. Monolayer and few-layer PdSe₂ flakes were prepared by micromechanical exfoliation of these bulk crystals. For optical, morphological, and device characterizations, clean silicon substrates with a 280 nm SiO₂ layer were used to support the flakes. For STEM characterization, the PdSe₂ flakes were transferred from the SiO₂ substrates to the TEM grid via a wet KOH/PMMA transfer method.¹⁹ The flakes were directly exfoliated onto a 0.5 mm thick commercially available quartz substrate for absorption spectroscopy measurements.

STEM Characterization. Thin PdSe₂ flakes were first prepared by mechanical exfoliation onto a SiO₂ substrate and then transferred with PMMA to Quantifoil gold TEM grids using a 0.25 M KOH solution to dissolve the SiO₂. The samples were baked at 150 °C in vacuum before STEM observation. The medium angle annular dark-field images (MAADF) were obtained using a Nion UltraSTEM100 microscope operated at 60 kV. The convergence angle of the electron beam is 30 mrad, and the inner detector half-angles used for high angle annular dark-field (HAADF) and MAADF images were 71 and 50 mrad, respectively. The images presented in the paper are filtered using a Gaussian function with a fwhm of 0.12 nm.

DFT Calculations. Plane-wave density functional theory (DFT) calculations were performed using the VASP package equipped with the projector-augmented-wave (PAW) method for electron-ion interactions.²⁰ The exchange-correlation interactions were considered in the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional.²¹ Van der Waals (vdW) interactions between the PdSe₂ layers were included using the vdW density functional method optPBE-vdW (denoted as optPBE).²² For bulk PdSe₂, both atoms and cell volume were allowed to relax (i.e., ISIF = 3) until the residual forces were below 0.001 eV/Å, with a cutoff energy of 350 eV and the 12 × 12 × 8 k-point sampling. The optimized bulk lattice constants obtained via optPBE are $a = 5.85$ Å, $b = 5.99$ Å, and $c = 7.95$ Å, were in good agreement with the experimental values ($a = 5.75$ Å, $b = 5.87$ Å, and $c = 7.69$ Å).^{23,24} Note that the out-of-plane direction is defined as the z-axis. Based on the fully relaxed geometries, the dynamic matrix was then calculated using the finite difference scheme implemented in the Phonopy software to obtain phonon frequencies and eigenvectors. Raman intensity calculations were then performed within the Placzek approximation using an in-house developed Raman modeling package. More details about DFT calculations are in the Supporting Information (SI).

Device Fabrication and Measurement. PdSe₂ crystals were exfoliated onto a silicon substrate with 280 nm thickness of SiO₂ layer. The location of suitable flakes was identified using a Nikon LV150 high-powered optical microscopy. AFM was performed to ascertain the thickness of the flakes. Electron beam lithography (FEI DB-FIB with Raith pattern software) was used for device fabrication. The metal contacts for the flakes, 5 nm of Ti followed by 30 nm Au, were deposited in vacuum using an electron beam evaporator. The FET device measurements were conducted using a Keithley 4200 semiconductor analyzer in a two-terminal configuration.

■ RESULTS AND DISCUSSION

Bulk PdSe₂ is a semi-metal noble transition metal dichalcogenide that was theoretically predicted recently to have a unique pentagonal structure in 2D layers, with a strong interlayer coupling and an extraordinarily high carrier mobility.^{24–26} As shown by the side view and projected top view of a 2D PdSe₂

monolayer in Figure 1b, it consists entirely of pentagonal rings with the vertices in a slightly asymmetrical boat conformation, which is similar to the puckered structure of BP (Figure 1a) that has hexagonal rings.²⁷ As shown in the figure, each Pd atom binds to four Se atoms in the same layer, and two neighboring Se atoms can form a covalent Se–Se bond.²⁸ To our knowledge, this pentagonal conformation has not yet been experimentally reported for any 2D materials structure, including graphene, other elemental 2D materials (also called Xenes), and TMDs.

Bulk PdSe₂ single crystals were grown by melting stoichiometric amounts of Pd powder and Se powder in an evacuated quartz ampoule under a vacuum condition of 10⁻⁶ Torr. The as-grown crystals are plate-like with a thickness around 4 mm. As shown in Figure 1c and Figure S1, bulk PdSe₂ displays *Pbca* symmetry (point group *D*_{2h}) with an orthorhombic lattice that contains four Pd and eight Se atoms in one unit cell.²⁸ The structure is made up of single layers of PdSe₂ stacking along the *c*-axis and held together mainly by van der Waals forces. From the top view, we can see that the monolayer PdSe₂ crystals are composed entirely of pentagonal rings, presenting an intriguing pattern that is known as the Cairo pentagonal tiling.¹⁵ This unique pentagonal structure has been predicted theoretically to be stable only for graphene and a few other 2D materials.^{15–17} In contrast to the structure of hexagonal 2D materials such as graphene, Xenes, and TMDs that have been reported experimentally, the PdSe₂ monolayer structure features unusual planar tetra-coordination of its Pd atoms, puckered pentagons with a vertical puckering distance, δ , of ~ 1.6 Å, as well as Se–Se bonds. Although the predicted interlayer binding energy of PdSe₂ (190 meV/atom)²⁴ is significantly higher than that of BP (40 meV/atom),²⁵ PdSe₂ mono- and few-layer structures were able to be isolated using micromechanical exfoliation by adhesive tapes, and as shown in Figure 1d, large areas (~ 30 μm) were obtained. The thickness of the monolayer crystals was verified from atomic force microscopy (AFM) to be ~ 0.6 nm as shown in Figure S2. The thickness of multilayered PdSe₂ crystals was inferred from AFM measurements and cross-calibrated by micro-Raman and micro-absorption spectroscopies as discussed in the SI. Interestingly, PdSe₂ exfoliates primarily into regular rectangular shapes, allowing the identification of its crystalline orientation (see Figure S2). As shown in Figure S3, the dynamical stability of the single- and few-layer PdSe₂ is confirmed by the absence of soft modes in the calculated phonon dispersions. Note that very small negative frequencies are still present in the calculated phonon dispersion of monolayer PdSe₂, but by switching to the LDA functional they can be nearly eliminated, suggesting that such negative frequencies are likely not due to structural instability.

The atomic structure of the PdSe₂ flakes was characterized by scanning transmission electron microscopy (STEM). Although we can exfoliate large monolayer PdSe₂ flakes onto a substrate and transfer it onto a TEM grid, it is hard to distinguish the pentagonal structure in the annular dark-field (ADF) image (Figure S4) due to the surrounding disordered region of the flakes, perhaps resulting from damage during transfer. Figure 2 shows the ADF image of few-layer PdSe₂ crystals, and although, even and odd layer numbers appear very different in ADF as shown in Figure 2a,b due to symmetry differences, the patterns agree very well with the image simulations²² shown in Figure 2c,d, respectively. Bulk PdSe₂ crystals exhibit *Pbca* space group symmetry and *D*_{2h} point group symmetry. In contrast, thin

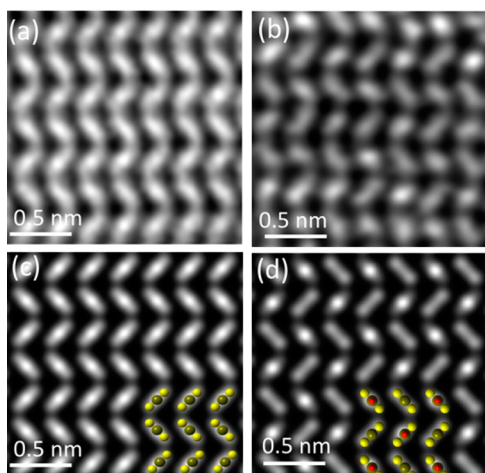


Figure 2. Atomic resolution structure of few-layer PdSe₂ crystals revealed by Z-contrast STEM images (top row) and corresponding simulated images (bottom row) of PdSe₂. (a,c) Even number of layers and (b,d) odd number of layers. Insets in (c,d) show atomic models of the corresponding STEM images.

flakes with either an odd or even number of layers belong to space group $P2_1/c$ (No. 14) and point group C_{2h} ($2/m$) with inversion symmetry or space group $Pca2_1$ (No. 29) and point group C_{2v} ($mm2$) without inversion symmetry, respectively. The corresponding fast Fourier transform (FFT) patterns of few-layer PdSe₂ in Figure S5a–c show the rectangular structure distinct from the hexagonal structure of other TMDs. Each flake has an identical lattice structure with similar diffraction patterns of (020) and (200), confirming the crystallinity of each flake. Electron energy loss spectroscopy (EELS) of the few-layer PdSe₂ flakes (Figure S5d,e) shows characteristic peaks of Pd N,M edges and Se M edges.

According to the calculated electronic band structures in Figure 3a,b, 1L PdSe₂ exhibits 1.3 eV indirect band gap and no band gap for the bulk. The 1.3 eV indirect band gap for a monolayer is quite close to its direct band gap (1.43 eV), making the PdSe₂ monolayer promising for optoelectronic applications. Similar indirect band gaps are observed in few-layer PdSe₂ as well (more details in Figure S6), indicating the intrinsic nature of this indirect band gap semiconductor compared to the indirect-to-direct band gap transition observed in other TMDs.⁵ Generally speaking, the valence band maximum (VBM) is located between the high-symmetry Γ and X (0.5, 0, 0) points while the conduction band minimum (CBM) is located between Γ and M (0.38, 0.5, 0) points, suggesting that it is not located along the high-symmetry lines like the commonly studied TMDs (MoS₂ family)³ and BP.²⁹ For the PdSe₂ systems, both the valence band edge and conduction band edge are contributed mostly by the Pd 4d-states and Se 4p-states, which indicates that the energy levels of both VBM and CBM (thus the band gap) are sensitive to the interlayer coupling and electronic hybridization.²⁴ The inset of Figure 3b shows the rectangular shape of the first Brillouin zone of PdSe₂ 2D crystals. To determine the thickness dependence of the indirect band gap, optical absorption measurements were carried out and Tauc plots were used to derive the band gaps from the absorption spectra as shown in Figure S7d–g. Figure 3c shows the optical band gaps versus the number of PdSe₂ layers. The large uncertainty in the band gaps (± 0.2 eV) can be explained by possible high amount of defects in the PdSe₂

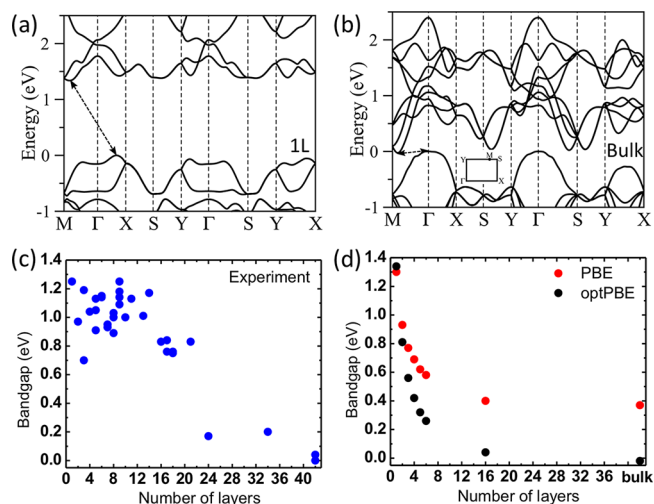


Figure 3. Calculated electronic band structures of (a) 1L and (b) bulk PdSe₂ by the optPBE method. The dashed arrows indicate the lowest energy transitions between the valence band maximum (VBM) and conduction band minimum (CBM). The VBM is set at 0 eV. Inset in (b) shows the Brillouin zones of PdSe₂ 2D crystals with high-symmetry points labeled. (c) Band gaps extracted from the Tauc plots for various number of PdSe₂ layers derived from the optical absorption spectra (see Figure S7 for more details). (d) Band gaps obtained from first-principles calculations: PBE and optPBE shown in red and black dots, respectively.

flakes. Another possible source of this uncertainty may be related to in-plane anisotropic absorption properties of PdSe₂.¹⁷ However, these data show a clear trend of decreasing band gap with increasing number of layers from ~ 1.3 eV (1L) to 0 eV (bulk) (within the uncertainty of ± 0.2 eV). This trend is consistent with the first-principles calculations (Figure 3d) although the calculated band gap is generally smaller than experimental one because DFT tends to underestimate the band gap due to its limitation to describe the long-range many-body interactions. Therefore, the experimentally observed band gap dependence for the thicker layers may reflect the importance of the many-body effects. In addition, both our absorption measurements and DFT calculations show a layer-dependent band gap that changes approximately from 0 eV (bulk) to 1.3 eV (monolayer). Note that the changes of the PdSe₂ band gap from bulk to monolayer are noticeably larger than those for MoS₂.⁵ Since Pd has more valence electrons than Mo (10 versus 6), it is expected that interlayer Pd and Se atoms are more hybridized, and that the interlayer coupling is stronger in this case.²⁴ This effect contributes to the strong layer-dependent band gaps for PdSe₂ and also for PtS(Se)₂ within the same group.^{30,31}

As shown in Figure 1c, the unit cell of bulk PdSe₂ is orthorhombic with space group $Pbca$ (No. 61, point group D_{2h}).²⁸ Unlike most well-studied hexagonal TMDs such as MoS₂,⁵ the symmetry of bulk PdSe₂ is comparable to BP, which is also orthorhombic (space group No. 64, point group D_{2h}).³² As a result, symmetry assignments of phonon modes for PdSe₂ resemble those for BP, and this indicates that 2D PdSe₂ flakes should have unique anisotropy due to their in-plane low symmetry. The unit cell of bulk PdSe₂ consists of two layers and 12 atoms, and thus there are 36 normal phonon modes at the Γ point whose irreducible representations are

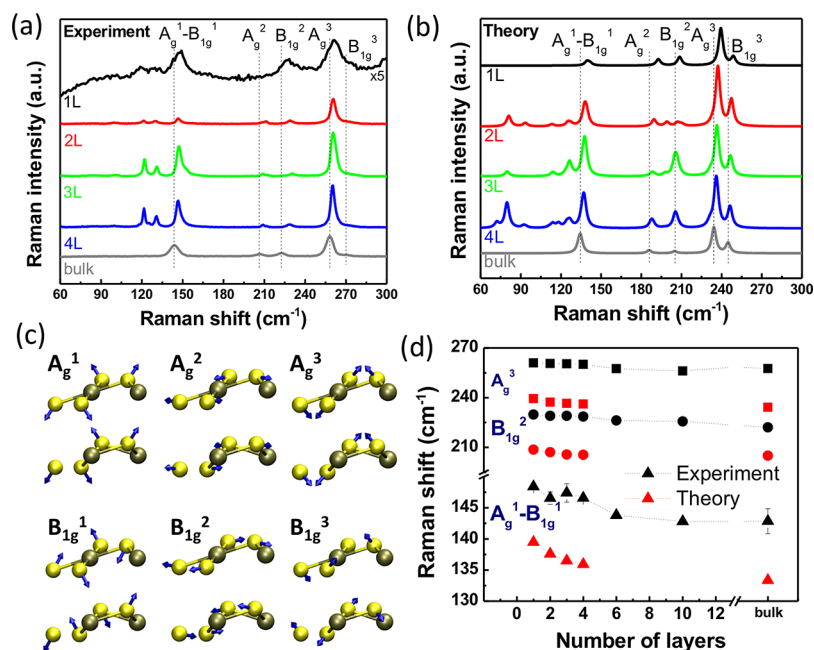


Figure 4. (a) Layer-dependent Raman spectra of PdSe₂ from 1L to bulk measured for an excitation laser wavelength of 532 nm. (b) Corresponding calculated Raman spectra by the optPBE method. In both (a) and (b), the dashed lines indicate positions of the Raman peaks for bulk PdSe₂. Note that the A_g¹-B_{1g}¹ label means the overlapping of two close peaks: A_g¹ and B_{1g}¹. For convenience, bulk notations of A_g and B_{1g} are also used for other systems. (c) Atomic displacements (blue arrows) of six Raman modes in bulk PdSe₂. (d) Comparison of the experimental (black) and theoretical (red) frequencies of Raman modes A_g¹-B_{1g}¹, B_{1g}², and A_g³ at different thicknesses. Although the calculated frequencies are systematically smaller than the experimental ones, the trend of the frequency shift versus thickness agrees.

$$\Gamma_{\text{bulk}} = 3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g} + 6A_u + 6B_{1u} + 6B_{2u} + 6B_{3u} \quad (1)$$

where 3A_g, 3B_{1g}, 3B_{2g}, and 3B_{3g} modes are Raman active. As shown in Figure 4a, we find that only A_g and B_{1g} modes can be observed in our unpolarized Raman measurements (more details in SI). This is confirmed by the theoretical Raman spectra shown in Figure 4b, where the bulk spectra (gray lines) exhibit five peaks. Although bulk PdSe₂ has 3 A_g modes (A_g¹, A_g², A_g³) and 3 B_{1g} modes (B_{1g}¹, B_{1g}², B_{1g}³), our calculations found that the A_g¹ and B_{1g}¹ modes are very close to each other with a frequency difference of less than 2 cm⁻¹, and subsequently a single mixed peak (denoted as A_g¹-B_{1g}¹) appears around 145 cm⁻¹ according to the measurements (around 134 cm⁻¹ according to the calculations). Detailed and strict symmetry assignments for all peaks are presented in Figure S8, but to further validate the peak symmetry assignments, polarized Raman measurements were carried out. As shown in Figure S9, in both the experimental and simulated polarized Raman spectra of PdSe₂, indeed only the three A_g peaks appear under $\bar{z}(x, x)z$ while the three B_{1g} peaks appear under $\bar{z}(x, y)z$ because the A_g and B_{1g} modes have dramatically different response behaviors to laser polarization due to their different Raman tensors (more details in SI). The atomic vibrations of these six Raman modes are illustrated in Figure 4c. It is interesting to point out that all of them mainly involve the vibrations of the Se atoms (blue arrows in Figure 4c). This can be ascribed to the unique structure in PdSe₂ (Figure 1c), in which each layer is actually a Se-Pd-Se trilayer with Pd atoms covalently bonded to four Se atoms on the top and bottom sublayers. It is also interesting to note that all five Raman peaks generally shift to higher frequency with the thickness reduction from bulk to 1L. Figure 4d shows both the experimental

(black) and theoretical (red) frequencies of the A_g¹-B_{1g}¹, B_{1g}², and A_g³ peaks at different thicknesses. Although the calculated frequencies are systematically smaller than the experimental ones (by about 9–20 cm⁻¹), the trend of the frequency versus thickness is in agreement. In addition, the significant shifts of Raman peaks around 5–9 cm⁻¹ from bulk to 1L for PdSe₂ are observed, which is different from the small shifts around 3–5 cm⁻¹ observed in MoS₂.³³ This anomalous shift behavior is attributed to the strong interlayer coupling and hybridization in PdSe₂, which also leads to the wide band gap variation as we discussed above. Our calculations also indicate that the in-plane lattice constants decrease with decreasing thickness because of the strong interlayer interaction in PdSe₂. For instance, the in-plane lattice parameters, *a* and *b*, are reduced by ~2% and ~1%, respectively, going from bulk to 1L PdSe₂. Such a lattice contraction can stiffen the bonds and enhance the restoring forces (we refer to this as the “lattice shrinking effect”), which is one of the main factors responsible for the increasing peak frequencies from bulk to 1L (more details in the SI).

To investigate the transport properties of 2D PdSe₂, field-effect transistor (FET) devices were fabricated using a two-terminal, back-gate configuration. Figure 5a shows the plot of the drain current (*I*_{ds}) as a function of back gate voltage (*V*_{bg}) for a typical 5L PdSe₂ device with 1.0 V drain bias. The linear behavior of the *I*_{ds}-*V*_{ds} characteristics shown in Figure S10a,b indicates good Ohmic contact. The device exhibits ambipolar transport with a slight asymmetry between holes and electrons. For this ~5 L device, electron-apparent field-effect mobility as high as 70 cm² V⁻¹ s⁻¹ was achieved at room temperature and an on/off ratio greater than 10⁵. Overall, we found higher mobilities for the electron carriers as compared with holes. To elucidate the layer-dependent electrical properties of 2D PdSe₂ crystals, the transfer characteristics for different numbers layers of PdSe₂ were measured and are shown in Figure S10c. We

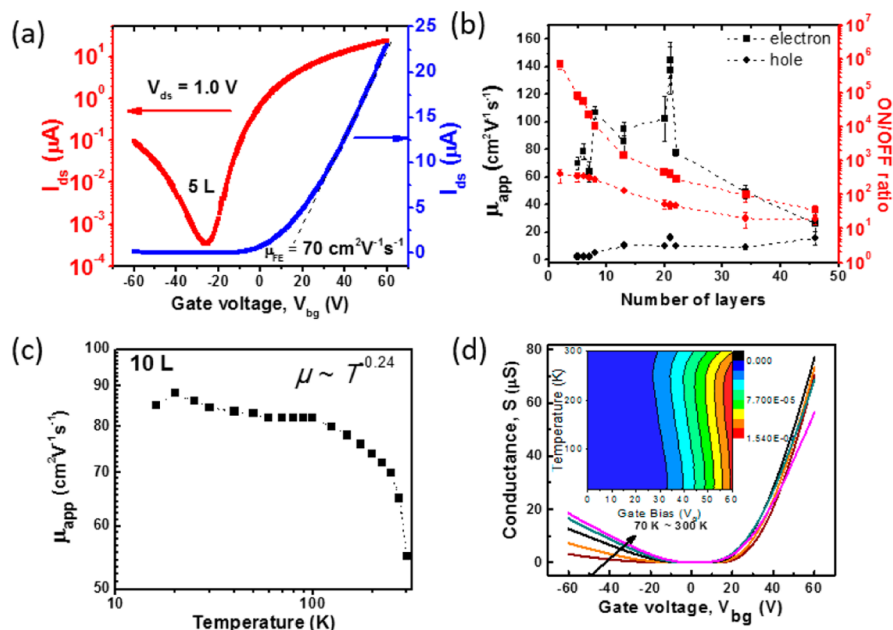


Figure 5. (a) Transfer curve of a typical ~5-layer PdSe₂ device, with both logarithmic and linear scales, showing ambipolar characteristics. (b) Electron and hole apparent mobility, and on/off ratio versus flakes thickness for PdSe₂ devices measured at room temperature. Black line indicates mobility curve, while red line indicates on/off ratio curves. Data points in squares and circles represent electron and holes, respectively. The electron mobilities are higher than hole mobilities, and thicker films consistently show lower on/off ratio than thinner flakes. (c) Electron-apparent mobilities measured at different temperatures for PdSe₂ flakes with a thickness of 10 layers. Below 100 K, the mobilities are independent of temperature, but above 100 K, the mobilities decrease with increasing temperature due to the phonon scattering, following a $T^{-\gamma}$ dependence with γ close to 0.24. (d) Conductance as a function of gate voltage for different temperatures for PdSe₂ flakes with a thickness of 10 layers. The crossing around ~40 V indicate the change in temperature dependence. Inset shows the color plot of the conductance as a function of temperature and gate bias.

observe distinct layer-dependent properties, in agreement with our optical characterization and electronic structure calculations. For example, as the number of layers increases, the gate control becomes negligible, which is consistent with a decrease in band gap. This is displayed in Figure 5b, where the on/off ratio for electrons decreases from $\sim 10^6$, for bilayer PdSe₂, to ~ 10 , for bulk PdSe₂. A similar trend also can be observed for the on/off ratio for holes. The low on/off ratio (< 10) observed in bulk PdSe₂ can be associated with a quasi-metallic behavior. While the on/off ratio decreases monotonically as the number of layers is increased, the electron mobility peaks at ~ 20 L, similar to that observed in BP.³⁴ The statistical analysis for the mobility and on/off ratios of our ~ 65 devices are presented in the SI, showing an average electron mobility of ~ 80 cm² V⁻¹ s⁻¹ with the highest one ~ 158 cm² V⁻¹ s⁻¹ (see Figure S11). Note that these values were measured without any materials treatment or device optimization, so perhaps with further device engineering, mobilities approaching the theoretical predicted value should be expected due to the low effective mass of noble transition metal dichalcogenides.²⁶ Interestingly, the PdSe₂ devices maintained their typical ambipolar behavior irrespective of the number of layers, with more symmetrical ambipolar behavior with increasing number of layers, which is very promising for high-performance 2D logic circuits. The layer dependence of the semiconductor-to-quasi-metal transition in PdSe₂ is also promising for fabricating single-material logic junction devices using 2D PdSe₂ crystals for both the channel and contact. This would eliminate the contact resistance due to scattering and Schottky barriers at the contact interface with the semiconducting channel.³⁵ It is important to note that unlike BP, PdSe₂ remains stable (at least up to 60

days for the present measurements) after exposure to air as shown in Figure S12.

The temperature dependence of the carrier mobility in 10 L PdSe₂ flakes shown in Figure 5c shows behavior similar to that found in other layered materials; i.e., the carrier mobility decreases at temperatures higher than ~ 100 K and saturates (or decreases slightly) at lower temperatures. The behavior of the mobility at low temperature is most likely due to the dominant charged impurity scattering mechanism. As the temperature increases, the mobility decreases due to phonon scattering, following a power law relation $\mu \sim T^{-\gamma}$, where γ is close to 0.24. The γ value for few-layer PdSe₂ is notably smaller than values in other 2D materials such as monolayer MoS₂ ($\gamma \approx 1.40$; ref 36), but agrees with that in few-layer BP ($\gamma \approx 0.5$; ref 9) and monolayer MoS₂ with double dielectric layers ($\gamma \approx 0.3$; ref 37). The decrease in the value of γ may be attributed to the suppression of the homopolar phonon modes due to the strong interlayer interaction in layered PdSe₂. Further theoretical and experimental work is needed to clarify the detailed mechanism. In addition, an increase in current modulation up to $> 10^9$ is observed for few-layer PdSe₂ as the temperature is lowered (see Figure S13). The plot of the temperature dependence of the two-terminal conductivity at different gate bias for the 10 L device is shown in Figure S14. With $V_{bg} < 40$ V, the conductivity of the 10 L device decreases with decreasing temperature, indicating insulating behavior, whereas for $V_{bg} > 40$ V, the temperature dependence is reversed, showing metallic behavior. The crossover from insulating to metallic conductance is shown in more detail in Figure 5d. Interestingly, this gate-bias-induced metal-insulator transition (MIT) behavior was only observed in our thinner devices (i.e., < 24 L). For thicker PdSe₂ devices, the conductance always increases

with increased temperature at all gate bias (Figure S15) suggesting there is no MIT in thick flakes of PdSe₂. This MIT behavior could be a result of quantum interference effects of weak and strong localization (more discussion in SI).

CONCLUSIONS

In summary, we have successfully fabricated and characterized few-layer PdSe₂ crystals, a new member of the 2D materials family. 2D PdSe₂ exhibits an anisotropically puckered pentagonal structure that was revealed by atomic-resolution scanning transmission electron microscopy. Micro-absorption spectroscopy and first-principles band structure calculations showed a wide band gap variation from ~0 (bulk) to ~1.3 eV (monolayer) in this material. Few-layer PdSe₂ devices exhibited excellent ambipolar semiconducting behavior with high room-temperature electron-apparent field-effect mobility (up to 158 cm² V⁻¹ s⁻¹). The Raman-active modes in PdSe₂ were identified by polarized Raman spectroscopy and first-principles calculations, and strong interlayer interactions were revealed from the large layer-dependent Raman peak shifts. In addition, in-plane anisotropic properties should be expected for this highly anisotropic material because of the low in-plane symmetry structure. Temperature-dependent conductance measurements of few-layer PdSe₂ devices revealed that a metal–insulator transition behavior exists only in thin flakes. In addition, compared to other buckled or puckered 2D materials, such as BP, 2D PdSe₂ exhibits much better air-stability (>60 days). Therefore, the discovery of new puckering pentagonal building blocks in 2D materials opens the possibility of both new emerging physics related to the low-symmetry structure and various disruptive applications such as low-energy electronics, piezoelectrics, enhanced thermoelectricity, and spintronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b04865.

Detailed descriptions of the characterizations, instrument parameters for the analytical techniques (AFM, absorption and Raman spectroscopy, and FET), additional AFM, STEM, Raman, FET device performance, charge transport, and detailed theoretical calculations of the electronic structure, phonon spectrum, and Raman spectrum (PDF)

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Notes

The authors declare no competing financial interest.

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