Broadband excitation spectrum of bulk crystals and thin layers of PtTe$_2$

Barun Ghosh,$^1$ Francesca Alessandro,$^{2,3}$ Marilena Zappia,$^2$ Rosaria Brescia,$^4$ Chia-Nung Kuo,$^5$ Chin Shan Lue,$^5$ Gennaro Chiarello,$^2$ Antonio Politano,$^{6,7}$ Lorenzo S. Caputi,$^2$ Amit Agarwal,$^{1,*}$ and Anna Cupolillo$^{2,†}$

$^1$Department of Physics, Indian Institute of Technology Kanpur, Kanpur - 208016, India
$^2$Department of Physics, University of Calabria, via Ponte Bucci, cubo 31/C 87036, Rende (CS) Italy
$^3$INFN, Sezione LNF, Gruppo Collegato di Cosenza, Cubo 31C, I-87036 Rende (CS), Italy
$^4$Electron Microscopy Facility, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
$^5$Department of Physics, National Cheng Kung University, 1 Ta-Hsueh Road 70101 Tainan, Taiwan
$^6$Istituto Italiano di Tecnologia-Graphene Labs via Morego, 30 16163 Genova, Italy
$^7$Dipartimento di Scienze Fisiche e Chimiche (DSFC), Universita dell’Aquila, Via Vetoio 10, I-67100 L’Aquila, Italy

(Dated: August 28, 2018)

We explore the broadband excitation spectrum of bulk PtTe$_2$, using electron energy loss spectroscopy and density functional theory. In addition to infrared modes related to intraband 3D Dirac plasmon and interband transitions between the 3D Dirac bands, we observe modes at 3.9, 7.5 and 19.0 eV in the ultraviolet region. The comparison of the excitation spectrum with the calculated orbital-resolved density of states allows us to ascribe spectral features to transitions between specific electronic states. Additionally, we study the thickness dependence of the high-energy plasmon in the PtTe$_2$ thin films. We show that, unlike graphene, the high-energy plasmon in PtTe$_2$ thin film gets red-shifted by $\sim$2.5 eV with increasing thickness.

I. INTRODUCTION

Recently, the PtX$_2$ (X=Se, Te, S) class of transition-metal dichalcogenides (TMDCs) have attracted a huge interest of the scientific community. This class of TMDCs combines promising application capabilities along with the fundamental physics interest arising from the existence of topological type-II Dirac fermions. As opposed to type-I Dirac materials, which have a closed Fermi surface with either an electron or a hole pocket, type-II Dirac materials have an unbounded Fermi surface with both electron and hole pockets. The presence of bulk topological Dirac node forces the existence of massless surface states. This provides massless charge carriers with ultrahigh mobility confined at the surface plane.

Thin layers of PtX$_2$ class of materials are equally interesting because of their air stability, high mobility, and superior gas sensing properties, among others. The quantum confinement effect dramatically changes the properties of the thin layers of PtTe$_2$ which undergo a metal-semiconductor transition with decreasing thickness. Apart from this, the monolayer exhibits a unique property: because of local dipole-induced Rashba effect, opposite spins with the same energy gets spatially separated on the opposite sides of the monolayer. This is known as spin layer locking and it can have potential applications in the electrically tunable spintronic devices.

Preceding discussions made it clear that PtX$_2$ class of materials has emerged as a promising material for the future electronics. While the band structure of PtTe$_2$ has been explored comprehensively, along with the Dirac plasmons (collective density excitations) in the infrared range of the electromagnetic spectrum, the high-energy excitations in PtTe$_2$ still remain unexplored. The comprehension of the excitation spectrum of collective modes in the visible-ultraviolet is crucial to develop broadband photodetectors, ultraviolet-imaging applications and broadband plasmonic devices. Monolayer PtTe$_2$ has the smallest energy band gap in the PtX$_2$ class of materials, offering it an advantage over the other members for applications in nano-electronics.

Motivated by this, in this paper we probe the broadband excitation spectrum of bulk crystals and thin layers of PtTe$_2$, using electron energy loss spectroscopy (EELS) complemented by detailed ab-initio calculations. EELS probes the broadband dielectric response of the system to a negatively charged probe, allowing for spectral contributions from both plasmonic modes and non-vertical transitions from valence-band to conduction-band electronic states. Therefore, EELS investigations supplement the studies of the absorption and emission processes of TMDCs in the long-wavelength limit involving only vertical transitions from occupied to unoccupied states. The nature of various experimentally probed EELS excitations is identified by means of calculations of the band-structure and the loss function based on density-functional theory (DFT). In addition to the bulk excitation spectrum, we also explore the changes in the broadband excitation spectrum of PtTe$_2$ on reducing its thickness to few layers. Contrarily to the case of graphene and phosphorene, a blue-shift of the high-energy plasmon frequency is observed for thin layers compared to the bulk.

The manuscript is organized as follows: In Sec. II we briefly describe the crystal structure, experimental details related to the growth and characterization of PtTe$_2$ along with that of the reflection EELS. This is followed by a discussion of the theoretical ab-initio calculation of the EELS spectrum and other computational details in Sec. III. The broadband EELS spectrum of bulk PtTe$_2$ is discussed in Sec. IV, followed by the discussion of the excitation spectrum of thin layers in Sec. V. Finally, we...
summarize our findings in Sec. VI.

II. GROWTH, CRYSTAL STRUCTURE, CHARACTERIZATION AND DETAILS OF EELS

A. Growth

Single crystals of PtTe$_2$ were prepared by the self-flux method. High-purity Pt (99.99 %) foil and Te ingot (99.9999 %) were mixed in the ratio of 1:17 and wrapped in a quartz tube under vacuum. The quartz tube was heated to 1000 °C, dwelled there for 8 hours, and slowly cooled at a rate of 3-5 °C/h to 500 °C. Successively, the excess Te flux was separated by centrifugation. The resulting crystals have typical dimensions of $8 \times 8 \times 1$ mm$^3$ with the c-axis perpendicular to the plates and can be easily cleaved. The structure of the grown crystals was examined by X-ray diffraction (Bruker D2 PHASER) using Cu K$_\alpha$ radiation and Laue diffraction at room temperature.

Thin flakes of PtTe$_2$ were obtained by liquid-phase exfoliation of bulk PtTe$_2$ in N-methylpyrrolidone (NMP).

B. Crystal Structure

Bulk PtTe$_2$ belongs to the large family of 1T-metal dichalcogenides with CdI$_2$ type crystal structure [space group P3m1(164)]. The bulk structure can be viewed as a collection of isolated monolayers stacked in the out of plane direction – see Fig. 1(a) and 1(b). In each of these monolayers there are three sublayers, Te-Pt-Te, where the central Pt atom is strongly bonded with six neighbouring Te atoms forming a hexagonal honeycomb structure. Both selected area electron diffraction (SAED) and low-energy electron diffraction (LEED) patterns shown in Fig. 1(d) and 1(e) match with $[0001]$-oriented flakes and bulk PtTe$_2$, respectively. Correspondingly, the XRD pattern only exhibits (00n) peaks as shown in Fig. 1(f).

C. Characterization

To demonstrate cleanliness, the surface has been characterized by means of vibrational spectroscopy and X-ray photoelectron spectroscopy, without finding any contamination (see appendix B, and C). Once prepared in ultra-high vacuum, the surface remains uncontaminated for a timescale of several weeks, thus ensuring sample stability. The low-energy electron diffraction (LEED) pattern shows sharp spots against a low background – see Fig. 1(e).

D. Electron Energy Loss Spectroscopy

The reflection EELS experiments were performed at room temperature by means of an EELS apparatus with two 50 mm hemispherical deflectors for both monochromator and analyzers, mounted in an ultra-high vacuum chamber at the University of Calabria, Italy. The pri-
mary electron beam impinging on the sample with an
incident angle $\theta_i$ of 43° with respect to the surface normal,
along the $\Gamma - K$ direction of the surface Brillouin zone.
The primary electron beam energy is $E_p = 100$ eV.

SAED and STEM-EELS analyses were carried out at room temperature on a FEI Tecnai G2 F20 TWIN TEM,
equipped with a Gatan Enfinium SE spectrometer at Istituto Italiano di Tecnologia, Genoa (Italy). For these
experiments a primary electron beam energy $E_p = 200$
keV and a collection angle of 13 mrad were used. Sam-
ple for TEM analyses were prepared by drop casting of
the flakes dispersion onto a holey carbon-coated Cu grid.
The EELS spectra were collected from flakes regions sus-
pended on holes in the carbon support film.

III. THEORY

A. Energy Loss function

The theoretical calculation of the electron energy loss function starts with the non-interacting density-density
response function ($\chi_{GG}^0$) for a periodic lattice. It is ob-
tained using the Adler-Wiser formula given by30,31,

$$\chi_{GG}^0(q, \omega) = \frac{1}{\Omega} \sum_{\mathbf{k}} \sum_{\mathbf{G}, \omega} f_{\mathbf{n}k} - f_{\mathbf{n}'k+q} \times$$

$$\langle \psi_{\mathbf{n}k} | e^{-i(q+\mathbf{G})\tau} \psi_{\mathbf{n}'k+q} \rangle_{\text{cell}} \langle \psi_{\mathbf{n}k} | e^{i(q+\mathbf{G})\tau} \psi_{\mathbf{n}'k+q} \rangle_{\text{cell}} \ .$$

The wave function $\psi_{\mathbf{n}k}$, eigenvalue $\epsilon_{\mathbf{n}k}$, and the corre-
sponding Fermi-Dirac occupation function $f_{\mathbf{n}k}$ at wave
vector $\mathbf{k}$ for the band with index $n$ are obtained from the
ground-state calculations performed using DFT.

The interacting density-density response function can be obtained within the framework of time-dependent
DFT (TDDFT) by solving a Dyson-like equation. Us-
ing a plane-wave basis for a periodic system, for a given
($\mathbf{q}, \omega$), it can be expressed as

$$\chi_{GG} = \chi_{GG}^0 + \sum_{G_1, G_2} \chi_{GG_1}^0(q, \omega) K_{G_1G_2}(q) \chi_{GG_2G'}(q, \omega),$$

where $G$ and $q$ are the reciprocal lattice vector and the
Bloch wave vector, respectively, and $K_{G_1G_2}$ is the in-
teraction kernel, including both the Coulomb or Hartree
term, as well as the exchange correlations.

Using the calculated $\chi_{GG}^0$, the dielectric matrix, $\epsilon_{GG}(q, \omega)$, can obtained as

$$\epsilon_{GG}^{-1}(q, \omega) = \delta_{GG'} + \frac{4\pi}{|q+G|^2} \chi_{GG}^0(q, \omega) .$$

The macroscopic dielectric constant can be obtained from
the dielectric matrix via the equation,

$$\epsilon_M(q, \omega) = \frac{1}{\epsilon_{GG}^{-1}(q, \omega)} .$$

The dynamical loss function, which is directly related to
the experimental excitation spectrum probed by EELS,
is now obtained from the macroscopic dielectric function,

$$\epsilon_{\text{Loss}}(q, \omega) = -\frac{3}{\epsilon_M(q, \omega)} .$$

B. Computational details

Electronic band structure calculations were performed
using a plane-wave basis set within the framework of
DFT, as implemented in the VASP package.33,34 We use the PAW pseudopotentials with 500 eV kinetic en-
cy cut-off for the plane-wave basis set.35 The exchange-
correlation part of the potential has been treated within
the framework of generalized approximation scheme de-
veloped by Perdew-Burke-Ernzerhof.36 Starting from the
experimental structure, we relax all the atomic positions
until the forces on each atom are less than 0.001 eV/Å. Spin-orbit interaction has been considered as a perturba-
tion and treated in a self-consistent manner.

In order to calculate the response functions we use the
GPAW code, which employs a real-space representation of
the PAW potentials.37–39 A kinetic energy cutoff of 500
eV has been used for the plane-wave basis set. We use a
$122 \times 122 \times 20$ $k$-grid to calculate the momentum depen-
dence of the loss function. To incorporate the local-field
effects, we use a plane-wave cutoff of 60 eV which cor-
responds to 85 plane waves. A broadening parameter
$\eta = 0.05$ eV is assumed in all calculations of the response
function.

IV. BROADBAND SPECTRUM OF BULK PtTe$_2$

The experimental broadband EELS spectra of PtTe$_2$
bulk sample, measured with an electron beam energy of
100 eV, is shown in Fig. 2(a). The broadband EELS spec-
trum shows distinctly resolved peaks at energies $\sim 0.5,
\sim 1.4, \sim 3.9, \sim 7.5$ and $\sim 19.0$ eV, among others. The
lowest energy peak at 0.5 eV is the intra-band gapped 3D
Dirac plasmon excitation in bulk PtTe$_2$, which disperses
with the momentum [see Fig. 2(e)]. It has been discussed
in detail in Ref. [18]. Here, we will focus on the remaining
inter-band excitations, which are relatively less disper-
sive compared to the intra-band 3D Dirac plasmon peak.
We find that their peak location and relative intensity is
FIG. 2. (a) Broadband EELS spectrum for bulk PtTe$_2$ measured in reflection mode with a primary electron beam energy of 100 eV. The EELS spectrum shows several distinct peaks at energies 0.5, 1.4, 3.9, 7.5 and 19.0 eV. The peak at 0.5 eV is dispersive and it is associated with the intra-band density excitations in PtTe$_2$. The other higher energy peaks correspond to inter-band transitions, which can be identified from the orbital-resolved DOS plot, shown in the panels (b) and (c). The corresponding orbital-resolved band-structure plots are shown in Fig. 3. The dominant transitions, corresponding to the observed EELS peaks, are marked by arrows. The experimental broadband EELS spectrum is also reasonably captured by the loss function obtained from ab-initio calculations, as shown in (d)-(f) for different momentum values, reported in the legend of panel (e). The 19.0 eV peak in (d) has the highest intensity in the ab-initio calculations. The other dominant intra-band peaks at 3.9 and 7.5 eV are resolved in panel (f).

In order to identify the inter-band transitions corresponding to the observed peaks in the EELS spectrum, we show the orbital-resolved density of states (DOS) in Fig. 2(b)-(c). The corresponding orbital-resolved band structure plot is shown in Fig. 3. The energetically lower valence band (VB) is situated approximately between -15 and -10 eV and it is mostly dominated by Te$_{5s}$ states. The upper VB extends from -7 eV up to the Fermi level and mostly comprises of Pt$_{5d}$ and Te$_{5p}$ orbitals. The lower conduction-band states till ~3 eV are also primarily formed by Pt$_{5d}$ and Te$_{5p}$ orbitals. The conduction-band states at higher energy have contributions mainly from the Pt$_{6p}$ and Te$_{5d}$ orbitals. Comparison of the orbital-resolved DOS with the observed spectral features in the broadband EELS spectrum allows us to identify the prominent states involved in the transitions. We find that the peaks at 3.9, 7.5 and 19.0 eV are predominantly connected to Pt$_{5d} \rightarrow$ Pt$_{5d}$; Te$_{5p} \rightarrow$ Te$_{5d}$; and Te$_{5s} \rightarrow$ Te$_{5d}$ transitions, respectively, as marked by arrows in Fig. 2(b)-(c). The theoretical loss function in Fig. 2(d)-(f) also captures the qualitative features of the experimental excitation spectrum reasonably well.

It is worth reminding that EELS peaks cannot precisely match the energies of single-particle transitions observed with optical spectroscopies, as maxima in the loss
function are related to the maxima in $-\text{Im}[1/\epsilon_M(\omega)]$. Conversely, optical transitions are identified with maxima in $\text{Im}[\epsilon_M(\omega)]$, that are actually shifted with respect to the maxima of $-\text{Im}[1/\epsilon_M(\omega)]$. Having discussed the EELS spectrum of the bulk PtTe$_2$ crystal, we now proceed to discuss the EELS spectrum of thin PtTe$_2$ layers in the next section.

V. BROADBAND SPECTRUM OF THIN PtTe$_2$ LAYERS

In this section, we explore the thickness dependence of the broadband EELS spectrum of PtTe$_2$ thin films. To this aim, we have employed the STEM-EELS technique, which affords the spatial resolution necessary to identify regions with different thickness within the flakes. As shown in Fig. 4(a), the liquid-phase exfoliation of PtTe$_2$ has produced flakes with inhomogeneous thickness. Therefore, for STEM-EELS experiments different thicknesses were probed on different areas of same fragments.

Previously, the thickness dependence of the high energy EELS peaks has been done for the case of $\sigma + \pi$ plasmons of graphene. In graphene, the plasmon energy shifts by about 10 eV when going from monolayer graphene to multilayers. Remarkably, a similar blue-shift has been detected by both reflection EELS in graphene layers epitaxially grown on silicon carbide, and by EELS-TEM in free-standing graphene flakes exfoliated from graphite. This is irrespective of the dissimilarities in the plasmon energy in the monolayer regime (10 eV in the latter case and 14.6 eV in the former one). This blue-shift of the plasmon energy in graphene with increasing thickness had been ascribed to the effect of interlayer Coulomb coupling. In contrast to graphene, the high energy plasmon peak in phosphorene does not show any thickness dependence.

Our STEM-EELS investigation suggests that in PtTe$_2$ the plasmon band changes in both line-shape and energy position as a function of thickness. Specifically, a symmetrical line-shape, centered at about 23 eV (Fig. 4c), is recorded for thinner flakes, whereas an asymmetrical line-shape, with a corresponding centroid around 20.5 eV, are revealed for thicker flakes. Thus, in contrast to graphene, and phosphorene the high energy plasmon peak in PtTe$_2$ is red-shifted with increasing thickness. However, the layer-dependent plasmon-energy shift in PtTe$_2$ is much lower (~2.5 eV) than that of graphene (~10 eV). The change in the line shape, with an asymmetric shape characterizing the thinner regions, is ascribable to the multiple contributions (i.e., due to regions with different thickness) to the spectra acquired in the thinner regions of the flakes. The presence of contributions from regions few nm away from the position of the electron beam is due to the delocalization of inelastic scattering, prominent in the low energy-loss range.
FIG. 4. (a) HAADF-STEM image of the fragmented PtTe$_2$ flake suspended on a hole in the amorphous carbon support film used for STEM-EELS analysis. The points A and B exhibit a lower thickness (lower brightness in HAADF-STEM mode) than point D, while the point C has the highest thickness in the flake. Only the zero-loss peak appears in the spectrum recorded at point E, i.e. 20 nm far from the PtTe$_2$ flake. (b) The broadband STEM-EELS spectra acquired for points A, B, C and D. In panel (b) the intensity is normalized to the zero-loss peak maximum, while in panel (c) it is normalized to that of the peak at ∼20 eV, in order to highlight the dissimilarities in the line-shape of the peaks corresponding to different thickness.

VI. CONCLUSIONS

We have probed the broadband excitation spectrum of bulk crystals and thin layers of PtTe$_2$, using EELS in reflection mode for bulk and STEM-EELS for thin layers. In the case of bulk PtTe$_2$ we find different modes in the ultraviolet regime at 3.9, 7.5 and 19.0 eV, in addition to the excitations associated to the 3D Dirac cones observed in the infrared range at 0.5 and 1.4 eV. These observations are well explained by the DFT-based orbital-resolved band-structure and DOS calculations. Specifically, we find that in bulk PtTe$_2$ the observed peaks at 3.9, 7.5 and 19.0 eV are predominantly connected to Pt$_{5d}$ → Pt$_{5d}$; Te$_{5p}$ → Te$_{5d}$; and Te$_{5s}$ → Te$_{5d}$ transitions, respectively. In thin layers, with decreasing thickness, the high-energy plasmon peak gets shifted from 20.5 to 23.0 eV. This red-shift with increasing thickness is in contrast to the blue-shift observed in case of graphene. Moreover, with increasing number of layers an increase in the anisotropy of the line-shape of the high-energy plasmon peak is observed. This peculiarity can be exploited for characterizing the thickness of PtTe$_2$ thin films. Similar physics is expected to play out in other members of the family, including PdTe$_2$ and PtSe$_2$, among others.

Appendix B: Surface chemical reactivity of PtTe$_2$ single crystals

To evaluate the surface chemical reactivity of PtTe$_2$, we have carried out high-resolution X-ray photoelectron spectroscopy (XPS) experiments (Fig. 6). We addressed firstly the evolution of Pt 4f and Te 3d core levels upon several treatments (O$_2$ dosage and air exposure), with respect to spectra measured for pristine PtTe$_2$. From the analysis of Te 3d core-level spectra (Fig. 6), we deduce that the as-cleaved undefected PtTe$_2$ surface is inert to oxygen exposure. In fact, only 3d$_{5/2}$ and 3d$_{3/2}$ core levels at the binding energies of 573.1 and 583.5 eV, corresponding to an oxidation state Te(0), are observed in Fig. 6 for both the pristine PtTe$_2$ (red curve) and the same surface exposed to a dose of $10^6$ L (1 L=1.33 × 10$^{-6}$ mbars) of oxygen.

Appendix A: Valence-band states in PtTe$_2$

As an additional check we explicitly check that there are no valence-band states below the -14 eV in PtTe$_2$, by calculating the band-structure over a wide energy range. The calculated band-structure is shown in Fig. 5: it is evident that there are no valence-band states in PtTe$_2$ from approximately -14 to -50 eV.

FIG. 5. Band structure of PtTe$_2$ over a wide energy region. Evidently, there are no energy states in between -13 eV to -50 eV.
FIG. 6. High-resolution XPS spectra of Pt-4f and Te-3d core levels taken for the pristine PtTe$_2$ sample (red curve) and the same surface exposed to 10$^6$ L of O$_2$ (dashed blue curve). For all spectra, the photon energy is 745 eV and the energy resolution is 0.1 eV.

O$_2$ at room temperature (dashed blue curve).

The Pt 4f doublet reported in Fig. 6 is observed at binding energies of 72.5 (4f$_{7/2}$) and 75.9 (4f$_{5/2}$) eV, respectively. Similar values of the binding energy for Pt-4f core levels have been reported for PtSe$_2$.$^{14,46}$

To further assess the surface chemical reactivity in PtTe$_2$-based systems, we have also carried out vibrational experiments by means of high-resolution electron energy loss spectroscopy (HREELS). Explicitly, we have exposed pristine PtTe$_2$ to water and oxygen. The corresponding vibrational spectra are reported in Fig. 7. For the case of pristine (undefected) PtTe$_2$, the vibrational spectrum remains featureless even after exposure of water and oxygen at room temperature (Fig. 7). Likewise, no vibrational peaks are revealed in the air-exposed undefected PtTe$_2$ surface (red curve in Fig. 7). Combined with the XPS results reported in Fig. 6, these data lead to the conclusion that undefected PtTe$_2$ does not react at room temperature with ambient gases. This finding has a particular interest in view of applications in optoelectronics based on PtTe$_2$.

* amitag@iitk.ac.in
† anna.cupolillo@fis.unical.it

1. Andres Castellanos-Gomez, “Why all the fuss about 2d semiconductors?” Nature Photonics 10, 202 (2016).
2. Liang Li, Weike Wang, Yang Chai, Huiqiao Li, Mingliang Tian, and Tianyou Zhai, “Few layered pts$_2$ phototransistor on hbn with high gain,” Advanced Functional Materials 27, 1701011 (2017).
3. Alexey A. Soluyanov, Dominik Gresch, Zhijun Wang, QuanSheng Wu, Matthias Troyer, Xi Dai, and B. Andrei Bernevig, “Type-ii weyl semimetals,” Nature 527, 495 EP – (2015).
4. Mingzhe Yan, Huaqing Huang, Kenan Zhang, Eryin Wang, Wei Yao, Ke Deng, Guoliang Wan, Hongyun Zhang, Masashi Arita, Haitao Yang, Zhe Sun, Hong Yao, Yang Wu, Shoushan Fan, Wenhui Duan, and Shuyun Zhou, “Lorentz-violating type-ii dirac fermions in transition metal dichalcogenide ptte2,” Nature Communications 8, 257 (2017).
5. M. S. Bahramy, O. J. Clark, B.-J. Yang, J. Feng, L. Bawden, J. M. Riley, I. Markovic, F. Mazzola, V. Sunko, D. Biswas, S. P. Coebl, M. Jorge, J. W. Wells, M. Landersson, T. Balasubramanian, J. Fujii, I. Vobornik, J. E. Rault, T. K. Kim, M. Hoesch, K. Okawa, M. Asakawa, T. Sasagawa, T. Eknapakul, W. Meevasana, and P. D. C. King, “Ubiquitous formation of bulk dirac cones and topological surface states from a single orbital manifold in transition-metal dichalcogenides,” Nature Materials 17, 21 (2017).
6. Han-Jin Noh, Jinwon Jeong, En-Jin Cho, Kyoo Kim, B. I. Min, and Byeong-Gyu Park, “Experimental realization of type-ii dirac fermions in a pdte$_2$ superconductor,” Phys. Rev. Lett. 119, 016401 (2017).
7. Kenan Zhang, Mingzhe Yan, Haoxiong Zhang, Huaqing Huang, Masashi Arita, Zhe Sun, Wenhui Duan, Yang Wu, and Shuyun Zhou, “Experimental evidence for type-ii dirac semimetal in ptse$_2$,” Phys. Rev. B 96, 125102 (2017).
8. Huaqing Huang, Shuyun Zhou, and Wenhui Duan, “Type-ii dirac fermions in the ptse$_2$ class of transition metal dichalcogenides,” Phys. Rev. B 94, 121117 (2016).
9. Tay-Rong Chang, Su-Yang Xu, Daniel S. Sanchez, Weifeng Tsai, Shih-Ming Huang, Guoqing Chang, Chuang-Han Hsu, Guang Bian, Ilya Belopolski, Zhi-Ming Yu, Shengyuan A. Yang, Titus Neupert, Hong-Tay Jeng, Hsin Lin, and M. Zahid Hasan, “Type-ii symmetry-protected topological dirac semimetals,” Phys. Rev. Lett. 119, 026404 (2017).
“Atomic and electronic structure of exfoliated black phosphorus,” Journal of Vacuum Science & Technology A 33, 060604 (2015).

44 C.C. Ahn, Transmission electron energy loss spectrometry in materials science and the EELS atlas (Wiley-VCH, 2004).

45 R.F. Egerton, Electron Energy-Loss Spectroscopy in the Electron Microscope, Language of science (Plenum Press, 1996).

46 Chanyoung Yim, Kangho Lee, Niall McEvoy, Maria OBrien, Sarah Riazimehr, Nina C. Berner, Conor P. Cullen, Jani Kotakoski, Jannik C. Meyer, Max C. Lemme, and Georg S. Duesberg, “High-performance hybrid electronic devices from layered ptse2 films grown at low temperature,” ACS Nano 10, 9550–9558 (2016).