1. Introduction

The emergence of novel topological phases has opened new avenues for science and technology.\textsuperscript{[1]} Especially, recently discovered Weyl/Dirac topological semimetals host massless relativistic quasiparticles arising from linear band crossing at the degenerate point, protected by crystalline symmetries.\textsuperscript{[2]}

Strongly tilted Dirac/Weyl dispersion arising from broken Lorentz symmetry can result in type-II Dirac/Weyl semimetals (Figure 1b), with the Weyl/Dirac node being located at the intersection point of an electron/hole pocket. Type-II Dirac/Weyl systems have unbounded electron and hole pockets at the Fermi surface with a large density of states at the Dirac/Weyl node, leading to a modulated effective mass and unconventional properties.\textsuperscript{[3]}

Transition-metal dichalcogenides PtTe\textsubscript{2}, PdTe\textsubscript{2}, and NiTe\textsubscript{2} deserve particular attention, due to the presence of type-II Dirac fermions. As a matter of fact, tilted Dirac cones afford a suitable platform for optoelectronics of dissipation-less carrier-transport, favored by their ultrahigh carrier mobility, and large nonsaturating magnetoresistance. Herein, it is shown that PtTe\textsubscript{2}, PdTe\textsubscript{2}, and NiTe\textsubscript{2} display high-speed terahertz (THz) detection capability at room temperature, which originates from their peculiar band structure with topologically protected electronic states. Furthermore, photodetectors based on their heterostructures are able to suppress dark current with high-performance detection of THz light. Furthermore, these crystals are stable in air and they can be easily exfoliated in nanosheets by liquid-phase exfoliation, due to the weak interlayer van der Waals bonds. The obtained results clearly establish that the type-II Dirac semimetals based on transition-metal ditellurides have immense research potential for addressing application-oriented issues for remote sensing and telecommunications.
Among the various topological materials, transition-metal ditelluride systems showing type-II Dirac fermions (PtTe$_2$, PdTe$_2$, and NiTe$_2$) have stimulated considerable interest in recent years for their technological potential.\(^4\) The existence of a tilted Dirac cone, observed in the vicinity of the Fermi level in PtTe$_2$ (−0.76 eV),\(^5\) PdTe$_2$ (−0.65 eV),\(^6\) and NiTe$_2$ (+0.02 eV)\(^7\) (Figure S1, Supporting Information) has ushered in the new era of exploration of topological superconductivity and anisotropic magneto-transport. This class of materials features graphene-like charge-carrier mobility and tunable photon absorption with even higher efficiency, which provides a promising platform for low-energy and high-sensitivity photodetection.

Herein, we use large-area, high-quality single crystals of MTe$_2$ (M = Pt, Pd, and Ni) to propose an experimental innovation of spoof surface plasmon polaritons (SPPs)-induced nonequilibrium electrons in a log-antenna-assisted subwavelength metal–MTe$_2$–metal (m–M–m) structure for the detection of microwave and terahertz wave band. To further improve the performance of the device, van der Waals heterostructure (vdW heterojunction) integration based on PdTe$_2$ is constructed, exhibiting the lower dark current and higher sensitivity at THz illumination.

2. Results and Discussion

High-quality MTe$_2$ crystals are crucial for fabricating high-performance optoelectronic and plasmonic devices. Due to the high melting points, the bulk crystals of MTe$_2$ are generally grown by the chemical vapor transport (CVT) and flux method,\(^8\) rather than with melt growth techniques. The CVT method provides high-quality crystals with low defect concentration. However, the entire process is lengthy and energy-intensive and chemical contamination from halogen is sometimes inherent. To achieve controlled and scalable growth of thin MTe$_2$, also the direct...
Tellurization of deposited Pt film, molecular beam epitaxy, or chemical vapor deposition (CVD) method were adopted. However, the structural and electronic properties of the PtTe monolayer on clean and selenium-passivated Pt surface represent semiconductor–metal interfaces, which do not display topological electronic states as bulk PtTe. We adopted both the flux and melt growth methods to prepare the bulk PtTe, NiTe, and PdTe crystals as starting materials (Figure 1a). MTe (M = Pt, Pd, and Ni) have a CaI2-type trigonal (1T) structures with a P3m1 space group, in which one M atom is surrounded by six Te atoms in a hexagonal repeating unit structure (Figure 1c,d). Raman spectrum of exfoliated MTe flake (Figure 1e) show two active bands located at 111 and 157 cm−1 for PtTe2,[8c], 75 and 134 cm−1 for PdTe2,[11c] 84 and 138 cm−1 for NiTe2,[13c] corresponding to the Eg and A1g optical phonon modes, respectively.

We fabricated an m–M–m structure of MTe2-based (M = Pt, Pd, and Ni) device. To optimize the detection, a symmetrically log-periodic antenna is designed to couple the low-energy photons into the subwavelength channel, achieving THz electrical gain (see Figure 2a). To verify the enhancement of spoof SPPs in a log-periodic antenna at the THz frequency, the finite difference time domain (FDTD) solutions are carried out with a horizontally polarized plane wave illumination at 0.30 THz (1.24 meV). The gain at both ends of the source and drain channels are particularly obvious and the magnitude is about 110 in the inset of Figure 2a. The perfectly linear current–voltage (I–V) curves in the dark reflect the good ohmic contact between the MTe2 (M = Pt, Pd, and Ni) flake and metallic stack after the device fabrication process, with a resistance smaller than 100 Ω in Figure 2b.

The photoresponse measurements are carried out using a lock-in technique, and THz radiation is generated from a VDI multiplier connected to a 40 GHz microwave source, covering the photon frequencies from 0.08 to 0.12 THz and 0.24 to 0.30 THz (see details in the Experimental section). Nonequilibrium carriers could be excited even under the low-energy THz photon of the order of few meV, due to the presence of the type-II Dirac cone in the vicinity of the Fermi energy. When an electromagnetic wave at normal incidence impinges onto the subwavelength channel, photocurrent might be induced by the interaction of the topological surface states and low-energy photon. Similar to graphene, the gapless nature of MTe (M = Pt, Pd, and Ni) offer alternative capability of ultrabroadband detection even down to THZ range. The THz detection capability of the device is characterized by photocurrent (Ip) in Figure 2c. The photocurrent can be expressed by Ip = Ihgh − Idark (Idark is the current without radiation at room temperature), and all time-resolved photoresponses show a high signal-to-noise ratio, characterizing a good photoelectric conversion ability. When an electrical bias (Vds) is applied in the drain, the photocurrent increases linearly for Vds varying from −0.1 to +0.1 V (Figure 2d), due to the increased drift-velocity of the carriers. The photocurrent of PdTe2-based device shows an obvious improvement even at room temperature. At a lower temperature of 77 K, we find a 2–3-fold enhancement in the photocurrent compared with that at 300 K, due to the increase in carrier mobility at 77 K.

However, such semimetals have been criticized for photodetection due to relatively high dark current, which reduces the detection sensitivity and increases the shot noise. To overcome this, we made a vdW heterojunction by stacking few-layer graphene with a PdTe2 flake, with a small lattice mismatch. In such 2D heterostructures, a larger electric field can be induced, compared with traditional bulk semiconductor heterostructure, due to the large charge transfer between the layers. To gain further

Figure 2. Photoelectric properties. a) Schematic of the PdTe2/PtTe2/NiTe2 THz photodetector with symmetrically log-periodic antenna. The channel length is 6 μm. b) The electrical characteristics of three devices. c) Time-resolved photosignal for room-temperature operation at 0.12 THz. d) Photocurrent of the PdTe2-based device at different temperatures. e) The current–voltage (I–V) curve of the vdW heterojunction device at the different drain–source voltage varying from −0.5 to 0.5 V. Inset: Optical microscopy image of vdW heterojunction. f) Photoresponse of the PdTe2–graphene vdW heterojunction device.
insights into the capacity of the PdTe₂-graphene device for THz photodetection, we plotted the electrical bias-dependent photosignals at photon frequencies of 0.04, 0.12, and 0.30 THz, as shown in Figure 2f. The magnitude of the photocurrent linearly increases as the bias voltage increases from −0.1 to 0.1 V. The vdW heterojunction device enables the superb capability for photodetection at low-energy frequency bands.

Ambient stability is crucial for optoelectronic devices which should work in air. Especially, both theoretical and experimental assessments of chemical stability of MTe₂ bulk crystals demonstrate superb chemical stability of pristine PtTe₂ and tendency to formation of oxide monolayer on the surface of PdTe₂, NiTe₂, and defective PtTe₂ (see Figure S2, Supporting Information), which just represents a passivation layer. Calculations demonstrate that oxidation of MTe₂ (M = Pt, Pd, and Ni) is an exothermic process with moderate magnitude of the enthalpies of decomposition of molecular oxygen (−50 to −120 kJ/O₂). This is consistent with experimentally observed removal of oxygen from the surface by annealing. Accordingly, MTe₂ (M = Pt, Pd, and Ni) can be used in nanoelectronics without any encapsulation.

Another relevant issue for technology is related to the possibility to produce inkjet-printed photodetectors based on bulk crystals exfoliated in liquid phase. The exfoliation of MTe₂ (M = Pt, Pd, and Ni) nanosheets in liquid phase can be considered as chemically safe process, as in liquid media only physical adsorption of water on defect sites (Te vacancies) is energetically favorable at room temperature and further decomposition of water is extremely unfavorable.

3. Conclusions

We have demonstrated a MTe₂-based (M = Pt, Pd, and Ni) photodetector with self-driven detection capability of low-energy photons in an ambient environment. In addition, we successfully demonstrated a high-performance photodetector based on a PdTe₂-graphene heterostructure that operates at THz wavelengths. The detectors fabricated have a sensitivity of microampsere in the self-powered operation. The ambient stability of MTe₂ (M = Pt, Pd, and Ni) crystals facilitates the nanofabrication process without any capping layer on the active channel. Furthermore, all MTe₂ (M = Pt, Pd, and Ni) crystals can be exfoliated in atomically thin layers by liquid-phase exfoliation. Accordingly, MTe₂ (M = Pt, Pd, and Ni) represents a very promising class of materials for low-energy optoelectronic application in next-generation communications using topological semimetal materials.

4. Experimental Section

Methods for single-crystal growth are reported in Section S1, Supporting Information.

The thin MTe₂ (M = Pt, Pd, and Ni) flakes were acquired by mechanically exfoliation from bulk crystal and quickly transferred onto a high-resitivity silicon (300 nm SiO₂) substrate. Then, log-periodic antenna electrodes were defined by ultraviolet lithography, electron-beam evaporation, and lift-off process. Concerning the preparation of the PdTe₂-graphene heterostructure, few-layer graphene with different thicknesses using the standard mechanical exfoliation method from the bulk material was transferred onto the SiO₂/Si substrate. Then, the PdTe₂ flakes were exfoliated and transferred onto the few-layer graphene to achieve the vdW heterojunction. Through the processes, including electron-beam lithography, electron-beam evaporation, lift-off, and bonding wire interconnection, the PdTe₂-graphene heterostructure devices were fabricated.

The I–V characteristic curve of photodetector was measured at room temperature using 4200 Semiconductor Analyzer. For photoresponse measurements, microwave frequency was tuned up to 20~40 GHz, connected to a microwave source (Agilent E8257D) with an electrical modulation and detected the closed-circuit photosignal using a preamplifier, a lock-in amplifier, and a high-speed sampling oscilloscope. The terahertz frequency was tuned up to 0.08~0.12 and 0.24~0.30 THz based on commercially available VDI synthesizer. The data of time-resolved photosignal were obtained directly from the high-speed sampling oscilloscope (1 GHz bandwidth).

Supporting Information

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

Acknowledgements

The support was provided by the State Key Program for Basic Research of China (nos. 2017YFA0305500 and 2018YFA0306204), the National Natural Science Foundation of China (nos. 61521005, 61875217, and 91850208), and the STCSM Grants (no. 1859078100 and 19590780100). Shanghai Municipal Science and Technology Major Project (grant no. 2019SHZDZX01). The project was funded by State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University (KF1809). The work was partially supported by the Ministry of Science and Higher Education of the Russian Federation (through the basic part of the government mandate, project no. FEUZ-2020-0060). B.G. and A.A. acknowledge funding from Science Education and Research Board (SERB) and Department of Science and Technology (DST), government of India.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

heterostructures, terahertz photodetectors, topological materials, transition-metal ditellurides, type-II Dirac semimetals

Received: April 17, 2021
Revised: April 28, 2021
Published online: May 16, 2021

[1] a) J. E. Moore, Nature 2010, 464, 194; b) A. A. Burkov, Nat Mater. 2016, 15, 1145; c) S. Klembt, T. H. Harder, O. A. Egorov, K. Winkler, R. Ge, M. A. Bandres, M. Emmerling, L. Worschech, T. C. H. Liew, M. Segev, C. Schneider, S. Hofling, Nature 2018, 562, 552; d) P. Liu, J. R. Williams, J. J. Cha, Nat. Rev. Mater. 2019, 4, 479.
[2] a) G. B. Osterhoudt, L. K. Diebel, M. J. Gray, X. Yang, J. Stanco, X. Huang, B. Shen, N. Ni, P. J. W. Moll, Y. Ran, K. S. Burch, Nat. Mater. 2019, 18, 471; b) Y. Tanaka, Z. Ren, T. Sato, K. Nakayama, S. Souma, T. Takahashi, K. Segawa, Y. Ando, Nat. Phys. 2012, 8, 800.

[3] a) H. J. Noh, J. Jeong, E. J. Cho, K. Kim, B. I. Min, B. G. Park, Phys. Rev. Lett. 2017, 119, 016401; b) A. A. Soluyanov, D. Gresch, Z. Wang, Q. Wu, M. Troyer, X. Dai, B. A. Bernevig, Nature 2015, 527, 495.

[4] a) M.-K. Lin, R. A. B. Villaos, J. A. Hleuyack, P. Chen, R.-Y. Liu, C.-H. Hsu, J. Avila, S.-K. Mo, F.-C. Chuang, T. C. Chiang, Phys. Rev. Lett. 2020, 124, 036402; b) X. Hu, K. P. Wong, L. Zeng, X. Guo, T. Liu, L. Zhang, Q. Chen, X. Zhang, Y. Zhu, K. H. Fung, ACS Nano 2020, 14, 6276; c) H. Xu, C. Guo, J. Zhang, W. Guo, C. N. Kuo, C. S. Lue, W. Hu, L. Wang, G. Chen, A. Politano, X. Chen, W. Lu, Small 2019, 15, 1903362; d) A. Politano, G. Chiarello, C.-N. Kuo, C. S. Lue, R. Edla, P. Torelli, V. Pellegrini, D. W. Boukhvalov, Adv. Funct. Mater. 2018, 28, 1706504; e) A. Politano, G. Chiarello, B. Ghosh, K. Sadhukhan, C.-N. Kuo, C. S. Lue, V. Pellegrini, A. Agarwal, Phys. Rev. Lett. 2018, 121, 086804; f) H. Ma, P. Chen, B. Li, J. Li, R. Ai, Z. Zhang, G. Sun, K. Yao, Z. Lin, B. Zhao, R. Wu, X. Tang, X. Duan, X. Duan, Nano Lett. 2018, 18, 3523.

[5] A. Politano, G. Chiarello, B. Ghosh, K. Sadhukhan, C. N. Kuo, C. S. Lue, V. Pellegrini, A. Agarwal, Phys. Rev. Lett. 2018, 121, 086804.

[6] 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. Cooil, M. Jorge, I. Vobornik, A. Politano, A. L. Vázquez de Parga, G. Benedek, D. Farías, R. Miranda,npj 2D Mater. Appl. 2021, 5, 25; b) S. Nappini, D. W. Boukhvalov, G. D’Olimpio, L. Zhang, B. Ghosh, C. N. Kuo, H. Zhu, J. Cheng, M. Nardone, L. Ottaviano, D. Mondal, R. Edla, J. Fuji, C. S. Lue, I. Vobornik, J. A. Yarmoff, A. Agarwal, L. Wang, L. Zhang, F. Bondino, A. Politano, Adv. Funct. Mater. 2020, 30, 2000915; c) L. Zhang, Z. Chen, K. Zhang, L. Wang, H. Xu, L. Han, W. Guo, Y. Yang, C. N. Kuo, C. S. Lue, D. Mondal, J. Fuji, I. Vobornik, B. Ghosh, A. Agarwal, H. Xing, X. Chen, A. Politano, W. Lu, Nat. Commun. 2021, 12, 1584; d) C. Guo, G. Chen, D. Wei, L. Zhang, Z. Chen, W. Guo, H. Xu, C.-N. Kuo, C. S. Lue, X. Bo, X. Wan, L. Wang, A. Politano, X. Chen, W. Lu, Sci. Adv. 2020, 6, eabb6500.

[7] B. Ghosh, D. Mondal, C.-N. Kuo, C. S. Lue, J. Nayak, J. Fuji, I. Vobornik, A. Politano, A. Agarwal, Phys. Rev. B 2019, 100, 195134.

[8] a) K. Zhang, M. Yan, H. Zhang, H. Huang, M. Arita, Z. Sun, W. Duan, Y. Wu, S. Zhou, Phys. Rev. B 2017, 96, 125102; b) Y. Zhao, J. Qiao, Z. Yu, P. Yu, K. Xu, S. P. Lau, W. Zhou, Z. Liu, X. Wang, W. Ji, Y. Chai, Adv. Mater. 2017, 29, 1604230; c) A. Politano, G. Chiarello, C.-N. Kuo, C. S. Lue, R. Edla, P. Torelli, V. Pellegrini, D. W. Boukhvalov, Adv. Funct. Mater. 2018, 28, 1706504.

[9] a) Y. Wang, L. Li, W. Yao, S. Song, J. T. Sun, J. Pan, X. Ren, C. Li, E. Okunishi, Y. Q. Wang, E. Wang, E. 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; b) M. Wang, T. J. Ko, M. S. Shawkat, S. S. Han, E. Okogbue, H. S. Chung, T. S. Bae, S. Sattar, J. Gil, C. Noh, K. H. Oh, Y. Jung, J. A. Larsson, Y. Jung, ACS Appl. Mater. Interfaces 2020, 12, 10839.

[10] M. Yan, E. Wang, X. Zhou, G. Zhang, H. Zhang, K. Zhang, W. Yao, N. Lu, S. Yang, S. Wu, T. Yoshikawa, K. Miyamoto, T. Okuda, Y. Wu, P. Yu, W. Duan, S. Zhou, 2D Mater. 2017, 4, 045015.

[11] a) Z. Wang, Q. Li, F. Besenbacher, M. Dong, Adv. Mater. 2016, 28, 10224; b) H. Ma, P. Chen, B. Li, J. Li, R. Ai, Z. Zhang, G. Sun, K. Yao, Z. Lin, B. Zhao, R. Wu, X. Tang, X. Duan, X. Duan, Nano Lett. 2018, 18, 3523.

[12] M. Bosnar, V. Caciuc, N. Atodiresei, I. Lontărić, S. Blügel, Phys. Rev. B 2020, 102, 115427.

[13] a) G. Anemone, P. Casado Aguilar, M. Garnica, F. Calleja, A. Al Taleb, C.-N. Kuo, C. S. Lue, A. Politano, A. L. Vázquez de Parga, G. Benedek, D. Farias, R. Miranda,npj 2D Mater. Appl. 2021, 5, 25; b) S. Nappini, D. W. Boukhvalov, G. D’Olimpio, L. Zhang, B. Ghosh, C. N. Kuo, H. Zhu, J. Cheng, M. Nardone, L. Ottaviano, D. Mondal, R. Edla, J. Fuji, C. S. Lue, I. Vobornik, J. A. Yarmoff, A. Agarwal, L. Wang, L. Zhang, F. Bondino, A. Politano, Adv. Funct. Mater. 2020, 30, 2000915; c) L. Zhang, Z. Chen, K. Zhang, L. Wang, H. Xu, L. Han, W. Guo, Y. Yang, C. N. Kuo, C. S. Lue, D. Mondal, J. Fuji, I. Vobornik, B. Ghosh, A. Agarwal, H. Xing, X. Chen, A. Politano, W. Lu, Nat. Commun. 2021, 12, 1584; d) C. Guo, G. Chen, D. Wei, L. Zhang, Z. Chen, W. Guo, H. Xu, C.-N. Kuo, C. S. Lue, X. Bo, X. Wan, L. Wang, A. Politano, X. Chen, W. Lu, Sci. Adv. 2020, 6, eabb6500.

[14] F. Giorgianni, E. Chiadroni, A. Rovere, M. Cestelli-Guidi, A. Perucchi, M. Bellaveglia, M. Castellano, D. Di Giovenale, G. Di Pirro, M. Ferrario, R. Pompili, C. Vaccarezza, F. Villa, A. Cianchi, A. Mostacci, M. Petrarca, M. Brahlek, N. Koirala, S. Oh, S. Lupi, Nat. Commun. 2016, 7, 11421.