Kitkaite NiTeSe, an Ambient-Stable Layered Dirac Semimetal with Low-Energy Type-II Fermions with Application Capabilities in Spintronics and Optoelectronics

Ivana Vobornik,* Anan Bari Sarkar, Libo Zhang, Danil W. Boukhvalov, Barun Ghosh, Lesia Pilai, Chia-Nung Kuo, Debasish Mondal, Jun Fujii, Chin Shan Lue, Mykhailo Vorokhta, Huaizhong Xing, Lin Wang,* Amit Agarwal,* and Antonio Politano*

The emergence of Dirac semimetals has stimulated growing attention, owing to the considerable technological potential arising from their peculiar exotic quantum transport related to their nontrivial topological states. Especially, materials showing type-II Dirac fermions afford novel device functionalities enabled by anisotropic optical and magnetotransport properties. Nevertheless, real technological implementation has remained elusive so far. Definitely, in most Dirac semimetals, the Dirac point lies deep below the Fermi level, limiting technological exploitation. Here, it is shown that kitkaite (NiTeSe) represents an ideal platform for type-II Dirac fermiology based on spin-resolved angle-resolved photoemission spectroscopy and density functional theory. Precisely, the existence of type-II bulk Dirac fermions is discovered in NiTeSe around the Fermi level and the presence of topological surface states with strong ($\approx 50\%$) spin polarization. By means of surface-science experiments in near-ambient pressure conditions, chemical inertness towards ambient gases (oxygen and water) is also demonstrated. Correspondingly, NiTeSe-based devices without encapsulation afford long-term efficiency, as demonstrated by the direct implementation of a NiTeSe-based microwave receiver with a room-temperature photocurrent of 2.8 $\mu$A at 28 GHz and more than two orders of magnitude linear dynamic range. The findings are essential to bringing to fruition type-II Dirac fermions in photonics, spintronics, and optoelectronics.

1. Introduction

The unusual properties of relativistic quasiparticles in Dirac and Weyl semimetals have generated considerable interest in recent years,[3] due to their high technological capabilities and for exploration of novel fundamental physics. More recently, the focus of the field has partially moved towards tilted Dirac/Weyl systems, which break the Lorentz symmetry and have no analog in quantum field theory. Depending on the degree of the tilt, materials can be classified as type-I or type-II Dirac/Weyl systems.[2] In type-I Dirac and Weyl semimetals, massless Dirac fermions with asymmetric linear dispersions are expected at the isolated Dirac or Weyl point. Type-II Dirac/Weyl fermions emerge at the topologically protected band touching points of the electron and hole pockets, and they show highly tilted Dirac cones along certain momentum directions.[2b] Type-II Dirac semimetals can be tuned to a Weyl semimetal[3] or topological crystalline insulator[4] when the time-reversal symmetry or the crystal symmetry is broken. Accordingly, they are ideal candidates for investigating topological phase transitions and potential device applications.

Recently, the transition-metal dichalcogenides (TMDs) TMX$_2$ (TM = palladium (Pd), platinum (Pt); X = tellurium (Te), selenium (Se)) were proposed to host type-II Dirac fermions.[5] However, the Dirac...
points reported in these materials are located deeply below the Fermi level, with a Dirac point energy ($E_D$) of 0.6 eV in PdTe$_2$,[5a] 0.8 eV in PtTe$_2$,[5b] and 1.2 eV in PtSe$_2$.[5c] The Dirac node far from the Fermi level smears out the signature of relativistic particles and the observed physical properties, such as transport, are mainly dominated by the nonrelativistic carriers.[8] On the other hand, in NiTe$_2$, the Dirac point is above the Fermi level (20 meV), corresponding to unoccupied electronic states.[9]

Here, by means of spin-polarized angle-resolved photoemission spectroscopy (spin-ARPES) and density functional theory (DFT), we demonstrate the existence of type-II bulk Dirac fermions in NiTeSe, with the energy of the Dirac point slightly below the Fermi level ($E_D = -0.23$ eV). Additionally, our surface-science investigations in near-ambient pressure conditions demonstrate the ambient stability of the NiTeSe surface. These findings make NiTeSe an excellent candidate for technological applications without the need for any encapsulation procedure. To validate NiTeSe-based optoelectronic applications, we fabricated an ambient-stable NiTeSe photodetector with an ultrafast response by integrating only a bow-tie-type antenna under millimeter-wave illumination. Definitely, the NiTeSe-based device exhibited improved performance compared to similar ones based on graphene, black phosphorus, topological insulators, and van der Waals semiconductors.

## 2. Results and Discussion

### 2.1. Band Structure and Spin Polarization

Kitkaita (NiTeSe) is a relatively unexplored natural mineral, observed in carbonate-bearing veinlets in Kuusamo, Finland.[10] NiTeSe crystallizes in the trigonal space group 164 (P-3m1). The crystal structure (Figure 1a,b) consists of individual layers held together by the weak interlayer van der Waals bonds. Specifically, the crystal structure can be depicted as a combination of the IT-NiTe$_2$ and IT-NiSe$_2$ structures, where the Ni atom occupies the 1a-Wycoff site and the 2d-Wycoff site is shared equally by the Se and Te atoms. The resultant point group is $D_{3d}$, which hosts an inversion center, a threefold rotation, along with three mirror planes.

Single-crystal samples of NiTeSe were grown by the slow cooling method, described in the Experimental Section. The Raman spectrum is dominated by an intense $E_g$ mode at 92 cm$^{-1}$ (Figure 1c, see Section S6, Supporting Information, for details regarding its assignment). Samples show an excellent stoichiometry and crystalline order (Figure 1d,e). Furthermore, no contaminants are present in the as-cleaved NiTeSe (see X-ray photoemission spectroscopy, X-ray photoelectron spectroscopy (XPS), survey in Figure S1, Supporting Information). The room temperature X-ray diffraction (XRD) pattern (Figure 1d) with Cu-K$_\alpha$ radiation shows only the (00l) Bragg peaks, which indicates that the measured plane surface of the crystal is the ab-plane. The low-energy electron diffraction (LEED) pattern in Figure 1e indicates that the cleaved surface has trigonal symmetry, consistent with the $D_{3d}$ point group.

Our ab initio calculations reveal the metallic nature of NiTeSe with multiple bands crossing the Fermi level, with evident analogies with respect to the case of NiTe$_2$.[9b] Specifically, similar to NiTe$_2$, NiTeSe displays the highly tilted type-II Dirac-like band crossing (highlighted in Figure 2a) along the $\Gamma$-A high symmetry direction. Interestingly, in contrast with the parent compounds PdTe$_2$, PtTe$_2$, PtSe$_2$, where the Dirac cone is buried below the Fermi level,[5a] in NiTeSe the Dirac point is in close vicinity (within $-0.23$ eV) of the Fermi level. Remarkably, contrarily to NiTe$_2$, the Dirac cone in NiTeSe is below the Fermi level, with superior applications capabilities for applications related to excitations of Dirac-cone electrons in occupied electronic states (e.g., plasmonics).

We find that, apart from the type-II Dirac crossing, NiTeSe hosts multiple band inversions in the Te-p and Se-p orbital manifold within the $-2$ to $+2$ eV energy range around the Fermi level. These series of inverted bands lead to exotic spin-polarized surface states over a wide range of energy. We demonstrate these surface states in Figure 2d,e along the $\Gamma$-M and $\Gamma$-K directions of the hexagonal surface Brillouin zone, along with the corresponding calculated surface band structure.

Along the $\Gamma$-M direction, there are three prominent features of the surface states in the investigated range of the binding energy ($E_{\text{bind}}$) ($0$--$2$ eV), that is, i) a parabolic electron pocket-like surface state adjacent to the Fermi level (indicated by the black arrow in Figure 2d), ii) a shoulder-like surface feature within 0.5 to 1.0 eV (red arrow in Figure 2d), and iii) a Dirac-like linear band crossing near 1.4 eV (white arrow in Figure 2d). All these surface states are well reproduced by our DFT calculations. A careful analysis of the conduction-band states reveals that the parabolic surface state pockets (black arrow in Figure 2d) near the Fermi level arise due to the band inversion in the upper conduction band. Considering that the corresponding Dirac crossing is located within unoccupied states (and thus cannot be measured in ARPES), the linear nature of these surface states is lost on moving away from the $\Gamma$ point, and they appear as parabolic electron pockets. Interestingly, these parabolic electron pockets are absent along the $\Gamma$-K direction, whereas the shoulder-like surface state and the Dirac crossing are clearly visible.

---

D. W. Boukhvalov  
College of Science  
Institute of Materials Physics and Chemistry  
Nanjing Forestry University  
Nanjing 210037, P. R. China

A. Politano  
INSTM and Department of Physical and Chemical Sciences  
University of L’Aquila  
via Vetoio, L’Aquila, AQ 67100, Italy  
E-mail: antonio.politano@univaq.it

A. Politano  
CNR-IMM Istituto per la Microelettronica e Microsistemi  
VIII strada 5, Catania I-95121, Italy

C.-N. Kuo, C. S. Lue  
1 Ta-Hsueh Road, Tainan 70101, Taiwan

D. W. Boukhvalov  
Theoretical Physics and Applied Mathematics Department  
Ural Federal University  
Mira Street 19, Ekaterinburg 620002, Russia

L. Piliai, M. Vorokhta  
Department of Surface and Plasma Science Prague  
Charles University  
V Holesovická 2, Prague 8, Prague 18000, Czech Republic

C.-N. Kuo, C. S. Lue  
Department of Physics  
National Cheng Kung University  
1 Ta-Hsueh Road, Tainan 70101, Taiwan

A. Politano  
INSTM and Department of Physical and Chemical Sciences  
University of L’Aquila  
via Vetoio, L’Aquila, AQ 67100, Italy  
E-mail: antonio.politano@univaq.it

A. Politano  
CNR-IMM Istituto per la Microelettronica e Microsistemi  
VIII strada 5, Catania I-95121, Italy
Owing to their topological nature, all these surface states are expected to show spin-momentum locking features. To provide an experimental validation, we carried out spin-polarized ARPES measurements. The spin-polarized ARPES results in Figure 3a clearly demonstrate the presence of large (up to 50%) spin polarization in these surface states. The value of the measured spin polarization is comparable to that observed in the parental compound NiTe2.[9a] The measured spin texture of the band dispersion is well reproduced by DFT calculations. Explicitly, the spin momentum locking of the surface state with the crossing at 1.4 eV is evident in both experiments and calculations along Γ-M (Figure 3a) and the Γ-K (Figure 3b) directions, respectively. Additionally, at the Fermi energy, the parabolic topological states with the opposite spin polarization have opposite velocities. Evidently, this finding has relevant consequences for spintronic applications. For example, in a device fabricated in such a way that the Γ-M direction is aligned along the channel, a positive bias would induce charge current along the channel, with spin polarization along the perpendicular direction, while the bias current in the opposite direction will show opposite spin polarization.

Previously, low-energy type-II Dirac fermions were claimed for Ir1-xPtxTe2, that is, Pt-doped IrTe2.[11] By using ARPES, it has been shown that the type-II Dirac fermions can be tuned through Pt doping, with Dirac point lying close to the Fermi level for x = 0.1.[12] However, Ir0.9Pt0.1Te2 does not exist in nature, while NiTeSe is a natural mineral (kitkaite)[10] enabling superior reproducibility and stability. Furthermore, by considering the cost of raw materials,[13] NiTeSe is hugely more sustainable for technology transfer than Ir0.9Pt0.1Te2, with a reduction of costs by even ≈400 times, owing to the relatively wide abundance of Ni on Earth compared to that one of precious and rare Ir and Pt elements.

For the sake of completeness, we point out that monolayer NiTeSe has an indirect band gap, as shown in Figure S6, Supporting Information.

2.2. Surface Chemical Reactivity and Ambient Stability

An important requirement to assess possible technological exploitation of type-II Dirac fermions in NiTeSe is...
Figure 2. a) Bulk band structure of NiTeSe including spin-orbit coupling. The type-II Dirac point along the Γ-A direction is highlighted in the red circle. b) The measured ARPES map n along the Γ-A direction (measured by varying the incident photon energy) with the red-dashed lines highlighting the tilted Dirac crossing. c) The bulk and the projected surface Brillouin zone of NiTeSe. d,e) The experimental ARPES map (right panel) and the theoretical spectral function (left panel) along the (d) M-Γ-M and the (e) K-Γ-K directions of the (001) surface Brillouin zone.

Figure 3. Spin-resolved surface states along the a) M-Γ-M and the b) K-Γ-K direction of the (001) surface Brillouin zone. The left and right panels show the spin polarization map from the DFT calculations and the experimental spin-ARPES maps, respectively. In the left panel of (a), the spin polarization (spin component perpendicular to the Γ-M direction) of the parabolic surface states near the Fermi energy is clearly noticeable, congruently with the measured spin polarization in the right panel. The helical spin polarization of the surface Dirac point located at Energy = −1.4 eV is evident in all four panels.
related to its ambient stability. Accordingly, we followed the evolution of core levels of NiTeSe upon exposure of its surface to humid and oxidative environments by means of XPS experiments in near-ambient pressure conditions (NAP-XPS). At first, the sample was subsequently exposed to 1 mbar of H₂O and O₂ for ≈1 h while collecting XPS spectra. Such an exposure corresponds to a maximum dose of 3 × 10⁹ L (1 L = 1.33 × 10⁻⁶ mbar s). Ni-2p core levels for as-cleaved NiTeSe and the same surface exposed to 1 mbar of H₂O and O₂ are reported in Figure 4a. Specifically, the E_{bin} for the Ni-2p₃/₂ component of the Ni 2p spin-orbit split doublet (Figure 4a) was recorded at 853.6 eV from the as-cleaved surface, with a satellite at 860.4 eV, as in other Ni-containing compounds. The spectral features remained practically unchanged upon H₂O and subsequent O₂ exposures. Correspondingly, Te-3d⁵/₂ (Figure 4b) core level for as-cleaved NiTeSe shows a single peak at about 572.8 eV. The observed E_{bin} of this component is consistent with previous reports for Te-containing alloys. The Te-3d spectrum remains unchanged after H₂O exposure, while O₂ dosage induces partial oxidation of Te with the appearance of a new component at E_{bin} = 575.9 eV, which can be ascribed to the formation of TeO₂ layer and a reduction of the NiTeSe peak intensity. However, the relative intensity of the TeO₂ peak is only about 3% in respect to the total Te signal, thus

**Figure 4.** a) Ni-2p₃/₂, b) Te-3d⁵/₂, and c) Se-3d core-level spectra collected from as-cleaved NiTeSe (brown curves) and from the same surface while being exposed to 1 mbar of H₂O (blue curves) and O₂ (green curves), up to a total dose of 3 × 10⁹ L. d) Ni-2p₃/₂, e) Te-3d⁵/₂, and f) Se-3d core-level spectra collected from NiTeSe after air exposure for 30 min (blue curves), 24 h (green curves), and 60 days (red curves). The incident photon energy is 1486 eV (Al Kα line) and the spectra are normalized to get the same area.
indicating relatively marginal oxidation of the surface. Finally, the corresponding Se-3d XPS spectra (Figure 4c) show two spin-orbit split doublets. The predominant doublet at $E_{\text{bin}}$ of 53.6 (J = 5/2) and 54.4 (J = 3/2) eV are assigned to Se-Ni-Te bonds, while the weak doublet at 54.2 (J = 5/2) and 55.0 (J = 3/2) eV belongs to Se-Ni-Se bonds.

With the aim to assess its ambient stability, the aging phenomena of as-cleaved NiTeSe were also followed by monitoring the evolution of Ni-2p$_{3/2}$ (Figure 4d), Te-3d$_{5/2}$ (Figure 4e), and Se-3d (Figure 4f) core levels upon exposure to ambient atmosphere. Quantitative analysis of core levels (see Section S2, Supporting Information, for more details) revealed the formation of passivation oxide skin of TeO$_2$ with a thickness of $\approx 7$ Å, formed after only 30 min of air exposure. The intensity of the components of oxide species gradually increases from $\approx 15\%$ (after 30 min in air) to $\approx 30\%$ (after 24 h in air) and to $\approx 50\%$ (60 days in air) of the total spectral area, with a saturation thickness of $\approx 13$ Å. Correspondingly, the Ni-2p$_{3/2}$ core level (Figure 4d) exhibited the NiO-related multiplet-split components at $E_{\text{bin}}$ of 853.7 and 855.4 eV with the satellite at 861.3 eV.[18] The relative intensity of the NiO signal was $\approx 35\%$ after 30 min in the atmosphere. It reaches 73% and 82% of the total Ni-2p$_{3/2}$ spectral area when storage in air is prolonged up to 24 h and to 60 days, respectively. The analysis of the O-1s core-level spectra (Figure S3, Supporting Information) further supports the proposed aging mechanism. O-1s showed two spectral contributions originating from NiO ($E_{\text{bin}} = 529.6$ eV) and TeO$_2$ ($E_{\text{bin}} = 532.0$ eV), whose intensity increased with the dosage. For the sake of completeness, we point out that the absence of spectral changes in Se-3d after only 30 min of air exposure. The intensity of the components of oxide species gradually increases from $\approx 15\%$ (after 30 min in air) to $\approx 30\%$ (after 24 h in air) and to $\approx 50\%$ (60 days in air) of the total spectral area, with a saturation thickness of $\approx 13$ Å. Correspondingly, the Ni-2p$_{3/2}$ core level (Figure 4d) exhibited the NiO-related multiplet-split components at $E_{\text{bin}}$ of 853.7 and 855.4 eV with the satellite at 861.3 eV.[18] The relative intensity of the NiO signal was $\approx 35\%$ after 30 min in the atmosphere. It reaches 73% and 82% of the total Ni-2p$_{3/2}$ spectral area when storage in air is prolonged up to 24 h and to 60 days, respectively.

2.3. Device Implementation

To assess the suitability of NiTeSe for technology transfer, we used exfoliated flakes of NiTeSe (Figure 5b) to fabricate photodetectors with uncapped active channels. The good stability and high-rate operation of NiTeSe-based devices were exploited to engineer a microwave receiver, whose relevance is associated to the next-generation six-generation wireless communication technology, mainly used in the field of national defense and civil communications.[19] We devised high-frequency photodetectors, depicted in Figure 5a, with metal-NiTeSe-metal configuration, within a bow-tie-type antenna including sub-wavelength channel spacing between two similar metallic contacts (see Experimental Section for details on fabrication). An optical micrograph of the device is shown in Figure 5a, in which the bow-tie-type antenna can accumulate more charges and enhance the microwave electric-field intensity along the direction of 6µm horizontal channel.[20]

The linear current-voltage curve in the dark indicates a perfect ohmic characteristic (Figure S5a, Supporting Information), consistent with the semimetal nature of NiTeSe in ARPES spectra in Figure 2. The current-voltage characteristics of the studied device under the ON/OFF modulated illumination of low-energy photons (40 GHz carrier-wave frequency) is shown in Figure S5a, Supporting Information. The NiTeSe-based device enabled highly efficient detection of microwave photons by directly converting the electromagnetic energy into a DC current, showing a large photocurrent ($I_{\text{ph}} = I_{\text{light}} - I_{\text{dark}}$) (inset of Figure 5c). To validate the detection performance of the NiTeSe devices, we measured the spectral response characteristics and response time in the 20–40 GHz range at a bias of 0.01 V, showing a photoresponse in the µA range in the microwave band (Figure 5d). Upon absorption of low-energy photons, the transition from valence to the conduction band is forbidden, owing to the Pauli-blockade principle. However, due to the presence of strongly anisotropic dispersion in the type-II Dirac semimetal NiTeSe (Figure 2), free carrier intraband transition at the Fermi surface of tilted Dirac cones is feasible upon irradiation in the microwave range (see the inset of Figure 5d).[21] Correspondingly, non-equilibrium carriers can be excited when the surface carriers couple strongly with the localized field in the channel by incident radiation. The non-equilibrium carriers under electrical bias are diffused unilaterally from one side to another side of the channel, generating a net photoconductive current. The time-resolved photoresponse at different bias voltages is well preserved with a good signal-to-noise ratio (Figure S5b, Supporting Information), indicating that our device is suited for the detection of microwaves.

The response time is an important figure of merit in the assessment of the performance of the photodetector. Specifically, the response time (Figure 5e), defined as the time measured from 10% to 90% on the rising edge (or 90% to 10% on the falling edge) of the photocurrent, is about 2 µs (5 µs), thus indicating an excellent performance in photoelectric detection and proving the real-time imaging capability. The response time of the NiTeSe-based device is compared with the long-wavelength detectors based on 2D materials and the commercial state-of-the-art long-wavelength detectors (Figure 5f), including SnSe$_2$ (46 µs), Bi$_2$Se$_3$ (60 µs), PtTe$_2$ (17 µs), Bi$_2$Te$_3$Se$_2$ (8 µs), graphene (22.26) (2 µs), black phosphorus (BP) (27) (15 µs), MoS$_2$ (26e) (6 s), and commercial bolometers (28) (1 ms). The response time of devices based on 2D materials is often limited by the intrinsic properties of the materials, such as the lifetime and transit time. On the other hand, the commercial bolometers are limited by the operating temperature of 4.2K (liquid helium), which greatly increased the cost.

For the sake of comparison, we fabricated the same device with BP and graphene. Figure 5g shows the photocurrent value in NiTeSe as a function of the incident power under direct comparison with similar devices fabricated with BP and graphene, exhibiting a larger linear dynamic range in the NiTeSe device. With a maximum microwave output power density of the microwave source of 2.5 mW/cm$^2$, the NiTeSe-based device has a maximum power of 2.5 mW cm$^{-2}$. The minimum power density achievable is 5.4 µW cm$^{-2}$. 
For the case of BP, the output power density ranges from a minimum of $20 \, \mu W \, cm^{-2}$ up to a maximum of $1.1 \, mW \, cm^{-2}$, while for graphene, a $15 \, \mu W \, cm^{-2}$–$1.6 \, mW \, cm^{-2}$ range is achieved. Accordingly, we can infer that our NiTeSe-based device exhibits an overall improved performance than similar devices fabricated with BP and graphene.

In the prospect of large-scale technological exploitation, the stability of device efficiency is crucial. Notably, the response time of the devised long-wavelength photodetector remained practically unchanged even after long-time storage (one month) in ambient atmosphere without any encapsulation (Figure 5c,h and Figure S5c, Supporting Information). The output photo-signal of the device, acquired with a high-speed sampling oscilloscope, showed a nearly constant rise/fall time. Accordingly, the excellent stability of our device, which does not display any decay even after prolonged air exposure, is fully validated.

3. Conclusions

Based on experiments and theory, we demonstrated the suitability of kitkaite (NiTeSe) for type-II Dirac fermiology, owing to the existence of type-II bulk Dirac fermions in NiTeSe just below the Fermi level. We show that in addition to the type-II Dirac crossing, NiTeSe hosts multiple band inversions above and below the Fermi level. This series of inverted bands lead to exotic spin-polarized surface states over a wide range of energy.
Remarkably, our surface-science experiments in near-ambient pressure conditions demonstrate that the NiTeSe surface is chemically inert towards ambient gases (oxygen and water). Combined with the low cost of constituting elements, these findings point NiSeTe as a promising candidate for exploring optoelectronic and spintronic applications.

We demonstrate the capabilities of NiSeTe for optoelectronics explicitly, by implementing a NiTeSe-based microwave detector with microsecond response speed and microampere magnitude photo-signal. The comparison with graphene, topological insulators, van der Waals semiconductors, and commercial bolometers clarifies that only graphene enables the same response speed, while all other systems have a much slower response time.

Our device shows a negligible deterioration in the photocurrent and in the response time over a timescale of 1 month without encapsulation. Room-temperature photocurrent reaches 2.8 μA at 28 GHz and the linear dynamic range is over more than two orders of magnitude. Our high-performance NiTeSe-based device is promising for ultrafast, stable, and highly sensitive long-wavelength photodetection and applications as a suitable component of the future detector array for fast imaging.

Accordingly, our results are crucial to bringing to fruition type-II Dirac fermions in photonics, spintronics, and optoelectronics.

4. Experimental Section

Single-Crystal Growth: Single crystals of NiTeSe were prepared using the slow cooling method. High-purity Ni (99.99%) sheet, Se powder (99.999%), and Te powder (99.9999%) were mixed in the ratio of 1:1:1 and sealed under vacuum in a cone-shaped quartz tube. The quartz tube was heated to 1050 °C, dwelled for 12 h, and slowly cooled at a rate of 2 °C h⁻¹ to 650 °C. The planar crystals with dimensions of 4 × 4 × 1 mm³ can be mechanically separated from the melts.

Theoretical Methods: All the DFT-based ab initio calculations were performed using the VASP package. A plane-wave basis set with a kinetic energy cutoff of 500 eV was used. The exchange-correlation part of pseudopotential was incorporated within the generalized gradient approximation scheme. A Monkhorst-pack k-grid of 12 × 12 × 8 was used for performing the Brillouin zone integration. Tight binding parameterizations were done using the Wannier90 code via the VASP2WANNIER interface. The electronic properties of NiTeSe were calculated using the virtual crystal approximation scheme by mixing the NiTe₂ and NiSe₂ tight binding hopping parameters in equal ratios. The semi-infinite surface states were computed within the iterative gradient approximation scheme.

A Monkhorst-pack k-grid of 12 × 12 × 8 was used for performing the Brillouin zone integration. Tight binding parameterizations were done using the Wannier90 code via the VASP2WANNIER interface. The electronic properties of NiTeSe were calculated using the virtual crystal approximation scheme by mixing the NiTe₂ and NiSe₂ tight binding hopping parameters in equal ratios. The semi-infinite surface states were computed within the iterative Green’s function formalism using the WannierTools package.

Spin-ARPES: Spin-ARPES experiments were carried out on the APE-LE beamline at Eletra synchrotron, described in Ref. [33]. Energy and angular resolution were 15 meV and 0.2°, respectively.

Near-Ambient Pressure XPS: Both UHV and NAP-XPS studies were performed at Surface Physics Laboratory in Prague using a custom-built (SPECS Surface Nano Analysis GmbH) XPS spectrometer equipped with a high-pressure (NAP) cell, monochromatized Al Kα X-ray source, and hemispherical electron analyzer Phoibos 3500 (see Ref. [34] for a description of the NAP-XPS equipment). The as-cleaved sample was loaded into the NAP cell and filled with 1 mbar of O₂ for approximately one hour. During this time the XPS spectra were collected in the presence of O₂. The same workflow at the same pressure was used for the H₂O exposure. The XPS measurements on aging phenomena of NiTeSe were performed by simply taking the sample from the spectrometer, bringing it into contact with air for a required time, and further measuring in UHV.

Device Fabrication: NiTeSe flakes were mechanically exfoliated with adhesive tape from bulk NiTeSe crystal and transferred onto a high-resistance silicon wafer capped with a thin oxide layer of SiO₂ (300 nm) in ambient environment. The bow-tie-type antenna electrodes were patterned by electron beam lithography, followed by electron-beam evaporation of 5 nm Cr/90 nm Au and lift-off.

Photocurrent Measurements: The current-voltage characteristic curve of the photodetector was measured by B2913a Semiconductor Analyzer using variable voltage mode at room temperature. For photoresponse measurements, the frequency was tuned up to 40 GHz, connected to a microwave source (Agilent E8257D) with an electrical modulation, and detected the closed-circuit photo-signal by using a preamplifier, a lock-in amplifier, and a high-speed sampling oscilloscope. The power flux intensity was calibrated by a TK100 power meter (2.5 mW cm⁻² at 0.04 THz). The data of response time were obtained directly from the high-speed sampling oscilloscope.

Supporting Information

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

Acknowledgements

I.V., A.B.S., and L.Z. contributed equally to this work. L.W. acknowledged support from the State Key Program for Basic Research of China (No. 2017YFA0303500, 2018YFA0306204), Shanghai Municipal Science and Technology Major Project (Grant No. 2019SHZDZX01), and the Science and Technology Commission of Shanghai Municipality (21ZR1473800). A.P. thanks CERIC-ERIC for the access to the NAP-XPS facility. D.W.B. acknowledged support from the Ministry of Science and Higher Education of the Russian Federation (through the basic part of the government mandate, Project No. FEUZ-2020-0060) and Jiangsu Innovative and Entrepreneurial Talents Project. This work has been partly performed in the framework of the nanoscience foundry and fine analysis (NFFA-MUR Italy Progetti Internazionali) facility. A.B., B.G., and A.A. acknowledge funding from Science and Engineering Research Board (SERB) and Department of Science and Technology (DST), government of India. A.A. thanks the HPC facility at IIT Kanpur for computational resources.

Open access funding provided by Università degli Studi dell’Aquila within the CRUI-CARE Agreement.

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

Dirac fermions, density functional theory calculations, device implementation, surface science, topological materials

Received: June 24, 2021
Revised: August 23, 2021
Published online: September 27, 2021
