#### Section SI. Computational Methods

In this study, the electronic structures of Pnma (no. 62) Nb<sub>3</sub>GeTe<sub>6</sub> were calculated using density functional theory, within the VASP code<sup>1</sup>. We also use the projector augmented wave (PAW)<sup>2</sup> method to deal with the interaction between the ion cores and valence electrons. The Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA)<sup>3</sup> was selected to describe the exchange and correlation functionals. For the Nb<sub>3</sub>GeTe<sub>6</sub> bulk, a plane-wave basis set cut-off of 500 eV and a Monkhorst-Pack special  $3 \times 8 \times 4$  k-point mesh were used in the Brillouin zone (BZ) integration. For the Nb<sub>3</sub>GeTe<sub>6</sub> surface, the Monkhorst-Pack special  $4 \times 8 \times 1$  k-point mesh was used in the surface BZ. The unit cell was optimized until the force and total energy were less than 0.005 eV/Å and  $1 \times 10^{-7}$  eV, respectively.

The electronic transport coefficients were calculated in the framework of the Boltzmann transport equation (BTE) within the constant relaxation time approximation (CRTA), as implemented in BoltzTraP<sup>4</sup>. The electronic transport coefficients can be derived from the calculated electronic structure, and the key point is to find the so-called transport distribution (TD) by solving the BTE. Then, the Seebeck coefficient and electrical conductivity can be calculated in term of TD. Within CRTA, the Seebeck coefficient can be directly evaluated from the band structure, while the electrical conductivity is calculated with relaxation time  $\tau$  as a constant. The phonon dispersion of unit cell of 2D Nb<sub>3</sub>GeTe<sub>6</sub> monolayer was checked based on density functional perturbation theory (DFPT).

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## Section SII. Structural Models

With the help of first-principles, the crystal structure of bulk Nb<sub>3</sub>GeTe<sub>6</sub> was totally relaxed, and the optimized lattice parameters were a = 6.465 Å, b = 11.558 Å, and c = 14.219Å, respectively. We should point out that the van der Waals corrections were considered according to the methods of Klimeš et al.<sup>5</sup> The lattice parameters obtained experimentally by Li and Carroll<sup>6</sup> were a = 6.435 Å, b = 11.524 Å, and c = 13.915Å, respectively. The results for the optimized lattice parameters in this current work are in good agreement with the experimental values listed above<sup>6</sup>.

Different views of crystal structure of this bulk can be observed in Fig. S1(a) and S1(b). Bulk Nb<sub>3</sub>GeTe<sub>6</sub> contains 40 atoms, i.e., 24 Te atoms, 12 Nb atoms, and 4 Ge atoms, respectively. In this unit cell, Te atoms occupy the 8d (-0.35454, 0.62533, 0.18211), 8d (-0.28409, 0.62616, 0.84054), and 8d (0.13462, 0.62924, 0.00670) sites, Nb atoms occupy the 4c (0.32719, 0.75, 0.16607), 4c (-0.19778, 0.75, 0.03285), and 4c (0.42522, 0.75, 0.92486) sites, and Ge atoms occupy the 4c (0.42522, 0.75, 0.92486) sites, respectively.

As shown in Fig. S1(c) and S1(d), different views are presented of Nb<sub>3</sub>GeTe<sub>6</sub> monolayer with optimized lattice constants a = 6.54 Å and b = 11.587 Å. To break the periodic symmetry in the c direction, for this monolayer, a vacuum layer of 15 Å in the c direction was added in this work.

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Fig. S1. (a) and (b) Different views of the crystal structure of bulk  $Nb_3GeTe_6$ ; (c) and (d) Different views of the crystal structure of monolayer  $Nb_3GeTe_6$ .

C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>22</sub>	C <sub>23</sub>	C <sub>33</sub>	C <sub>44</sub>	C <sub>55</sub>	C <sub>66</sub>
113.515	11.93	23.589	47.956	12.423	99.084	8.861	12.577	36.673

# Section SIII. Calculated elastic constants C<sub>ij</sub> (GPa)

Table S1. Calculated elastic constants of Pnma type Nb<sub>3</sub>GeTe<sub>6</sub> bulk.

The mechanical stability of this system can be evaluated by the following necessary conditions:

Criteria (i) C<sub>11</sub> > 0;.

Criteria (ii)  $C_{11} \times C_{22} > C_{12}^2$ ;

Criteria (iii)  $C_{11} \times C_{22} \times C_{33} + 2C_{12} \times C_{13} \times C_{23} - C_{11} \times C_{23}^2 - C_{22} \times C_{13}^2 - C_{33} \times C_{12}^2 > 0$ ;

Criteria (iv)  $C_{44} > 0$ ;.

Criteria (iv) C<sub>55</sub> > 0;.

Criteria (iv)  $C_{66} > 0$ .

From the calculated elastic constants (see Table S1), it is confirmed that bulk  $Nb_3GeTe_6$  fulfills all the above-mentioned conditions and thus is mechanically stable.





Fig. S2. Calculated orbital-resolved band structures of Pnma Nb<sub>3</sub>GeTe<sub>6</sub> bulk.

### Section SV. Symmetry analysis

#### 3D Nb<sub>3</sub>GeTe<sub>6</sub>

3D Nb<sub>3</sub>GeTe<sub>6</sub> has a Pnma space, the generators for it are: the inversion symmetry P, glide mirrors  $M_x ((x,y,z) \rightarrow (-x+1/2,y+1/2,z+1/2))$  and glide mirrors  $M_y ((x,y,z) \rightarrow (x+1/2,-y+1/2,z))$ . It also preserves time reversal symmetry T.

In R2 region, the nodal ring is accidental and protected by two independent symmetries, i.e.,  $M_x$  and PT symmetries. This nodal line will not maintain if the band inversion disappears due to this nodal line in R2 is formed by two bands at  $\Gamma$  point with band inversion.

In R1 region, each k point on S-R for 3D Nb<sub>3</sub>GeTe<sub>6</sub> is invariant under  $M_x$ , each Bloch state on this path can be chosen as the eigenstate  $|u\rangle$  of  $M_x$ . S-R is an invariant subspace of the combined anti-unitary  $M_yT$ . On this path, one has  $(M_yT)^2 = e^{ik_x} = -1$ , it means that there must exist a Kramer-like degeneracy oh this path. Furthermore, S-R is also the invariant subspace for  $M_{z'}M_x$ . The commutation between these two operators are  $M_xM_z = -e^{ik_x + ik_z}M_zM_x$ , that means  $\{M_{x'}M_z\} = 0$  on this path. Such that there is another double degeneracy on this path. Therefore, S-R is a fourfold degenerate path, degenerate states are  $\{|u\rangle, M_yT|u\rangle, M_z|u\rangle$ ,  $M_zM_yT|u\rangle$ . Hence, when SOC is ignored, there should be a fourfold degenerate nodal line in R1 region, which is in a good agreement with our DFT calculated results.

#### 3D Nb<sub>3</sub>GeTe<sub>6</sub> (with SOC)

For S-X path, it is the invariant subspace for  $S_z = PM_z:(-x + \frac{1}{2}, -y, z + 1/2)$ . We chose each Bloch state as the eigenstate  $|u\rangle$  of  $S_z$ . The eigenvalue is given by  $g_z = \pm i e^{ik_z/2}$ . As shown in the figure S3, at S  $(\pi, 0, \pi)$ ,  $g_x = \pm 1$ , each Kramers pair  $|u\rangle$  and T  $|u\rangle$  at S should have same  $g_x$ . However, at X  $(\pi, 0, 0)$ ,  $g_x = \pm i$  each  $|u\rangle$  and T  $|u\rangle$  at X should have opposite  $g_x$ . Therefore, a partner-switching from S to X will form a hourglass ban structure. Due to the presence of PT symmetry, every band is double degenerate, it is a Dirac like hourglass along S-X direction. The similar analysis also applies to the path S-R.



Figure S3: Schematic figure of the hourglass-like Dirac point along X-S path.

### Section SVI. Carrier relaxation time at 300K

We calculated the carrier relaxation time at 300K using the deformation potential theory (Phys. Rev. 1950, 80, 72–80.; Sci. Rep. 2016, 6, 19830.). For two-dimensional systems, the relaxation time is calculated as

$$\tau = \frac{\mathbf{h}^3 C_{2D}}{k_B T m_d^* E_l^2},$$

where  $C_{2D}$  is elastic modulus and can be determined by  $C_{2D} = \frac{1}{S_0} \frac{\partial^2 E}{\partial (\Delta l/l_0)^2}$ , a second order of the total energy with respect to deformation  $\Delta l/l_0$ , and  $S_0$  is the area of the unit cell. The factor  $E_1$  is DP constant, which is calculated as  $E_l = \frac{\partial E_{edge}}{\partial (\Delta l/l_0)}$ , the slop of the energies at the valence or conduction edges as a function of  $\Delta l/l_0$ . And  $m_d^*$  is the average effective mass and defined by  $m_d^* = \sqrt{m_{X-S}^* m_{\Gamma-X}^*}$ . Calculated results are listed in following table S2 and figure

S3.

Table S2 Calculated DP constant ( $E_1$ ), elastic modulus ( $C_{2D}$ ), effective mass, carrier mobility and relaxation time at 300 K.

E <sub>l</sub> (eV)	C <sub>2D</sub> (eVÅ <sup>-2</sup> )	$m_{X-S}^{*}(\mathbf{m_e})$	$m^*_{\Gamma-X}(\mathbf{m_e})$	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	τ (10 <sup>-14</sup> s)
5.44	11.12	4.39	1.59	11.08	2.76



Figure S4: (a) calculated total energy as a function of deformation  $\Delta l/l_0$ ; (b) Fermi-vacuum energy as a function of deformation  $\Delta l/l_0$ ;