Anomalous Dirac Plasmons in 1D Topological Electrides

Jianfeng Wang,1 Xuelei Sui,2,1 Shiwu Gao,1 Wenhui Duan,2,4 Feng Liu,3,4,6 and Bing Huang1,1

1Beijing Computational Science Research Center, Beijing 100193, China
2Department of Physics and State Key Laboratory of Low-Dimensional Quantum Physics, Tsinghua University, Beijing 100084, China
3Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA
4Collaborative Innovation Center of Quantum Matter, Beijing 100084, China

DOI: 10.1103/PhysRevLett.123.206402

The plasmon opens up the possibility to efficiently couple light and matter at subwavelength scales. In general, the plasmon frequency, intensity, and damping are dependent on the carrier density. These dependencies, however, are disadvantageous for stable functionalities of plasmons and render fundamentally a weak intensity at low frequency, especially for the Dirac plasmon (DP) widely studied in graphene. Here we demonstrate a new type of DP, emerging from a Dirac nodal-surface state, which can simultaneously exhibit a density-independent frequency, intensity, and damping. Remarkably, we predict the realization of anomalous DP (ADP) in 1D topological electrides, such as Ba3CrN3 and Sr3CrN3, by first-principles calculations. The ADPs in both systems have a density-independent frequency and high intensity, and their frequency can be tuned from terahertz to midinfrared by changing the excitation direction. Furthermore, the intrinsic weak electron-phonon coupling of anionic electrons in electrides affords an added advantage of low-phonon-assisted damping and hence a long lifetime of the ADPs. Our Letter paves the way to developing novel plasmonic and optoelectronic devices by combining topological physics with electrode materials.

© 2019 American Physical Society
FIG. 1. (a) Density dependences of plasmon frequency and intensity. (Green curve) The usual plasmon following a $\omega \sim n^\alpha$ scaling ($\alpha = 1/2, 1/3, 1/4$ for parabolic metals, DNP, and DNL semimetals, respectively). (Red curve) Our proposed ADP following the $\omega \sim n^0$ scaling. The brightness of the color indicates the intensity of the plasmon [15]. (b) (Left) Schematic plot for 1D electrode, where the orange channels denote the anionic electrons. (Inset) A band crossing of a single anionic plot for 1D electrides, where the orange channels denote the anionic electrons. (Right) The crossing points along the $k_z$ direction. (c) Schematic illustration of the phonon-assisted damping for the Dirac plasmon. The plasmon may enter the intraband Landau region and decay into electron-hole pairs via phonon scattering or by emitting a phonon. This damping pathway is naturally suppressed in electrides.

(i.e., 1D and 2D), have provided a platform to create novel DPs beyond graphene [16,17,43,44]. For a TSM, the “relativistic” effective mass of quasiparticles is $n$ dependent, as $m_r \propto n^{1/3}$ and $n^{1/2}$ for Dirac nodal point (DNP) and Dirac nodal line (DNL), respectively [15]. Consequently, the $n^{1/2}$ scaling in the classical plasmon frequency is partially offset by $m_r$, resulting in $\omega_{\text{DNP}} \sim n^{1/3}$ and $\omega_{\text{DNL}} \sim n^{1/4}$ for DNP and DNL, respectively [16,17,43]. Interestingly, we realize when the dimensionality of band crossing is further increased to 2D DNS [45,46], $m_r$ becomes proportional to $n$, to completely offset the $n^{1/2}$ scaling in the frequency. Consequently, the plasmon frequency of a DNS semimetal becomes independent of $n$, fundamentally different from all the known plasmons [see Fig. 1(a)].

Using the dynamical dielectric function based on random phase approximation (RPA) [15] and the Lindhard function of Dirac systems [16], one can obtain the noninteracting irreducible polarizability of DNS in the long-wavelength limit as

$$\Pi(q, \omega) = \frac{g S v_F^2 q^2 \cos^2 \theta}{4 \pi^2 \omega^2} + O(q^4/\omega^4),$$

where $g$ is the degeneracy factor, $S$ is the DNS area, $v_F$ is the Fermi velocity along the normal direction of DNS, and $\theta$ is the angle between $q$ and the normal direction of DNS.

One then deduces the long-wavelength plasmon frequency as [15]

$$\hbar \omega_{\text{DNS}} = \sqrt{\frac{g e^2 S h v_F \cos^2 \theta}{\pi^2 k}} + O(q^2).$$

As shown by the red line in Fig. 1(a), the long-wavelength plasmon of DNS exactly follows $\omega_{\text{DNS}} \sim n^0$. Moreover, the DNS has a constant high DOS near $E_F$ [15], which produces a constant strong plasmon intensity. Consequently, an ADP has an inherently $n$-independent frequency and high intensity. As indicated by Eq. (2), the frequency of ADP depends solely on the direction of plasmon excitation (a $| \cos \theta |$ function), providing a simple way to continuously tune its frequency. In addition, the $n$-independent DOS makes the phonon-assisted damping of ADP immune to carrier density, as discussed later.

Though the DNS states were proposed theoretically [45,46], they have not been observed in experiments due to the lack of ideal materials. Here we predict that the DNS states and ADPs can be realized in 1D topological electrides. Electrides are known as special ionic solids, in which excess electrons trapped in the cavities serve as anions [47–50]. They are classified into 0D, 1D, and 2D electrides according to the dimensionality of confinement [51]. The anionic electrons with low work function may enter the intraband Landau region and decay into electron-hole pairs via phonon scattering or by emitting a phonon. This damping pathway is naturally suppressed in electrides.
Figure 2(a) shows that the conduction and valence bands are degenerate along the high-symmetry paths $A–L–H–A$, but split along $\Gamma–A$, $M–L$, and $K–H$. Actually, such band degeneracy occurs at all points in the $k_z = \pi/c$ plane, as confirmed by plotting the bands [Fig. 2(d)] along an arbitrary line $P_1–P–P_2$ perpendicular to the $k_z = \pi/c$ plane at an arbitrary $P$ point in the plane [see Fig. 2(b)]. So, the band crossing takes place throughout the BZ boundary to form a perfect DNS state [orange plane in Fig. 2(b)]. It is noted that the DNS near $E_F$ is not completely flat due to a small interchannel coupling.

The DNS state is protected by a nonsymmetric symmetry [15,45]. $\text{Ba}_3\text{CrN}_3$ has time-reversal symmetry $T = K$, with $K$ being the complex conjugation, inversion symmetry $I$, and screw rotation symmetry $S_z = \{C_2\}_{c/2}$. Two compound symmetries, $IT$ and $IS_z$, are preserved in the $k_z = \pi/c$ plane, and their anticommutation ensures a twofold band degeneracy in the entire $k_z = \pi/c$ plane [15,45]. When SOC effect is included, this degeneracy is lifted but the SOC gap is negligibly small due to the unique nature of anionic electrons [see Fig. 2(d)]. Similar conclusions are drawn for $\text{Sr}_3\text{CrN}_3$ [15].

After establishing an ideal DNS state in $\text{Ba}_3\text{CrN}_3$, we investigate its plasmonic excitations. Under RPA, the collective plasmon mode can be determined by the dynamical dielectric function $\epsilon(q, \omega) = 1 - V(q)\Pi(q, \omega)$, where $V(q) = 4\pi e^2/|q|^2$. In the long-wavelength limit ($q \to 0$), a noninteracting irreducible polarizability is given by [16,56]

$$\Pi(q, \omega) = -\frac{2}{(2\pi)^3} \int d^3k \sum_{l,l'} |(k + q, l')\epsilon^{q}\tau| |k, l|^2 \times \frac{n_F(E_{k,l}) - n_F(E_{k+q,l'})}{\hbar\omega + E_{k,l} - E_{k+q,l'} + i\eta},$$

where $n_F$ is the Fermi-Dirac distribution function and $\eta$ is the broadening of the plasmon mode. The collective plasmon mode is defined at zeros of the complex dynamical dielectric function. It is more convenient to calculate the electron energy loss spectrum (EELS), i.e., $\text{EELS} = -\text{Im}[1/\epsilon(q, \omega)]$, whose broadened peaks indicate the plasmons [56]. Along the $z$ direction, we calculate the long-wavelength limit ($q = 0.001$ $\text{Å}^{-1}$) dielectric function of $\text{Ba}_3\text{CrN}_3$ and the EELS at $T = 300$ K, as shown in Fig. 3(a). A sharp plasmon peak with high intensity appears for $\text{Re}[\epsilon(q, \omega)] = 0$. Simultaneously, the $\text{Im}[\epsilon(q, \omega)] \to 0$, indicating a weak direct damping rate. The plasmon excitation energy of 0.125 eV corresponds to a frequency of $\sim30$ THz in the mid-IR range. As shown in Fig. 3(b), the parabolic plasmon dispersion (3D dielectric screening) lies above the region of intraband Landau damping, consistent with the sharp peak of plasmon; it indicates that the direct decay into electron-hole pairs is almost forbidden.

In Fig. 3(c), we plot the plasmon frequency versus $n$ and excitation direction angle $\theta$ at the long-wavelength limit. Remarkably, at any fixed excitation direction, the plasmon frequency keeps a constant value ($\omega \sim n^0$) for a significantly
large range of \( n \) up to \( \sim 3 \times 10^{20} \text{ cm}^{-3} \) (i.e., within the energy range of linear band dispersion [15]), consistent with our predicted feature of ADP. Meanwhile, the high intensity of ADP remains almost unchanged for different \( n \) [15] because of a constant DOS within the same energy range. On the other hand, the ADP frequency depends on \( \theta \) and can be continuously tuned, following a \(|\cos \theta|\) function [black curve in Fig. 3(c)], which agrees well with our model [Eq. (2)]. It is noted that the plasmon mode along the \( x \) direction (i.e., \( \theta = 90^\circ \)) has a small excitation energy (\( \sim 20 \text{ meV} \)) and enters the particle-hole continuum at large \( q \) [15], whereas the nonzero frequency for \( \theta = 90^\circ \) is due to a small dispersion in the \( xy \) plane of the DNS band. Moreover, the high intensity of ADP is almost maintained for different \( \theta \), as confirmed by our calculations [15]. Thus, by changing \( \theta \), a high-intensity ADP with a frequency tuned from terahertz to mid-IR can be continuously tuned, following a \(|\cos \theta|\) function [black curve in Fig. 3(c)], which agrees well with our model [Eq. (2)]. It is noted that the realization of \( n \)-independent ADP requires two conditions: 1D Dirac spectrum (\( \sim 30 \text{ meV} \) near \( E_F \) for Ba\(_3\)CrN\(_3\)) and a long-wavelength limit. Once the plasmon frequency reaches the quadratic dispersion region, it becomes \( n \)-dependent. The 2D classical plasma also has \( n \)-independent DOS and hence high intensity, but its frequency is \( n \)-dependent (\( \omega \sim n^{1/2} \)), differing from ADP. In addition, we find the ADP frequency is robust against strain, due to the nature of loosely bound anionic electrons [15].
for the occupied DNS band of anionic electrons and for an unoccupied band of atomic bound electrons are shown in Fig. 4(c). Strikingly, the former is much smaller than the latter over the entire BZ. Correspondingly, the scattering rate of anionic electrons at low energy is much lower than that of atomic bound electrons at high energy, as shown in Fig. 4(d). As a result, the plasmon relaxation time is $\sim 130$ fs (at $T = 300$ K) [57] for the DNS states, even longer than that of graphene plasmons at high carrier density [31,61]. The low electron scattering of graphene is mostly contributed to by the low DOS near $E_F$, while the carrier doping will inevitably result in a rapid increase of scattering rate [31,38]. In contrast, the ultrawave $e$–ph coupling and nearly constant DOS exist in a wide energy range for Ba$_3$CrN$_3$, leading to a low phonon scattering rate over a large range of doping [Fig. 4(d)].

In conclusion, we demonstrate an ADP excited by a DNS state in a 1D electrode, which exhibits an anomalous density-independent frequency, intensity, and damping. It can help realize stable functionalities of plasmons in changeable environments, enable a low-frequency plasmon with high intensity, and lead to long-lived plasmons at high carrier density.

The authors thank L. Kang and X. Zhang for helpful discussions. The authors at Beijing acknowledge the support from the Science Challenge Project (Grant No. TZ2016003), MOST of China (Grants No. 2017YFA0303404 and No. 2016YFA0301001), NSFC (Grants No. 11574024, No. 11674188, and No. 11334006), and NSAF U1930402. F. L. acknowledge NSFC (Grants No. 11574024, No. 11674188, and No. 2017YFA0303404 and No. 2016YFA0301001), discussions of symmetry protection and topological invariant of nodal surface, and $e$-ph coupling calculation tests of Ba$_3$CrN$_3$, which also includes Refs. [16–38].

See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.123.206402 for details of three different 3D topological semimetals (DNP, DNL, and DNS) and their plasmon excitation derivations, the proof of density dependence of plasmon intensity, computational methods, electronic and plasmonic properties of Ba$_3$CrN$_3$ and Sr$_3$CrN$_3$, discussions of symmetry protection and topological invariant of nodal surface, and $e$-ph coupling calculation tests of Ba$_3$CrN$_3$, which also includes Refs. [16–38].

J. Chen et al., Optical nano-imaging of gate-tunable graphene plasmons, Nature (London) 487, 77 (2012).

D. Rodrigo, O. Limaj, D. Janner, D. Etezadi, F. J. G. de Abajo, V. Pruneri, and H. Altug, Mid-infrared plasmonic biosensing with graphene, Science 349, 165 (2015).

1. S. A. Maier, Plasmonics: Fundamentals and Applications (Springer, New York, 2007).
2. W. L. Barnes, A. Dereux, and T. W. Ebbesen, Surface plasmon subwavelength optics, Nature (London) 424, 824 (2003).
3. E. Ozbay, Plasmonics: Merging photonics and electronics at nanoscale dimensions, Science 311, 189 (2006).
4. D. K. Gramotnev and S. I. Bozhevolnyi, Plasmonics beyond the diffraction limit, Nat. Photonics 4, 83 (2010).
5. S. Lal, S. Link, and N. J. Halas, Nano-optics from sensing to waveguiding, Nat. Photonics 1, 641 (2007).
6. H. A. Atwater and A. Polman, Plasmonics for improved photovoltaic devices, Nat. Mater. 9, 205 (2010).
7. C. Clavero, Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices, Nat. Photonics 8, 95 (2014).
8. F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, Graphene photonics and optoelectronics, Nat. Photonics 4, 611 (2010).
9. F. H. L. Koppens, D. E. Chang, and F. J. G. de Abajo, Graphene plasmonics: A platform for strong light-matter interactions, Nano Lett. 11, 3370 (2011).
10. L. Ju, B. Geng, J. Hong, C. Girit, M. Martin, Z. Hao, H. A. Bechtel, X. Liang, A. Zettl, Y. R. Shen, and F. Wang, Graphene plasmonics for tunable terahertz metamaterials, Nat. Nanotechnol. 6, 630 (2011).
11. A. N. Grigorenko, M. Polini, and K. S. Novoselov, Graphene plasmonics, Nat. Photonics 6, 749 (2012).
12. Z. Fei et al., Gate-tuning of graphene plasmons revealed by infrared nanoimaging, Nature (London) 487, 82 (2012).
13. J. Chen et al., Optical nano-imaging of gate-tunable graphene plasmons, Nature (London) 487, 77 (2012).
14. D. Rodrigo, O. Limaj, D. Janner, D. Etezadi, F. J. G. de Abajo, V. Pruneri, and H. Altug, Mid-infrared plasmonic biosensing with graphene, Science 349, 165 (2015).
P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. N. P. Armitage, E. J. Mele, and A. Vishwanath, Weyl and C.-K. Chiu, J. C. Y. Teo, A. P. Schnyder, and S. Ryu, K. M. Borysenko, J. T. Mullen, E. A. Barry, S. Paul, Y. G. R. Chen, H. C. Po, J. B. Neaton, and A. Vishwanath, H. Watanabe, H. C. Po, M. P. Zaletel, and A. Vishwanath, Filling-Enforced Gaplessness in Band Structures of the 230 Space Groups, Phys. Rev. Lett. 117, 096404 (2016).

R. Chen, H. C. Po, J. B. Neaton, and A. Vishwanath, Topological materials discovery using electron filling constraints, Nat. Phys. 14, 55 (2018).

S. A. Parameswaran, Topological “Luttinger” invariants protected by non-symmetric symmetry in semimetals, arXiv:1508.01546.

K. M. Borysenko, J. T. Mullen, E. A. Barry, S. Paul, Y. G. Semenov, J. M. Zavada, M. B. Nardelli, and K. W. Kim, First-principles analysis of electron-phonon interactions in graphene, Phys. Rev. B 81, 121412(R) (2010).

C.-K. Chiu, J. C. Y. Teo, A. P. Schnyder, and S. Ryu, Classification of topological quantum matter with symmetries, Rev. Mod. Phys. 88, 035005 (2016).

N. P. Armitage, E. J. Mele, and A. Vishwanath, Weyl and Dirac semimetals in three-dimensional solids, Rev. Mod. Phys. 90, 015001 (2018).

A. A. Burkov, M. D. Hook, and L. Balents, Topological nodal semimetals, Phys. Rev. B 84, 235126 (2011).

H. Weng, X. Dai, and Z. Fang, Topological semimetals predicted from first-principles calculations, J. Phys. Condens. Matter 28, 303001 (2016).

Z. Yan, P.-W. Huang, and Z. Wang, Collective modes in nodal line semimetals, Phys. Rev. B 93, 085138 (2016).

A. Poliziano, G. Chiarello, B. Ghosh, K. Sadhukhan, C.-N. Kuo, C. S. Lue, V. Pellegrini, and A. Agarwal, 3D Dirac Plasmons in the Type-II Dirac Semimetal PrTe$_2$, Phys. Rev. Lett. 121, 086804 (2018).

Q.-F. Liang, J. Zhou, R. Yu, Z. Wang, and H. Weng, Node-surface and node-line fermions from nonsymmorphic lattice symmetries, Phys. Rev. B 93, 085427 (2016).

W. Wu, Y. Liu, S. Li, C. Zhong, Z.-M. Yu, X.-L. Sheng, Y. X. Zhao, and S. A. Yang, Nodal surface semimetals: Theory and material realization, Phys. Rev. B 97, 115125 (2018).

J. L. Dye, Electrides: Ionic salts with electrons as the anions, Science 247, 663 (1990).

J. L. Dye, Electrides as anions, Science 301, 607 (2003).

S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka, and H. Hosono, High-density electron anions in a nanoporous single crystal: [Ca$_2$Al$_2$BO$_4$]$_n$(4e$^-$), Science 301, 626 (2003).

K. Lee, S. W. Kim, Y. Toda, S. Matsuishi, and H. Hosono, Dicalcium nitride as a two-dimensional electrode with an anionic electron layer, Nature (London) 494, 336 (2013).

L. A. Burton, F. Ricci, W. Chen, G.-M. Rignanese, and G. Hautier, High-throughput identification of electrides from all known inorganic materials, Chem. Mater. 30, 7521 (2018).

M. Hirayama, S. Matsuishi, H. Hosono, and S. Murakami, Electrides as a New Platform of Topological Materials, Phys. Rev. X 8, 031067 (2018).

H. Buljan, M. Jablan, and M. Soljačić, Damping of plasmons in graphene, Nat. Photonics 7, 346 (2013).

A. Woessner, M. B. Lundeberg, Y. Gao, A. Principi, P. A. González, M. Carrega, K. Watanabe, T. Taniguchi, G. Vignale, M. Polini, J. Hone, R. Hillenbrand, and F. H. L. Koppens, Highly confined low-loss plasmons in graphene-boron nitride heterostructures, Nat. Mater. 14, 421 (2015).

X. Zeng, S. Zhao, Z. Li, and J. Yang, Electron-phonon interaction in a Ca$_3$N monolayer: Intrinsic mobility of electron, Phys. Rev. B 98, 155443 (2018).

Z. F. Wang and F. Liu, Self-Assembled Si(111) Surface States: 2D Dirac Material for THz Plasmonics, Phys. Rev. Lett. 115, 026803 (2015).

The calculated electron scattering rate by Eq. (4) [red or blue dots in Fig. 4(d)] is not the true plasmon damping rate due to the transport factor (see Refs. [27,58] for details). Using the methods in Refs. [27,59,60], we have calculated the phonon-assisted plasmon damping rate for Ba$_3$CrN$_3$, as shown in Fig. 4(d) (black triangles). The resulting plasmon lifetime is longer than the electron relaxation time. Most importantly, however, is that the main conclusion, i.e., the phonon-assisted plasmon damping being independent of carrier densities, is drawn consistently.

A. Principi, M. Carrega, M. B. Lundeberg, A. Woessner, F. H. L. Koppens, G. Vignale, and M. Polini, Plasmon losses due to electron-phonon scattering: The case of graphene encapsulated in hexagonal boron nitride, Phys. Rev. B 90, 165408 (2014).

D. Novko, Dopant-induced plasmon decay in graphene, Nano Lett. 17, 6991 (2017).

A. M. Brown, R. Sundararaman, P. Narang, W. A. Goddard III, and H. A. Atwater, Non-radiative plasmon decay and hot carrier dynamics: Effects of phonons, surfaces and geometry, ACS Nano 10, 957 (2016).

Although the relaxation time of 130 fs is not so long compared to that of a graphene plasmon at a low carrier density (e.g., see Refs. [32,33]), it can be maintained over a large range of carrier concentrations; i.e., it is indeed longer than graphene plasmon at a high carrier density (e.g., 20 fs in Ref. [31]). The phonon-assisted damping can, in principle, be ultralow because of the weak electron-phonon coupling for anionic electrons. The non-negligible value of phonon scattering in our system, however, is due to the high DOS of the nodal-surface state.