Energy loss spectrum and surface modes of two-dimensional black phosphorus

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Abstract
The structural features and the electron energy loss spectrum of black phosphorus (BP) have been experimentally analyzed and they are discussed based on a theoretical calculation. The low-energy loss spectra of typical samples reveal that the emerging high-mobility two-dimensional material BP often exhibits both bulk and surface plasmon modes. The surface modes of BP are strongly thickness dependent. Electrodynamic analysis indicates that the Fuchs–Kliewer-like surface plasmon modes consist of two branches with different charge symmetry: the upper side and lower side have the same charge polarity as the lower branch and the opposite charge polarity to the upper branch. This study provides fundamental insight into the characteristic nature of BP plasmonics.

1. Introduction
Surface plasmon is a type of surface electromagnetic mode propagation along the interface between the metal like medium and the dielectrics. The amplitude of the electric field decays exponentially away from the interface. Surface plasmonics of particular interest because they offer an efficient method for light manipulation [1]. In the past decade, as an important subject of surface plasmonic investigations, graphene plasmonics has provided a variety of gate-controlled optoelectronic applications, such as light harvesting and optical sensing [2, 3]. In addition to the unique electronic structure of graphene, graphene plasmonic devices can confine light in atomic thickness, resulting in dramatically enhanced local fields owing to graphene’s two-dimensional (2D) nature. However, replaceable 2D plasmonic materials are still lacking. Exploration of new 2D plasmonic building blocks in novel material systems is highly desirable to advance the field of plasmonics. As a result, a number of 2D materials in addition to graphene have been successfully prepared, including hexagonal boron nitride, transition metal dichalcogenides, and black phosphorus (BP) [4–6]. Among these emerging 2D systems, BP is one of the most promising candidates because of its remarkable electronic and photonic properties, such as its high carrier mobility (5200 cm² V⁻¹ s⁻¹ at room temperature), thickness-dependent direct bandgap, and gate-tunable optoelectronic properties [7–10]. A variety of experimental studies have been performed to investigate the structural and physical properties of BP by scanning tunneling microscopy [11], atomic force microscopy, Raman spectroscopy [12], and the electron loss spectroscopy [13, 14]. Although theoretical and experimental studies have demonstrated the potential of BP as a promising plasmonic platform [15–21], systematic analysis of the thickness-dependent surface modes in the low energy loss spectrum is still lacking. In the present work, we reveal that few-layer BP exhibits both bulk and surface plasmon modes in the visible and ultraviolet regions by electron energy loss spectroscopy (EELS) in transmission electron microscopy (TEM). The surface modes of BP are strongly thickness dependent. We performed an ab initio calculation of the dielectric function of BP. Based on the anisotropic dielectric function and electrostatic approximation, we also calculated the contribution of the...
thickness-dependent anisotropic surface modes to the low energy loss spectrum. The theoretical results are in good qualitative agreement with the experimental results.

2. Experimental

Crystalline BP is a typical sensitive material when exposed to ambient O2 and H2O, and it shows visible structural degradation [22]. Although the mechanism is still not completely understood, the presence of electrons/light has been shown to either initiate or accelerate this degradation [14]. Thus, the pristine BP samples in this study were handled with minimal ambient light exposure, and prior structural/compositional analyses were performed to ensure that the BP flakes selected for study were not significantly altered. In the experimental measurements, BP crystalline plates with thicknesses of 1–10 layers in distilled water solvent were dropped onto a 400 mesh copper grid on which carbon nanotubes were grown. After the distilled water vaporized, the BP nanoplates were attached to the nanotubes. The EELS measurements were performed with a JEOL-2100F electron microscope equipped with a Gatan spectrometer operating at a voltage of 200 kV. A collection semi-angle of more than 100 mrad was used. The TEM images were recorded with a JEM-ARM200 TEM (JEOL Inc.). High-resolution real space microscopy and EELS were performed for free-standing BP supported by carbon nanotubes on the edges. The advantage of using the carbon nanotubes as a scaffold for the flakes is that it can avoid introducing the background from the substrate in the EELS. Also, the surface electromagnetic modes are sensitive to the dielectric functions of the mediums above and below the interface along which it propagates. So, the spectroscopic feature and plasmonic behavior of the BP supported on the carbon nanotubes are different from the ones of the BP deposited on a flat substrate.

A TEM image of the sample at low magnification is shown in figure 1(a). It clearly shows that the BP crystalline plates are supported by the carbon nanotubes. A high-resolution real space image and the EELS spectrum of the BP plates are shown in figures 1(c) and (d), respectively. The crystal structure and lattice symmetry were investigated by TEM observations and electron diffraction along the main axis directions. All of the obtained experimental data can be well indexed to the Cmca orthorhombic unit cell with lattice parameters of \( a = 3.313 \text{ Å}, b = 4.376 \text{ Å}, \) and \( c = 10.478 \text{ Å} \). The structural image in figure 1(c) is for an exfoliated BP flake viewed along the [001] crystallographic direction, where P atomic columns can be directly observed. The schematic structural model is shown in figure 1(b), which is consistent with previously reported structures as AA stacking [13, 23]. The core energy loss spectrum in figure 1(d) clearly shows that the phosphorus L23 peak is located at 132 eV. Its shape is consistent with what has been observed with the pristine BP [14].

The low-energy loss spectrum recorded at 200k magnification with an exposure time of 1 s in the image mode is shown in figure 2. The thickness of the crystalline samples was analyzed as follows. First, the zero loss
peaks were isolated and the elastic scattering counts \( I_0 \) were recorded. The total counts \( I_t \) were also recorded. The mean free path was estimated by the equation

\[
\lambda \approx \frac{106F(E_0/E_m)}{\ln(2\beta E_0/E_m)},
\]

where \( F \) is the relativistic factor, \( E_0 \) is the incident electron energy, \( \beta \) is the semi-collection angle, and \( E_m \) is the mean energy loss estimated by the empirical formula \( E_m \approx 7.6Z^{0.36} \), in which \( Z \) is the atomic number of the sample. The crystal thickness (\( t \)) values of the examined samples were then estimated by the log-ratio method: \( t/\lambda = \ln(I_t/I_0) \).

### 3. Data analysis

The thickness-dependent energy loss spectrum is dominated by the bulk loss of BP at around 19 eV, and the energy loss associated with excitation of the surface modes on the upper and lower surface of the crystal plate appears as a broad plateau. With increasing thickness, both features in the EELS spectrum become stronger. The plasmons around 20 eV in BP has been reported recently by Nicotra et al [16] for both the zigzag and armchair directions. The weak shoulder observed in the EELS spectrum around 10 eV is identified as a single-particle transition from the \( 2G^+ \) band, derived from \( p_z \) orbitals, whose wave function has alternating signs between nearest neighbors. To extract the contributions of the surface modes, we removed the zero loss peaks by the reflected tail fit function. The bulk contributions in the experimental EELS spectra were then calculated using the jellium model. The bulk plasmon frequencies \( E_p \) and full widths at half-maximum of the plasmon peaks \( E_p \) were fitted to the experimental data using the following equation:

\[
\text{Im}(-1/\varepsilon(E)) = \frac{E(\Delta E_p)E_p^2}{(E^2 - E_p^2)^2 + (E\Delta E_p)^2},
\]

where \( E \) is the energy. The fitted bulk losses were then removed and the surface loss contributions remain, which are shown in figure 3.

We performed an \textit{ab initio} calculation of the electronic structure of BP with the Vienna \textit{ab initio} simulation package. Two layers of phosphorus atoms stack as the AA type. A 4.37 Å \times 3.31 Å \times 10.47 Å unit cell with eight atoms was constructed. The projector augmented-wave approach and the generalized gradient approximation exchange-correlation function were used in the calculation. We used 500 eV as the energy cutoff of the wave functions and a 21 \times 21 \times 7 \textit{K}-point mesh. The obtained anisotropic dielectric functions of BP in the \( X \), \( Y \), and \( Z \) directions shown in figure 4 were used as the input parameters in the following calculation of the EELS spectrum.

We will now discuss the theoretical calculation and analysis of the EELS spectrum of BP. Because of the difficulty of an accurate calculation of the EELS spectrum for the biaxial material, the analytical analysis in the present study is confined to the calculation of the EELS spectrum of the uniaxial-type thin film. The EELS data of the uniaxial crystals have the same in-plane dielectric functions as the dielectric functions along the \( x \)- and \( y \)-axis directions, whereas the out-of-plane dielectric function (i.e. the dielectric function of the \( z \)-axis direction) is different. The biaxial nature of BP was considered and EELS calculation was separately performed for the \( XZ \) and...
YZ planes. The analytical analysis was performed in the manner of nonretarded approximation. Similar analysis of the electron energy loss probability of uniaxial thin films has been performed for graphite [25, 26] and hexagonal boron nitride [27], in which the theoretical results are in good agreement with the experimental measurements. We started with separate calculations of the guided modes, bulk loss, and Begrenzungseffekt. The total electron energy loss probability is the sum of the three contributions.

The typical results for a 5 nm thick hypothetical uniaxial thin film with the in-plane dielectric function equal to the calculated dielectric functions for the x- and y-axis directions and the out-of-plane dielectric function equal to the calculated z direction dielectric function is shown in figure 5. A bulk plasmon peak at 19 eV is the prominent feature in both situations. The plateaus below 19 eV in the loss functions are contributed by the surface guided modes confined by the upper and lower boundaries of the thin flakes. The energy transfer from the bulk mode to the guided modes is described by the Begrenzungseffekt. The total loss functions are the sum of the loss functions obtained from the bulk modes, guided modes, and Begrenzungseffekt, which have similar profiles as the experimental data.

To further understand the structural features of the EELS spectrum, we plot the dispersion of the guided modes and bulk modes in log scale in figure 6. The dispersions of the relevant modes calculated with the X and Z direction dielectric functions are shown in figures 6(a) and (c), and the counterparts calculated with the Y and Z direction dielectric functions are shown in figures 6(b) and (d). Figures 6(a) and (b) are the bulk mode dispersion at 19 eV. Figures 6(c) and (d) are the guided mode dispersion below 19 eV. The guided modes split into two branches in both sets of plots. The lower branches below 14 eV in both sets of plots correspond to the lower branch of the surface plasmon pointed out by Kliewer and Fuchs [28, 29], while the upper branches between 14 and 19 eV are the upper branch of the surface plasmon. The calculated dielectric functions of the X, Y, and Z

![Figure 3](image1.png)
Figure 3. Contributions of the surface modes to the EELS spectra.

![Figure 4](image2.png)
Figure 4. The dielectric functions of BP in X, Y, Z directions obtained from the \textit{ab initio} calculation.
directions above 10 eV have negligible differences, so we can approximately treat BP as a homogenous material in this region. The dielectric function $\varepsilon = 0$ at 19 eV indicates the position of the bulk plasmon, while the dielectric function $\varepsilon = -1$ at 14 eV acts as the asymptotic line of the upper and lower branches of the surface plasmon. Another important feature is that the surface loss function has a local maximum at about 0.7 eV. This is consistent with the fact that small but obvious peaks appear at a frequency below 2 eV in the experimental data.

**Figure 5.** (a) Loss functions of a 5 nm thick uniaxial thin film with the calculated $X$ direction dielectric functions as the in-plane dielectric function and the calculated $Z$ direction dielectric function as the out-of-plane dielectric function. (b) Loss functions of a 5 nm thick uniaxial thin film. The calculated $Y$ direction dielectric function is set as the in-plane dielectric function and the calculated $Z$ direction dielectric function is set as the out-of-plane dielectric function.

**Figure 6.** Dispersion of the bulk modes for a 5 nm thick uniaxial slab obtained with the in-plane and out-of-plane dielectric functions set as the calculated BP dielectric functions in $x$ and $z$ direction (a) and in $y$ and $z$ direction (b). Dispersion of the surface guided modes for a 5 nm thick uniaxial slab obtained with the in-plane and out-of-plane dielectric functions set as the calculated BP dielectric functions in $x$ and $z$ direction (c) and in $y$ and $z$ direction (d).
We will now discuss the fundamental features of the total loss functions and guided mode loss functions for samples with different thicknesses (figure 7). The bulk loss monotonically increases with increasing thickness, as expected. However, the guided mode behavior is more complicated. The main peak of the surface loss moves to higher energy with increasing thickness, which is consistent with the experimental data for the surface loss part of the spectrum (figure 3). The thickness dependence of the data shown in figure 3 mainly comes from two aspects. First, the shape change of the curves with thickness of 7.76, 10.58, 15.79 nm mainly comes from the thickness dependence of the surface mode dispersion as pointed out by [27]. Second, what we measured are actually the stacks of BP flakes, especially for the thicker regions. So the surface mode contributions from the upper and lower sides of the slabs add together. It also induces thickness dependence to our data.

4. Conclusions

BP has been investigated by high-resolution electron microscopy and EELS. The orthorhombic crystal structure and crystal lattice constants were determined by real space measurement, as well as diffraction analysis. We also calculated the anisotropic dielectric function of BP by an *ab initio* method. Quasistatic analysis was performed and the EELS spectrum was analyzed within the frame of classical electrodynamics. The biaxial nature of BP was considered and EELS calculation was separately performed with the dielectric functions of BP in *X*, *Z* direction and *Y*, *Z* direction. The contributions of the bulk and surface plasmons were separately measured and calculated. The Fuchs–Kliewer-like surface plasmon modes within the BP slab are observed and the data are well supported by analytical analysis. The fast electron can act as a pulsed white light source with evanescent components and efficiently stimulate the surface plasmons along the surface of BP. The lower branch of Fuch Kliewer modes with smaller energies than 14 eV has the same charge polarity on the upper surface and lower surface of the slab while the upper branch of Fuch Kliewer modes with larger energies than 14 eV has the opposite charge polarity on the upper surface and lower surface of the slab. BP shows potential as a future 2D optoelectronic material and it has possible applications in plasmonic devices.

![Figure 7. Thickness-dependent total loss function (a) and (b) and surface loss function of BP (c) and (d). The loss functions calculated with the *X* and *Z* direction dielectric functions are shown in (a) and (c), and the counterparts calculated with the *Y* and *Z* direction dielectric functions are shown in (b) and (d).](image-url)
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References

[1] Barnes W L, Dereux A and Ebbesen T W 2003 Surface plasmon subwavelength optics Nature 424 824
[2] Grigorenko A, Polini M and Novoselov K 2012 Graphene plasmonics Nat. Photon. 6 749
[3] Koppens F, Chang D E and de Abajo F J G 2011 Graphene plasmonics: a platform for strong light–matter interaction 2011 Nano Lett. 11 3370
[4] Agarwal A, Vitiello M S, Viti L, Cupollolo A and Politano A 2018 Plasmonics with two-dimensional semiconductors: from basic research to technological applications Nanoscale 10 8938
[5] Miro P, Audiffred M and Heine T 2014 An atlas of two-dimensional materials Chem. Soc. Rev. 43 6537
[6] Bhimanapati G, et al. 2015 Recent advances in two-dimensional materials beyond Graphene ACS Nano 9 11509
[7] Ling X, Wang H, Huang S, Xia F and Dresselhaus M S 2015 The renaissance of black phosphorus Proc. Natl Acad. Sci. 112 4523–30
[8] Viti L, Hu J, Coquillat D, Politano A, Knap W and Vitiello M S 2016 Efficient Terahertz detection in black–phosphorus nano-transistors with selective and controllable plasma-wave, bolometric and thermoelectric response Sci. Rep. 6 20474
[9] Sun Z, Xie H, Tang S, Yu X F, Guo Z, Shao J, Zhang H, Huang H, Wang H and Chu P K 2015 Ultrasmall black phosphorus quantum dots: synthesis and use as photothermal agents Angew. Chem. Int. Ed. 127 11688
[10] Castellanos-Gomez A 2015 Black phosphorus: narrow gap, wide applications J. Phys. Chem. Lett. 6 4280
[11] Zhang C, Lian J, Yi W, Jiang Y, Liu L, Hu H, Xiao W, Du S, Sun L and Gao H 2009 Surface structures of black phosphorus investigated with scanning tunneling microscopy J. Phys. Chem. C 113 18823–6
[12] Castellanos-Gomez A, Vicarelli L, Prada E, Island J O, Narasimha-Acharya K, Blanter S I, Groenendijk D J, Buscema M, Steele G A and Alvarez J 2014 Isolation and characterization of few-layer black phosphorus 2D Mater. 1 025001
[13] Wu R J, Topsakal M, Low T, Robbins M C, Haratipour N, Jeong J S, Wentzcovitch R M, Koester S J and Mkhoian K A 2015 Atomic and electronic structure of exfoliated black phosphorus J. Vac. Sci. Technol. A 33 060604
[14] Favron A, Gaufrès E, Fossard F, Phaneuf-L’Heureux A L, Tang N Y W, Lèvesque P L, Loiseau A, Leonelli R, Francoeur S and Martel R 2015 Photooxidation and quantum confinement effects in exfoliated black phosphorus Nat. Mater. 14 826
[15] Gisho B, Kumar P, Thakur A, Chauhan Y S, Bhowmick S and Agarwal A 2017 Anisotropic plasmons, excitons, and electron energy loss spectroscopy of phosphorene Phys. Rev. B 96 035422
[16] Nicotra G et al. 2018 Anisotropic ultraviolet-plasmon dispersion in black phosphorus Nanoscale 10 21918
[17] Lee I H, Martin-Moreno L, Mohr D A, Khaliqi K, Low T and Oh S H 2018 Anisotropic acoustic plasmons in black phosphorus ACS Photonics 5 2208
[18] Liu Z and Aydin K 2016 Localized surface plasmons in nanostuctured monolayer black phosphorus Nano Lett. 16 3457
[19] Low T, Roldán R, Wang H, Xia F, Avouris P, Moreno L M and Guinea F 2014 Plasmons and screening in monolayer and multilayer black phosphorus Phys. Rev. Lett. 113 106802
[20] Abate Y, Gámez S, Li Z, Babicheva V, Javani M H, Wang H, Cronin S B and Stockman M I 2017 Ultrafast optical response in monolayer phosphorene Nano Lett. 17 16162
[21] Huber M A et al. 2017 Femtosecond photo-switching of interface polaritons in black phosphorus heterostructures Nat. Nanotechnol. 12 207
[22] Abellan G, Lloret V, Mundloch U, Marcia M, Neiss C, Geuling A, Varela M, Hauke F and Hirsch A 2016 Noncovalent functionalization of black phosphorus Angew. Chem. Int. Ed. 55 14557
[23] Dai J and Zeng X 2014 Bilayer phosphorene: effect of stacking order on bandgap and its potential applications in thin-film solar cells J. Phys. Chem. Lett. 5 1289
[24] Egerton R 1996 Electron Energy Loss Spectroscopy in the Electron Microscope (Berlin: Springer)
[25] Chen C and Silcox J 1975 Detection of optical surface guided modes in thin graphite films by high-energy electron scattering Phys. Rev. Lett. 35 389
[26] Chen C and Silcox J 1979 Calculations of the electron-energy-loss probability in thin uniaxial crystals at oblique incidence Phys. Rev. B 20 3605
[27] Goyadzinov A A, Konečná A, Chuvilin A, Vélez S, Dolado I, Nikitín A Y, Lopatin S, Gasanov M, Hueso L E and Aizpurua J 2017 Probing low-energy hyperbolic polaritons in van der Waals crystals with an electron microscope Nat. Commun. 8 95
[28] Kliwer K and Fuchs R 1966 Optical modes of vibration in an ionic crystal slab including retardation: I. Nonradiative region Phys. Rev. 144 495
[29] Lourenço-Martins H and Kociak M 2017 Vibrational surface electron-energy-loss spectroscopy probes confined surface-phonon modes Phys. Rev. X 7 041059