

Dynamical Tuning of Graphene Plasmonic Resonances by Ultraviolet Illuminations

Yunyun Dai, Yuyu Xia, Tao Jiang, Ang Chen, Yiwen Zhang, Yujie Bai, Guiqiang Du, Fang Guan, Shiwei Wu, Xiaohan Liu,* Lei Shi,* and Jian Zi*

One of the unique features of plasmonic resonances in graphene structures is the enabled tunability through external means. Up to now, electrical gating is extensively adopted to tune graphene plasmonic resonances. This method is, however, limited unfortunately only to graphene structures with electrical connections. Here, a simple and efficient method to tune graphene plasmonic resonances by ultraviolet illuminations in a dynamical and reversible way is demonstrated. It is purely an optical means and can be applied to all kinds of graphene structures without introducing electrodes, ion-gel, or conducting layers required in electrical gating, which is of great significance especially for isolated graphene structures. The optical tuning method could shed new light on graphene-based tunable devices.

Structured graphene, such as graphene ribbons and disks can support interesting plasmonic resonances in the mid- and far-infrared ranges,^[1–10] showing many unique properties like deep subwavelength confinement, high enhancement of optical nearfields, and tunability.^[11–21] To tune graphene plasmonic resonances, electrical gating has been dominantly used.^[22–29] For instance, plasmonic resonances in graphene ribbon arrays^[25] could be tuned in a range over 500 cm^{-1} with a gate voltage varying from -20 to -130 V . By using an ion gel,^[30] a broad tunable range around 1000 cm^{-1} was realized with a low gate voltage of about 4 V .

By utilizing the gate-controlled dynamical tuning, graphene plasmonic resonances could have potential applications in optoelectronics^[31–34] such as tunable sensors^[25,26] and modulators.^[25,30] Nevertheless, the method of electrical gating

has some disadvantages. To realize a dynamical tuning, graphene structures should have electrical connections. As a result, electrodes, ion gels, or conducting substrates have to be introduced to attain an electrical connection. The method has been successfully applied to graphene sheets and ribbons. However, it is especially difficult and challenging for isolated graphene structures such as graphene disks.^[35,36] Moreover, intrinsic absorptions from either conducting substrates or ion gels are inevitable, which may degrade considerably graphene plasmonic resonances. Thus, to find a way to tune plasmonic resonances in all kinds of

graphene structures without the introduction of electrical connections is of great significance.


In this paper, we develop a simple and efficient method to tune graphene plasmonic resonances by UV illuminations. We show that UV illuminations can induce a dynamical tuning of plasmonic resonances in all kinds of graphene structures both with and without electrical connections. Factors that influence this tuning process including the operating wavelength, power density, and illumination time of UV light sources are discussed.

Plasmonic resonances in both graphene and graphene structures depend strongly on their Fermi levels,^[4] E_F . Consequently, a variation of the Fermi level can lead to a change in plasmonic resonances. To show UV illuminations can induce a change in the Fermi level, we measure the response of resistance and transmission spectra of graphene samples on an insulating BaF_2 substrate. The UV source used is a 355 nm solid-state laser. **Figure 1a** shows the resistance of graphene changing with time upon UV illuminations at different power densities. Once the UV laser is switched on, the resistance undergoes an increase with time and reaches saturated values a few minutes later. If switching off the UV laser, the resistance decreases with time and resumes the original values without UV illuminations eventually. Obviously, the larger the power density of the UV laser is, the higher the resistance is. Correspondingly, the resuming time needed after switching off the UV laser is more. Physically, a change in resistance means a variation of the carrier concentration in graphene samples induced by UV illuminations. A higher resistance corresponds to a lower carrier concentration, implying a lower Fermi level. Thus, the time-dependent resistance measurements show unambiguously that the Fermi level of graphene can be modified by UV illuminations in a dynamical and reversible way.

Dr. Y. Dai, Y. Xia, Dr. T. Jiang, Dr. A. Chen, Y. W. Zhang, Y. J. Bai, Dr. F. Guan, Prof. S. Wu, Prof. X. Liu, Prof. L. Shi, Prof. J. Zi
Department of Physics
Key Laboratory of Micro- and Nano-Photonic Structures
(Ministry of Education), and State Key Laboratory of Surface Physics
Fudan University
Shanghai 200433, China
E-mail: lshi@fudan.edu.cn; liuxh@fudan.edu.cn; jzi@fudan.edu.cn

Prof. G. Q. Du
School of Space Science and Physics
Shandong University at Weihai
Weihai 264209, China

Prof. S. Wu, Prof. X. Liu, Prof. L. Shi, Prof. J. Zi
Collaborative Innovation Center of Advanced Microstructures
Nanjing 210093, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adom.201701081>.

DOI: 10.1002/adom.201701081

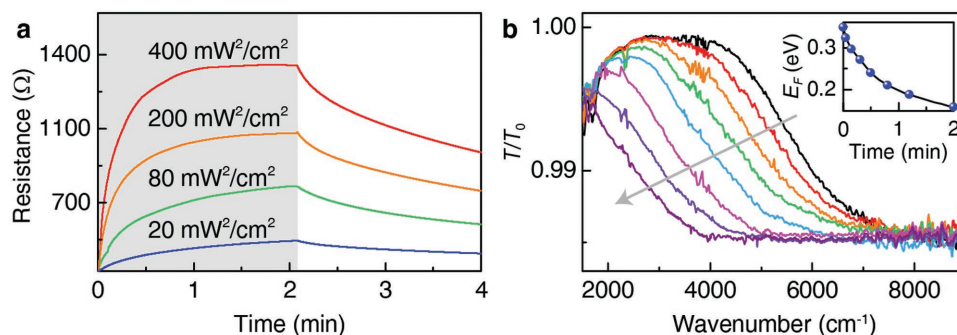


Figure 1. Optical tuning of the graphene Fermi level under UV illuminations. a) Graphene resistance as a function of time at different power densities of UV illuminations. The UV laser is switched on at zero time and then switched off after about 2 min. b) Normalized transmission spectra T/T_0 upon UV illuminations with power density of 200 mW cm^{-2} at different time. The black line corresponds to the spectrum when the UV laser is just switched on. The gray arrow indicates the direction of time. The inset shows the extracted graphene Fermi level at different time.

To determine quantitatively the change in the Fermi level of graphene under UV illuminations, we measure the time-dependent transmission spectra of graphene samples. Figure 1b displays the transmission spectra T normalized by data of the substrate without graphene T_0 upon UV illuminations at different time. Obviously, T/T_0 spectra exhibit overall a distinct threshold structure with a sharp drop above a threshold frequency. Note that the onset of interband transitions results in an abrupt increase in the real part of the optical conductivity of graphene with photon energy increasing across $2|E_F|$. As a result, the threshold structures found in real optical conductivity or T/T_0 spectra are due to the onset of interband transitions^[23,37] at $2|E_F|$. The central frequency of the threshold structure, the threshold frequency, corresponds thus to $2|E_F|$, from which the Fermi level can be extracted. After switching on the UV laser, the threshold structure in T/T_0 spectra shows a systematic shift toward a lower frequency with time and comes to a standstill eventually. The corresponding threshold frequency shifts from 5680 to 2580 cm^{-1} , implying that the absolute value of the Fermi level $|E_F|$ shifts from 0.35 to 0.16 eV . In other words, the Fermi level of graphene can be tuned in a range of about 0.19 eV .

To investigate the tunability of plasmonic resonances with UV illuminations, we measure the optical spectra of structured graphene on a BaF_2 substrate. The fabrication process of graphene structures is given in the experimental section. Figure 2a shows the extinction spectra $1 - T/T_0$ for an electrically connected graphene ribbons upon UV illuminations at different time, where T and T_0 are the transmittance with and without the graphene structure, respectively. In the absence of UV illuminations, there is a prominent peak around 1060 cm^{-1} in the extinction spectrum, corresponding to the excitation of a plasmonic resonance in graphene ribbons. Upon UV illuminations, the plasmonic resonance shows a redshift in frequency with time together with a continuous intensity decreasing. Figure 2b shows the measured extinction spectra for graphene patterned with hole arrays. The structure displays a resonant peak positioned at about 1100 cm^{-1} in the absence of UV illuminations. With the onset of UV illuminations, the peak frequency is decreased with time. Obviously, in the above two cases the graphene plasmonic resonances in graphene structures with electrical connections can be dynamically tuned in a range

over 200 cm^{-1} within 1 min upon UV illuminations. By using simulations, we can extract the Fermi level from the measured extinction spectra (shown in the Supporting Information). The Fermi level of the graphene nanostructure sample (Figure 2a) shifts from 0.31 to 0.18 eV upon UV illumination, which is consistent with the results shown in Figure 1b, despite that the original Fermi levels of different graphene samples could be different. Note that the tuning range in wavenumber of graphene plasmonic resonances is different in four types of nanostructures. This could be attributed to the differences of either the original Fermi level or the geometric size (ribbon width) of different graphene samples (details shown in the Supporting Information).

Figure 2c,d shows the change in the measured extinction spectra with time for isolated graphene rectangles and disks upon UV illuminations, respectively. Obviously, the resonant peaks stemming from the plasmonic resonances in the isolated graphene structures shift the peak frequency with illuminating time. In other words, the dynamical tuning of plasmonic resonances in isolated graphene structures is realized by UV illuminations. This cannot be achieved by common electrical gating methods for isolated graphene structures laid on an insulating substrate.

We also measure extinction spectra for the isolated graphene structures outside the region of UV illuminations. The spectra are identical to those inside the illumination region in the absence of UV illuminations as expected. This suggests that we can achieve a spatial tuning of graphene plasmonic resonances by using spatially modified UV illuminations.

Many parameters of the light sources, such as the operating wavelength, power density, and illuminating time may influence the dynamical tuning of graphene plasmonic resonances. To explore such effects, we measure the time-dependent frequency of a plasmonic resonance in graphene ribbons (the same as in Figure 2a) for the illuminations with different wavelength and power density. Figure 3a shows the results for three light sources with different operating wavelengths, while their power density is fixed. All light sources used are solid-state lasers. For the 479 nm light source, the frequency of the plasmonic mode is almost unchanged over time upon illuminations. In contrast, for the UV light sources it shows a redshift in frequency with time. The shorter UV

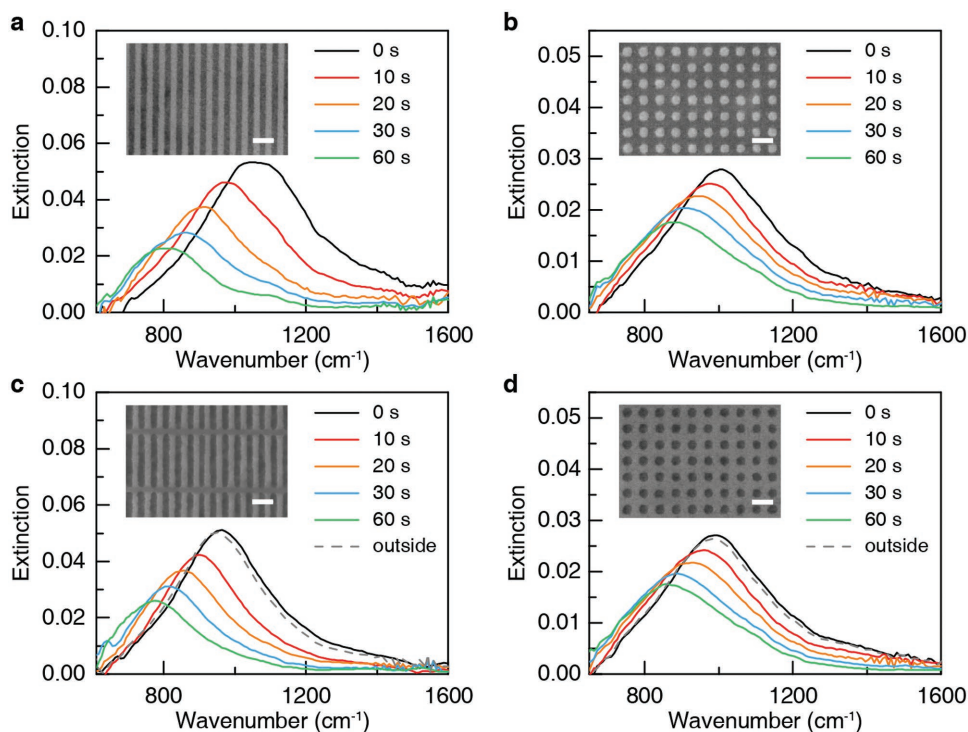


Figure 2. Optical tuning of plasmonic resonances in structured graphene under UV illuminations. The measured extinction spectra of a) graphene ribbons with a width of 60 nm and a period of 120 nm; b) graphene patterned with hole arrays with a diameter of 80 nm and a period of 160 nm; c) isolated graphene rectangles with a width of 70 nm, a length of 500 nm, and horizontal and vertical periods of 120 and 550 nm respectively; and d) isolated graphene disks with a diameter of 80 nm and a period of 160 nm upon UV illuminations with wavelength of 355 nm and power density of 200 mW cm^{-2} at different time. Black lines are the spectra at the beginning of UV illuminations and colored lines are the spectra at different illuminating time. Dashed lines are the spectra outside the region of UV illuminations. Insets show the SEM images of patterned graphene structures on a BaF_2 substrate with dark and gray regions representing graphene and substrate, respectively. Scale bars: 200 nm.

light source causes a larger frequency shift than the longer one. These facts indicate that the tunability of plasmonic resonances depends strongly on the photon energy of the illuminating light source.

Figure 3b shows the effects of the power density of illuminations. Obviously, a higher power density results in faster tuning and a larger tuning range as well. For intense enough UV light, the response could be even dramatically shortened to dozens of seconds. Therefore, by changing the operating wavelength and power density of the UV illuminations, the tuning process of

plasmonic resonances in graphene structures can be controlled rather accurately.

To reveal the tuning mechanism, extinction spectra of the graphene ribbons are measured in different gas atmospheres upon UV illuminations. For the graphene ribbons in air, with the onset of the UV light the frequency of the plasmonic mode undergoes a decrease in frequency with time, as shown in Figure 4a. Once the UV light is switched off after about 2 min, the frequency of the plasmonic mode shows an increase with time. About an hour later, it resumes to the original

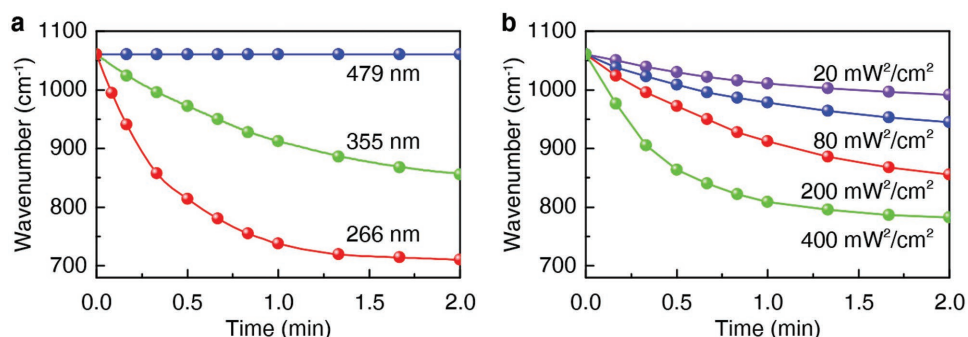


Figure 3. Effects of the wavelength and power density of the UV light source. a) Time-dependent frequency of a plasmonic mode in graphene ribbons upon illuminations for the light source with different operating wavelengths of 479, 355, and 266 nm. The power density is fixed at 200 mW cm^{-2} . b) Data for UV illuminations with different power densities. The wavelength of the light source is 355 nm.

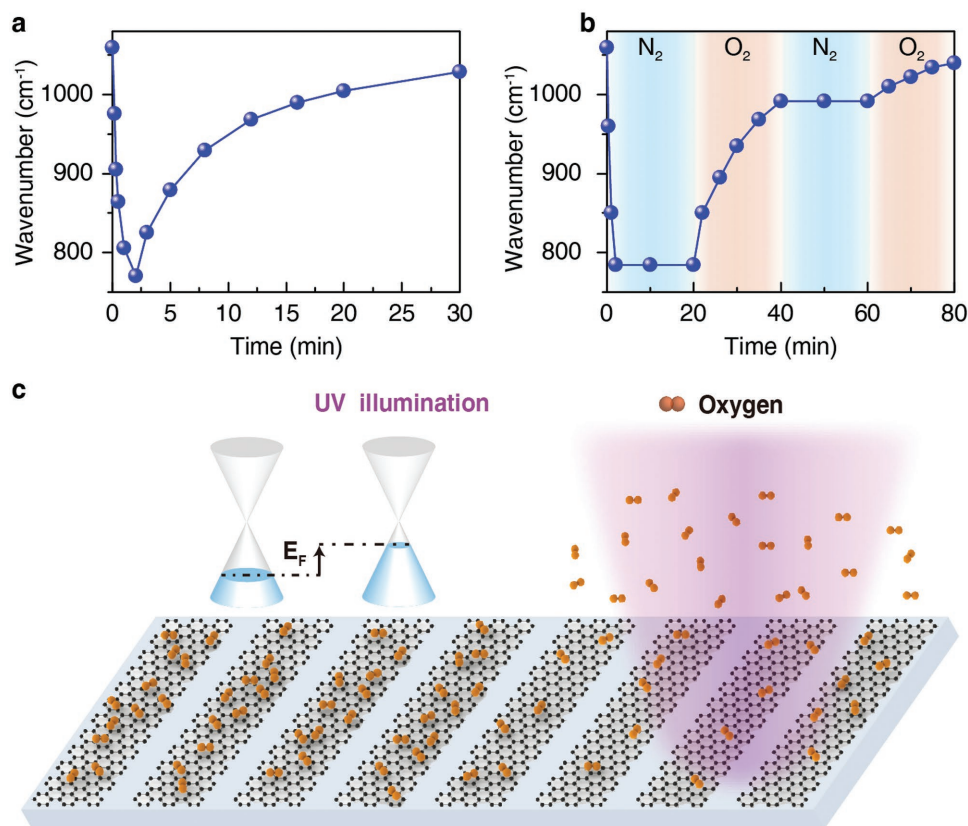


Figure 4. Tuning mechanism. a) Time-dependent frequency of a plasmonic mode in graphene ribbons in air upon illuminations. b) Data for the graphene ribbons in different gas atmospheres. Light blue (yellow) regions stand for the nitrogen (oxygen) atmosphere. In (a,b), the light source is 355 nm solid-state laser and the power density is 200 mW cm^{-2} . The source is switched on at zero time and then switched off after about 2 min. c) Schematic of adsorption and desorption of O_2 on graphene with UV illuminations, leading to the change in the Fermi level.

value without UV illuminations (shown in the Supporting Information).

Figure 4b shows the data for the graphene ribbons in the nitrogen or oxygen gas atmosphere. The nitrogen (oxygen) atmosphere is obtained simply by blowing the samples in a transparent chamber with the nitrogen (oxygen) gas. In the nitrogen atmosphere, with the onset of UV illuminations the frequency of the plasmonic mode undergoes a decrease in frequency with time until the light source is switched off after about 2 min, similar to that in air. Unlike that in air, it remains unchanged in the nitrogen atmosphere without UV illuminations, which can be clearly seen in two time intervals from 2 to 20 min and from 40 to 60 min. After changing to the oxygen atmosphere, however, the frequency of the plasmonic resonance begins to increase with time. These results indicate that oxygen rather than nitrogen is the due cause of the dynamical tuning.

Note that the major constituents of air are nitrogen and oxygen. When exposed to air, graphene may adsorb atmospheric oxygen, leading to a transfer of electrons from graphene to oxygen by forming negatively charged oxygen ions and p-type graphene,^[38] as shown in Figure 4c. The Fermi level will shift accordingly to a negative value away from the Dirac point. And It has been theoretically predicted that the adsorption energy of oxygen on graphene varies from -2.9 eV (around 427 nm) to -3.36 eV (around 370 nm) at different oxygen adsorption

concentration.^[39] Upon light illuminations, the bonds between oxygen and graphene can be broken if the photon energy is larger than their adsorption energy, resulting in oxygen desorption and back injection of electrons into graphene.^[40,41] The desorption of oxygen will thus cause an increase in the Fermi level toward the Dirac point.

The behaviors of plasmonic resonances in graphene structures in different gas atmospheres upon UV illuminations shown in Figure 4 can be understood in terms of oxygen adsorption and desorption. For graphene structures in air or oxygen atmosphere, the onset of UV illuminations will cause oxygen desorption and simultaneously a decrease in the Fermi level, leading to a redshift of the resonant frequency with time. With the removal of the illuminations, graphene can adsorb oxygen again and eventually attains saturated adsorption, leading to a blue-shift of the resonant frequency with time and approaching a saturated value eventually. The standstill of the resonant frequency in the nitrogen atmosphere without UV illuminations can be understood by the fact that there is neither oxygen adsorption nor desorption. Therefore, the desorption and adsorption of oxygen could satisfactorily explain the dynamical tuning of the plasmonic resonances in graphene structures by UV illuminations. Note that water vapor could also affect the tuning of the graphene Fermi level,^[38] which deserves further investigation.

We have demonstrated a dynamical tuning of plasmonic resonances in graphene structure by using UV illuminations. This tuning is reversible and could be easily controlled by the operating wavelength, power density, and illuminating duration time of UV light sources. The tuning mechanism is attributed to the desorption of oxygen induced by UV illuminations which causes a change in the Fermi level of graphene. Our tuning method is purely optical, implying that one does not need to introduce electrodes, ion gels, or conducting substrates in order to attain electrical connections. As a result, our method can be even applied to isolated graphene structures which are hard to achieve with electrical gating methods. Upon UV illuminations with specially designed patterns, we can realize graphene plasmonic structures in a continuous graphene layer.^[42] Thus, our optical tuning method with UV illuminations may shed new light on the dynamical control of plasmonic resonances in graphene structures and the development of novel graphene-based plasmonic devices as well.

Experimental Section

Structure Fabrications: A large-area chemical vapor deposition (CVD) grown graphene sheet was first transferred onto a BaF₂ substrate. Graphene structures were fabricated in a 100 × 200 μm² area at the center of the graphene layer using standard e-beam lithography followed by oxygen plasma etching. Fabricated samples were then exposed to Br₂ vapor for 30 s to increase doping.^[43]

Resistance Measurements: For resistance measurements, the size of the graphene channel is about 400 × 400 μm², and Cr/Au electrodes of 5/50 nm thickness were deposited onto the graphene sheet in vacuum using stencil masks. The resistance was measured at room temperature in air by Keithley 2400 Sourcemeter with time upon UV illuminations with different power densities.

Spectral Measurements: A Bruker Vertex 70 FTIR microspectrometer was used for mid-infrared spectral measurements. All measurements were performed at room temperature in air with a 355 nm solid-state laser at power density of 200 mW cm⁻² unless otherwise specified.

For measurements inside or outside the illuminated region, UV light was coupled into a fiber (1 mm in diameter) and focused on a sample by using an objective lens (15×), so that only a part of the sample (about 66 μm in diameter) was illuminated.

Supporting Information

Supporting Information is available from the Wiley Online Library.

Acknowledgements

Y.D. and Y.X. contributed equally to this work. L.S. thanks Prof. Wenzhong Bao and Prof. Huguen Yan for helpful discussion. The sample fabrications was conducted at Fudan Nano-fabrication Lab and Shanghai synchrotron radiation facility (2017-SSRF-PT-001333). The work was supported by 973 Program (2015CB659400), China National Key Basic Research Program (2016YFA0301100 and 2016YFA0302000) and NSFC (11774063 and 11727811). The research of L.S. was further supported by Science and Technology Commission of Shanghai Municipality (17ZR1442300), State key laboratory of surface physics (ZA2014-01 and KF2015-04), Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, and the Recruitment Program of Global Youth Experts (1000 plans).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

dynamical tuning, graphene, mid-infrared, nanophotonics, plasmonics

Received: October 11, 2017

Revised: December 12, 2017

Published online: January 22, 2018

- [1] A. N. Grigorenko, M. Polini, K. S. Novoselov, *Nat. Photonics* **2012**, *6*, 749.
- [2] F. J. García De Abajo, *ACS Photonics* **2014**, *1*, 135.
- [3] T. Low, P. Avouris, *ACS Nano* **2014**, *8*, 1086.
- [4] F. H. L. Koppens, D. E. Chang, F. Javier García De Abajo, *Nano Lett.* **2011**, *11*, 3370.
- [5] F. Xia, H. Wang, D. Xiao, M. Dubey, A. Ramasubramaniam, *Nat. Photonics* **2014**, *8*, 899.
- [6] Z. Fei, A. S. Rodin, G. O. Andreev, W. Bao, A. S. McLeod, M. Wagner, L. M. Zhang, Z. Zhao, M. Thiemens, G. Dominguez, M. M. Fogler, A. H. Castro Neto, C. N. Lau, F. Keilmann, D. N. Basov, *Nature* **2012**, *487*, 82.
- [7] J. Chen, M. Badioli, P. Alonso-Gonzalez, S. Thongrattanasiri, F. Huth, J. Osmond, M. Spasenovic, A. Centeno, A. Pesquera, P. Godignon, A. Zurutuza Elorza, N. Camara, F. Javier Garcia De Abajo, R. Hillenbrand, F. H. L. Koppens, *Nature* **2012**, *487*, 77.
- [8] S. Xiao, X. Zhu, B. Li, N. A. Mortensen, *Front. Phys.* **2016**, *11*, 026103.
- [9] Q. Guo, F. Guinea, B. Deng, I. Sarpkaya, C. Li, C. Chen, X. Ling, J. Kong, F. Xia, *Adv. Mater.* **2017**, *29*, 1700566.
- [10] D. Ogletree, P. Schuck, A. Weber-Bargioni, N. Borys, S. Aloni, W. Bao, S. Barja, J. Lee, M. Melli, K. Munechika, S. Whitelam, S. Wickenburg, *Adv. Mater.* **2015**, *27*, 5693.
- [11] H. Yan, T. Low, W. Zhu, Y. Wu, M. Freitag, X. Li, F. Guinea, P. Avouris, F. Xia, *Nat. Photonics* **2013**, *7*, 394.
- [12] H. Yan, X. Li, B. Chandra, G. Tulevski, Y. Wu, M. Freitag, W. Zhu, P. Avouris, F. Xia, *Nat. Nanotechnol.* **2012**, *7*, 330.
- [13] X. Zhu, W. Wang, W. Yan, M. B. Larsen, P. Bøggild, T. G. Pedersen, S. Xiao, J. Zi, N. A. Mortensen, *Nano Lett.* **2014**, *14*, 2907.
- [14] Y. Y. Dai, A. Chen, Y. Y. Xia, D. Z. Han, X. H. Liu, L. Shi, J. Zi, *Opt. Express* **2016**, *24*, 20021.
- [15] S. Thongrattanasiri, F. H. L. Koppens, F. Javier Garcia De Abajo, *Phys. Rev. Lett.* **2012**, *108*, 047401
- [16] W. Gao, J. Shu, C. Qiu, Q. Xu, *ACS Nano* **2012**, *6*, 7806.
- [17] M. Jablan, H. Buljan, M. Soljačić, *Phys. Rev. B* **2009**, *80*, 245435
- [18] J. Christensen, A. Manjavacas, S. Thongrattanasiri, F. H. L. Koppens, F. Javier García De Abajo, *ACS Nano* **2012**, *6*, 431.
- [19] E. H. Hwang, S. Das Sarma, *Phys. Rev. B* **2007**, *75*, 205418.
- [20] T. R. Zhan, F. Y. Zhao, X. H. Hu, X. H. Liu, J. Zi, *Phys. Rev. B* **2012**, *86*, 165416.
- [21] Y. Dai, X. Zhu, N. A. Mortensen, J. Zi, S. Xiao, *J. Optics* **2015**, *17*, 065002.
- [22] Z. Fang, Y. Wang, A. E. Schather, Z. Liu, P. M. Ajayan, F. Javier García De Abajo, P. Nordlander, X. Zhu, N. J. Halas, *Nano Lett.* **2014**, *14*, 299.
- [23] L. Ju, B. Geng, J. Horng, C. Girit, M. Martin, Z. Hao, H. A. Bechtel, X. Liang, A. Zettl, Y. R. Shen, F. Wang, *Nat. Nanotechnol.* **2011**, *6*, 630.
- [24] V. W. Brar, M. S. Jang, M. Sherrott, J. J. Lopez, H. A. Atwater, *Nano Lett.* **2013**, *13*, 2541.

- [25] D. Rodrigo, O. Limaj, D. Janner, D. Etezadi, F. Javier García De Abajo, V. Pruneri, H. Altug, *Science* **2015**, *349*, 165.
- [26] H. Hu, X. Yang, F. Zhai, D. Hu, R. Liu, K. Liu, Z. Sun, Q. Dai, *Nat. Commun.* **2016**, *7*, 12334.
- [27] S. Kim, M. S. Jang, V. W. Brar, Y. Tolstova, K. W. Mauser, H. A. Atwater, *Nat. Commun.* **2016**, *7*, 12323.
- [28] D. Rodrigo, A. Tittl, O. Limaj, F. J. García De Abajo, V. Pruneri, H. Altug, *Light: Sci. Appl.* **2017**, *6*, e16277.
- [29] X. Yang, X. Kong, B. Bai, Z. Li, H. Hu, X. Qiu, Q. Dai, *Small* **2015**, *11*, 591.
- [30] H. Hu, F. Zhai, D. Hu, Z. Li, B. Bai, X. Yang, Q. Dai, *Nanoscale* **2015**, *7*, 19493.
- [31] F. Bonaccorso, Z. Sun, T. Hasan, A. C. Ferrari, *Nat. Photonics* **2010**, *4*, 611.
- [32] Q. Bao, K. P. Loh, *ACS Nano* **2012**, *6*, 3677.
- [33] J. Li, L. Niu, Z. Zheng, F. Yan, *Adv. Mater.* **2014**, *26*, 5239.
- [34] V. W. Brar, M. C. Sherrott, M. S. Jang, S. Kim, L. Kim, M. Choi, L. A. Sweatlock, H. A. Atwater, *Nat. Commun.* **2015**, *6*, 7032.
- [35] Z. Fang, S. Thongrattanasiri, A. Schlather, Z. Liu, L. Ma, Y. Wang, P. M. Ajayan, P. Nordlander, N. J. Halas, F. Javier Garcia De Abajo, *ACS Nano* **2013**, *7*, 2388.
- [36] H. Cheng, S. Chen, P. Yu, W. Liu, Z. Li, J. Li, B. Xie, J. Tian, *Adv. Opt. Mater.* **2015**, *3*, 1744.
- [37] Z. Q. Li, E. A. Henriksen, Z. Jiang, Z. Hao, M. C. Martin, P. Kim, H. L. Stormer, D. N. Basov, *Nat. Phys.* **2008**, *4*, 532.
- [38] S. Ryu, L. Liu, S. Berciaud, Y. Yu, H. Liu, P. Kim, G. W. Flynn, L. E. Brus, *Nano Lett.* **2010**, *10*, 4944.
- [39] J. Ito, J. Nakamura, A. Natori, *J. Appl. Phys.* **2008**, *103*, 113712.
- [40] Z. Luo, N. J. Pinto, Y. Davila, A. T. C. Johnson, *Appl. Phys. Lett.* **2012**, *100*, 253108.
- [41] M. Z. Iqbal, M. W. Iqbal, M. F. Khan, J. Eom, *Phys. Chem. Chem. Phys.* **2015**, *17*, 20551.
- [42] P. A. Huidobro, M. Kraft, S. A. Maier, J. B. Pendry, *ACS Nano* **2016**, *10*, 5499.
- [43] N. Jung, N. Kim, S. Jockusch, N. J. Turro, P. Kim, L. Brus, *Nano Lett.* **2009**, *9*, 4133.