Circularly polarized extreme ultraviolet high harmonic generation in graphene

Zi-Yu Chen* and Rui Qin*

National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang 621999, China

E-mail: ziyuch@caep.ac.cn; qinrui.phy@outlook.com

Abstract

Circularly polarized extreme ultraviolet (XUV) radiation is highly interesting for investigating chirality-sensitive light-matter interactions. Recent breakthroughs enable generation of such light sources via high harmonic generation (HHG) from rare gases. There is a growing interest in extending HHG in gases to solids, especially 2D materials, which holds great promise to develop ultra-compact solid-state photonic devices and provide insight into electronic properties of the material itself. However, HHG in graphene driven by terahertz to mid-infrared fields reported so far only generate low harmonic orders, and furthermore no harmonics with circularly polarized drivers. Here, using first-principles simulations within a time-dependent density-functional theory framework, we show that it is possible to generate HHG extending to the XUV spectral region in monolayer extended graphene excited by near-infrared lasers. Moreover, we demonstrate that a single circularly polarized driver is enough to ensure HHG in graphene with circular polarization. The corresponding spectra reflect the threefold rotational symmetry of the graphene crystal. Extending HHG in graphene to the XUV regime and realizing circular polarization represent an important step towards the development of novel nanoscale attosecond photonic devices and numerous applications.
such as spectroscopic investigation and nanoscale imaging of Berry phase, topological properties, magnetic-related and ultrafast spin dynamics in graphene and other 2D materials.

**Keywords**

high harmonic generation; extreme ultraviolet; circular polarization; 2D materials

**Introduction**

Circularly polarized radiation source in the extreme ultraviolet (XUV) spectral regions is a unique and powerful tool for probing chirality-sensitive light-matter interactions, from photoionization in chiral molecules\(^1\) to magnetic properties in solid-state materials.\(^2\) There has been a quest for generating such light sources on the table-top scale. Table-top XUV source is generally produced through high harmonic generation (HHG), an extremely non-linear optical process up-converting driving laser frequency, in rare gases. However, it had been believed circularly polarized high harmonics could not be generated for many years, because electron trajectory undergoes lateral drifting in a circularly polarized driving field so that the electron cannot recollide with its parent ion. In the past few years, intensive efforts have been made towards circular HHG. Use of two counter-rotating circularly polarized laser fields has lead to the breakthrough of circularly polarized high harmonic\(^3\) and isolated attosecond pulse\(^6\) generation experimentally. Later, it was numerically demonstrated that circularly polarized XUV and attosecond pulses can also be generated via HHG from relativistic plasma surfaces.\(^7\)\(^8\)

Recently, there has been a growing interest to extend HHG and related techniques to solid-state systems. HHG in solids not only offers a novel approach to XUV and attosecond photonics, but also provides a new platform to study structure and ultrafast strong-field dynamics in the condensed phase. XUV HHG has been generated in bulk crystals\(^9\)\(^–\)\(^13\) and
demonstrated useful for probing electronic properties, such as reconstruction of bandgap,
retaining energy dispersion profile of conduction band, and measurement of Berry curva-
ture. In contrast to atomic HHG, HHG driven by a single-color circularly polarized laser
field is shown to be possible in bulk solids. Generation of circularly polarized XUV HHG
has been predicted in cubic Si and MgO crystals.

Apart from bulk crystals, nonperturbative HHG in two-dimensional (2D) materials has
also attracted much attention, as they exhibit distinct electronic properties compared
to the bulk. In particular, HHG in graphene, the most popular and promising 2D material
with zero band gap and massless Dirac fermions, has been actively studied both theoretically
and experimentally. With linear energy dispersion, graphene is expected to
display strong nonlinear optical responses. However, the highest harmonic order observed
in extended undoped graphene so far has been limited to less than the 10th order driven by
laser wavelength from terahertz (THz) to mid-infrared, which hampers the possibility of
developing graphene-based compact XUV sources. In addition, several groups have studied
ellipticity dependence of HHG in graphene yet come out with conflicting results. Yoshikawa
et al. show that HHG can be enhanced at a small non-zero laser ellipticity, while Taucer
et al. and Baudisch et al. present an atomic-HHG-like monotonic ellipticity dependence.
Moreover, the reported ellipticity dependences suggest that HHG is greatly suppressed by using circularly polarized driving field. These lead one to question whether circularly polarized
XUV high harmonics can be generated in graphene or not.

In this work, we perform, to our knowledge, the first ab initio calculations of HHG
in monolayer graphene based on the framework of time-dependent density-functional the-
ory (TDDFT). We use the Octopus package and follow the approach introduced by
Tancogne-Dejean et al. Employing more intense light pulse at a higher frequency (1.55
eV), simulation results show high harmonics up to the 21st order can be obtained with a
pump intensity of 6 TW/cm², and thus HHG in graphene can be extended to the XUV spec-
tral regions. We then study ellipticity dependence of HHG in graphene. The results show
that it is possible to generate high harmonics in graphene with a single circularly polarized driving pulse. The corresponding spectra reflect both the centrosymmetry and threefold rotational symmetry of the graphene crystal. Moreover, we demonstrate the generated high harmonics are also circularly polarized. These predictions show the strong potential of circularly polarized XUV HHG in 2D materials as novel ultra-compact XUV photonic sources and in enabling nanoscale imaging and spectroscopic investigation of spin, magnetic, and other chirality-related phenomena in 2D materials.

**Results**

![Graph showing typical waveforms](image1)

Figure 1: (a) Typical waveforms of the applied vector potential (red) and induced electronic current (blue). The 800 nm near-infrared laser has a pulse duration of 15 fs and intensity of 6 TW/cm². (b) Intensity scaling for the 7th harmonic, showing nonperturbative characteristic of the HHG process studied here, especially for intensity above 3 TW/cm². High harmonic spectra (c) up to the 15th order with a driving intensity of 3 TW/cm² and (d) up to the 21st order with a driving intensity of 6 TW/cm², demonstrating the possibility of HHG in graphene extending to the XUV spectral region. The inset of panel (c) shows the crystal structure of monolayer graphene and the definition of the armchair (AC) and zigzag (ZZ) directions.

Typical waveforms of the applied vector potential (red line) and induced electronic current
(blue line) are shown in Figure 1(a). The temporal evolution of the induced current tends to follow the driving laser profile. Distortion and nonlinear response in the current profile can also be seen, which lead to harmonic components in the radiation spectrum. Mid-infrared laser pulses with wavelength of 3.1 $\mu$m$^{26}$ and 4.8 $\mu$m$^{25}$ are used in previous experimental study of HHG in graphene. Here we perform simulations with near-infrared (1.55 eV; 800 nm) light excitation for the first time. Figure 1(b) shows the intensity of 7th-harmonic radiation (blue dots) as a function of the driving laser intensity $I_L$ in the range of 1.5 TW/cm$^2$ and 6 TW/cm$^2$. For $I_L > 3$ TW/cm$^2$, the harmonic intensity scales as $I_L^2$ (orange line) at the highest pump intensity, in agreement with the previous studies.$^{25,26}$ This power law dependence clearly shows the HHG process in this intensity range is in the nonperturbative regime, whereas it should behave as $I_L^7$ dependence (dashed green line) for the 7th harmonic in the perturbative limit. As we are interested in HHG in the nonperturbative regime, simulation results with $I_L > 3$ TW/cm$^2$ are considered in the following.

Figure 1(c) shows the harmonic spectrum generated with a pump laser intensity of 3 TW/cm$^2$. High harmonics up to the 15th orders are obtained. As the laser intensity is further increased to 6 TW/cm$^2$, the corresponding high harmonic spectrum (shown in Fig. 1(d)) covers the 21st order of the fundamental frequency (1.55 eV), well extending to the XUV spectral region. Only odd harmonic orders are present, reflecting the centrosymmetric nature preserved in the crystal lattice. Orienting the linearly polarized fundamental field along the armchair (AC) and zigzag (ZZ) directions of the crystal result in different HHG spectra. The difference is pronounced for higher-order harmonics. Therefore, graphene, though with isotropic Dirac cone, gives rise to anisotropic emission of high harmonics. This is because the band structure is isotropic only in the vicinity of the Dirac points while exhibits strong anisotropy away from the Dirac points, in agreement with previous discussions.$^{32}$

We note that the laser intensity ($I_L > 3$ TW/cm$^2$) required for nonperturbative HHG in graphene in our simulations is larger than the reported value (1.7 TW/cm$^2$) in experiments.$^{25}$ Yet, we believe that our simulations results are being performed in the regime without
damage of the material. We justify our choice of the parameters as following.

First, quite different laser parameters are used in our simulations from those in the experiments. On the one hand, the used laser pulse duration is 15 fs, much shorter than the 70 fs and 25 fs in the experiments. For the same intensity, a shorter pulse duration means less energy contained in the pulse, and thus less energy deposited in the material. Then the material is less likely to be damaged. This is in consistence with the reported damage threshold of $\sim 1.7$ TW/cm$^2$ for the 25 fs laser being larger than $\sim 0.55$ TW/cm$^2$ for the 70 fs laser in the experiments.

On the other hand, the laser wavelength is 800 nm in our simulations, much shorter than the 3.1 $\mu$m and 4.8 $\mu$m used in the experiments. For a shorter laser wavelength, the ponderomotive energy ($U_p \propto I_L \lambda_L^2$) is smaller, which means electrons acquire less energy from the laser field for averaged laser cycles, and thus less damage is possible. This may explain the experimentally measured single-shot damage threshold of graphene as high as $\sim 3$ TW/cm$^2$ irradiated by a 790 nm laser though with a long pulse duration of 50 fs.

We also note that with a laser intensity of 1.7 TW/cm$^2$ and wavelength of 4.8 $\mu$m, harmonics up to the 9th order are observed in the experiments, while in our simulations, with a similar intensity of 1.5 TW/cm$^2$ but a shorter wavelength of 800 nm, the obtained harmonic order is lower, i.e., 7th harmonic is very weak and 9th order is hardly distinguishable,
as shown in Fig. 2(a). In fact, from Fig. 1(b), we see that in our simulations HHG with the 1.5 TW/cm² and 800 nm laser has not even reach the well defined nonperturbative regime yet.

Second, compared with perfect crystals used in simulations, samples used in real experiments usually contain defects and impurities, which can lead to lowered damage threshold. With this in mind, considering the damage threshold being $\sim 3$ TW/cm² for a 790 nm and 50 fs laser in experiments, it is reasonable to expect a higher damage threshold for the 800 nm and 15 fs laser in our simulations, not to mention the laser pulse duration is also shorter.

Furthermore, we present the distinctive frequency spectrum driven by a very high laser intensity of $1 \times 10^{14}$ W/cm², i.e., far above the damage threshold, in Fig. 2(b). The spectrum now becomes quite noisy without well defined harmonic peaks at odd harmonic orders. Moreover, the spectrum does not show intensity decay with increasing harmonic frequency. In contrast, the clean and well defined odd-order harmonic spectra decaying with frequency in Figs. 1(c)–(d) show strong evidence that in these simulations the laser intensity is indeed below the damage threshold of the materials.

Figure 3: Evolution of the HHG spectrum as a function of time, i.e., spectrogram of the HHG process for laser polarization orientating along the (a) ZZ and (b) AC direction respectively, revealing high harmonic emission in phase at each field peak, suggesting intraband contribution is the dominate mechanism for the HHG in this study. The white curves are the waveform of the laser pulses. The pump laser intensity is 3 TW/cm². Colorbar represents spectral intensity (arb. units) in logarithmic scale.

The mechanisms responsible for nonperturbative HHG in solids can be attributed to
interband transition and intraband contribution. The former corresponds to direct electron-hole recombination, similar to the three-step mode of gas HHG, and thus trajectories can be observed in the spectrogram, i.e., a 2D map of the emission in time and frequency. The latter mechanism corresponds to carriers accelerated within the energy bands driven by the laser field, and thus the harmonics are emitted in phase at each laser peak when the acceleration is maximum. To gain insight into the physical dynamics underlying XUV emission in our calculations, we performed a time-frequency wavelet analysis of the harmonic emission. Figures 3(a)-(b) show the spectrograms with pump intensity of 3 TW/cm² for laser polarization along the ZZ and AC directions, respectively. It clearly shows the high harmonics are emitted as discrete bursts in phase at each peak of the laser field corresponding to maximum electron acceleration. This in-phase signature in the spectrograms, instead of recombination trajectories, indicates intraband contribution being the dominate mechanism in the HHG process we studied here, in agreement with previous model calculations for HHG in graphene driven by a mid-infrared laser pulse.

Figure 4: Ellipticity dependence of the peak harmonic intensity for different harmonic orders. The major axis of the elliptical polarization of the driving field is fixed relative to the (a-d) ZZ and (e-h) AC directions. The driving field intensity is 3 TW/cm². For each harmonic order, intensity of the field components parallel ($I_\parallel$) or perpendicular ($I_\perp$) to the major axis of the laser polarization is normalized by the maximum intensity between the two ($\max\{I_\parallel, I_\perp\}$). The total intensity ($I_{\text{total}} = I_\parallel + I_\perp$) is normalized by the maximum $I_{\text{total}}$. For the 5th and 7th harmonics, harmonic intensity is non-zero with circularly polarized driving pulse, in contrast to the 3rd and 9th harmonics.
Figure 4 illustrates the ellipticity dependence of the peak intensity of the 3rd, 5th, 7th, and 9th harmonic radiation. The major axis of the elliptical polarization of the driving laser is fixed relative to either the ZZ or the AC direction of the crystal. The incident pulse energy is constant while changing the ellipticity. For each harmonic order, the plotted intensity of the field components parallel ($I_\parallel$) or perpendicular ($I_\perp$) to the major axis of the laser polarization is normalized by the maximum intensity between the two ($\max\{I_\parallel, I_\perp\}$); while the total intensity ($I_{\text{total}} = I_\parallel + I_\perp$) is normalized by the maximum $I_{\text{total}}$. HHG in graphene studied here displays complex ellipticity dependence. We observe different dependence trend for different harmonic orders. For the 3rd harmonics, $I_\parallel$ decreases gradually as increasing ellipticity, while $I_\perp$ is enhanced at a finite laser ellipticity and then drops. These features are consistent with the essential results reported by Yoshikawa et al.\textsuperscript{25} On the other hand, the monotonic decrease of $I_\parallel$ and $I_{\text{total}}$ with ellipticity is in agreement with the observations of Taucer et al.\textsuperscript{26} and Baudisch et al.\textsuperscript{27} The fact that different intensity is measured may explain the discrepancy between the previous results. Apart from the 3rd harmonic, other harmonic orders show distinct ellipticity dependence. For the 5th and 7th harmonics, $I_\parallel$ and $I_{\text{total}}$ firstly drop and then increase (except for the 7th harmonic at AC configuration where they decrease monotonically), while $I_\perp$ gradually increase with ellipticity. For the 9th harmonics, all the intensities display similar ellipticity dependence, i.e., gradually increasing to maximum values before decreasing close to zero. These results show the possibility of tuning and enhancing harmonic emission in graphene by using a finite ellipticity of the driving field.

We note that for the 5th and 7th harmonics, the harmonic yield $I_\perp$ for circularly polarized driver is higher than a linearly polarized driver. This is easily understandable, as the driving component in the perpendicular direction increases with the laser ellipticity. Yet, in some cases (see Figs. 4(b),(c) and (f)), the overall harmonic yield for circularly polarized driver is still higher than a linearly polarized driver. This has not been reported before. We attribute this to the higher photon energy (1.55 eV) and higher laser intensity employed.
here. In this case, deeper electron bands are involved in the HHG process. As mentioned earlier, the band structure is isotropic in the vicinity of the Dirac cone but highly anisotropic away from the Dirac point. Since a circularly polarized laser can drive carriers to explore the energy band along different directions, it may experience more anharmonicity than just exploring one direction driven by a linearly polarized driver. Therefore, it is possible to get higher harmonic yield for a circularly polarized driver. Previous experiments used much lower photon energy and laser intensity. The HHG process may thus in a markedly different scenario that only involves the bands near the Dirac cone, where the charge carriers re-encounter the lowest energy point twice per field cycle driven by linearly polarized fields while exhibit spiraling trajectories with canceled anharmonic response in the Dirac potential driven by circularly polarized fields, as illustrated by Baudisch et al.\textsuperscript{27}. Then the harmonic yield is lower for circularly polarized driver in these studies.

Figure 5: (a) High harmonic spectra in graphene driven by a single circularly polarized laser field with intensity of 6 TW/cm\textsuperscript{2}. Every third harmonic order is missing, reflecting the threefold rotational symmetry of the graphene crystal. 3D plots of the electric field vector (purple) of the (b) 11th and (c) 13th harmonic demonstrate the generated high harmonics are circularly polarized. Also shown in panels (b) and (c) are the waveforms of the two orthogonal electric field components \(E_x\) (green) and \(E_y\) (blue), as well as the projection of \(E_x - E_y\) (gray).

The fact that strong harmonics can be generated by a circularly polarized driver is in contrast to atomic gas harmonics, where a single circularly polarized laser cannot generate harmonics. To better illustrate the HHG in graphene, we plot the harmonic spectra driving by a circularly polarized laser with a higher intensity of 6 TW/cm\textsuperscript{2} in Fig. 5(a). Up to 19th harmonic can be observed. An essential feature is that only the harmonic orders of
$n = 3m \pm 1 \ (m = 1, 2, 3, \cdots )$ are present, while every third one with $n = 3m$ is missing. This selection rule is a signature of threefold rotational symmetry preserved in the interaction system, similar to the cases of HHG driven by two-color counter-rotating circularly polarized laser fields from gases\textsuperscript{4,35,36} or plasmas.\textsuperscript{37} The selection rule can be deduced from simple arguments based on symmetry and conservation laws for energy, parity, and spin angular momentum.\textsuperscript{4,17,35–37} Therefore, this spectral feature clearly reflects the threefold rotational symmetry property of the graphene lattice, since the circularly polarized field is isotropic in the polarization plane. Thus the HHG spectrum provides a purely optical method of probing symmetric properties of 2D materials.

More importantly, the generated high harmonics are also circularly polarized. To demonstrated this, we show the 3D plot of the electric field vector of the 11th and 13th harmonic order in Figs. 5(b) and (c), respectively. It can be seen clearly that the polarization state of the high harmonics is indeed circular. This is also true for the 5th and 7th harmonics. Similar to the case of HHG driven by bicircular fields,\textsuperscript{4,37} the alternative harmonic orders exhibit opposite helicity, in consistent with the argument based on symmetry and conservation laws mentioned above.\textsuperscript{4,17,35–37} Generation of circularly polarized high harmonics extending to the XUV spectral region by a single-color laser pulse in 2D materials may open a door for developing novel ultra-compact photonic devices and new spectroscopy and imaging techniques for investigating chirality-phenomena at nanoscale. Besides, using cycle-level driving laser pulse, it should be possible to generate isolated attosecond XUV pulse with circular polarization in graphene, which can be useful for applications such as probing ultrafast chiral electronic and spin dynamics.

**Discussion**

In summary, we have investigated HHG in graphene driven by in-plane near-infrared laser fields using an *ab initio* approach based on TDDFT. The HHG processes are proven to be
in the nonperturbative regime. The calculated spectra show high harmonics well extending to the XUV spectral region can be generated in graphene. Spectrogram of the HHG suggests intraband contribution is the dominate mechanism responsible for the HHG in this study. Ellipticity dependence for different harmonic orders is analysed, which shows HHG is possible driven by a single circularly polarized laser field in graphene. The corresponding harmonic spectra, reflecting the threefold rotational symmetry of graphene crystal, may offer a purely optical method for probing symmetric properties of 2D materials. Moreover, the corresponding high harmonics are demonstrated to be circularly polarized. The predictions of this study, extending the limit of existing graphene-based HHG sources to the XUV spectral region and adding a new degree of freedom of polarization state, may have impact on many applications such as developing on-chip attosecond XUV photonic devices at nanoscale, imaging of Berry phase and chirality, and measurement of magnetic and ultrafast spin dynamics in graphene and other 2D materials.

**Methods**

Graphene structures are studied by using the semiperiodic supercell model, where a hexagonal primitive cell contains two carbon atoms. We optimize the graphene structure, and the C-C bond length is found to be 1.413 Å. Vacuum space of 30 Bohr, including 3 Bohr of absorbing regions on each side of the monolayer, is chosen to eliminate the interactions between adjacent graphene sheets and avoid reflection in the spectral region of interest. The Octopus package\(^{38-40}\) is employed to perform the simulations. The ground state electronic structures and geometric structure relaxation are performed within the density functional theory (DFT) framework in the local density approximation (LDA).\(^{41}\) Time evolution of the wave functions and time-dependent electronic current are calculated by propagating the Kohn-Sham equations in real time and real space\(^{42}\) within the time-dependent DFT (TDDFT) framework in the adiabatic LDA (ALDA). The real-space spacing is 0.4 Bohr. A
60 × 60 × 1 Monkhorst-Pack k-point mesh for the BZ sampling is used, and the sampling is
scaled according to the size of the supercells. The fully relativistic Hartwigs, Goedecker,
and Hutter (HGH) pseudopotentials are adopted.

The laser is described in the velocity gauge. The Ti:sapphire laser pulse has a wavelength
of $\lambda_L = 800$ nm (corresponding to a photon energy of 1.55 eV) and pulse duration of $\tau = 15$ fs. The pulse envelope profile is sin-squared and the carrier-envelope phase is taken to be
$\Phi = 0$. The peak laser intensity is in the range of $I_L = 1.5 \times 10^{12}$ W/cm$^2$ and $I_L = 6 \times 10^{12}$
W/cm$^2$. The laser field is normally incident onto the graphene sample so that the driving
electric field is in the plane of the monolayer.

The HHG spectrum was calculated from the time-dependent electronic current $j(r, t)$ as:

$$\text{HHG}(\omega) = \left| \mathcal{F}\mathcal{T} \left( \frac{\partial}{\partial t} \int j(r, t) \, d^3r \right) \right|^2,$$

where $\mathcal{F}\mathcal{T}$ denotes the Fourier transform.

References

1. Garcia, G. A.; Nahon, L.; Daly, S.; Powis, I. Vibrationally induced inversion of photo- 
etron forwardbackward asymmetry in chiral molecule photoionization by circularly polarized light. Nat. Commun. 2013, 4, 2132.

2. von Korff Schmising, C.; Pfau, B.; Schneider, M.; Günther, C. M.; Giovannella, M.; Perron, J.; Vodungbo, B.; Müller, L.; Capotondi, F.; Pedersoli, E. et al. Imaging ultrafast demagnetization dynamics after a spatially localized optical excitation. Nat. Photonics 2014, 112, 217203.

3. Ferré, A.; Handschin, C.; Dumergue, M.; Burgy, F.; Comby, A.; Descamps, D.; Fabre, B.; Garcia, G. A.; Gneaux, R.; Merceron, L. et al. A table-top ultrashort light source in the extreme ultraviolet for circular dichroism experiments. Nat. Photonics 2015, 9, 93–98.
4. Kfir, O.; Grychtol, P.; Turgut, E.; Knut, R.; Zusin, D.; Popmintchev, D.; Popmintchev, T.; Nembach, H.; Shaw, J. M.; Fleischer, A. et al. Generation of bright phase-matched circularly-polarized extreme ultraviolet high harmonics. *Nat. Photonics* **2015**, *9*, 99–105.

5. Hickstein, D. D.; Dollar, F. J.; Ellis, P. G. J. L.; Knut, R.; Hernández-García, C.; Zusin, D.; Gentry, C.; Shaw, J. M.; Fan, T.; Dorney, K. M. et al. Non-collinear generation of angularly isolated circularly polarized high harmonics. *Nat. Photonics* **2015**, *9*, 743–750.

6. Huang, P.-C.; Hernández-García, C.; Huang, J.-T.; Huang, P.-Y.; Lu, C.-H.; Rego, L.; Hickstein, D. D.; Ellis, J. L.; Jaron-Becker, A.; Becker, A. et al. Polarization control of isolated high-harmonic pulses. *Nat. Photonics* **2018**, *12*, 349–354.

7. Chen, Z.-Y.; Pukhov, A. Bright high-order harmonic generation with controllable polarization from a relativistic plasma mirror. *Nat. Commun.* **2016**, *7*, 12515.

8. Ma, G.; Yu, W.; Yu, M. Y.; Shen, B.; Veisz, L. Intense circularly polarized attosecond pulse generation from relativistic laser plasmas using few-cycle laser pulses. *Opt. Express* **2016**, *24*, 10057.

9. Ghimire, S.; DiChiara, A. D.; Sistrunk, E.; Agostini, P.; DiMauro, L. F.; Reis, D. A. Observation of high-order harmonic generation in a bulk crystal. *Nature Physics* **2011**, *7*, 138–141.

10. Schubert, O.; Hohenleutner, M.; Langer, F.; Urbanek, B.; Lange, C.; Huttner, U.; Golde, D.; Meier, T.; Kira, M.; Koch, S. W. et al. Sub-cycle control of terahertz high-harmonic generation by dynamical Bloch oscillations. *Nature Photonics* **2014**, *8*, 119–123.

11. Vampa, G.; Hammond, T. J.; Thiré, N.; Schmidt, B. E.; Légaré, F.; McDonald, C. R.;
Brabec, T.; Corkum, P. B. Linking high harmonics from gases and solids. *Nature* 2015, 522, 462–464.

12. Ndabashimiye, G.; Ghimire, S.; Wu, M.; Browne, D. A.; Schafer, K. J.; Gaarde, M. B.; Reis, D. A. Solid-state harmonics beyond the atomic limit. *Nature* 2016, 534, 520523.

13. You, Y. S.; Reis, D. A.; Ghimire, S. Anisotropic high-harmonic generation in bulk crystals. *Nature Physics* 2017, 13, 345349.

14. Vampa, G.; Hammond, T.; Thiré, N.; Schmidt, B.; Légaré, F.; McDonald, C.; Brabec, T.; Klug, D.; Corkum, P. All-Optical Reconstruction of Crystal Band Structure. *Physical Review Letters* 2015, 115, 193603.

15. Luu, T. T.; Garg, M.; Kruchinin, S. Y.; Moulet, A.; Hassan, M. T.; Goulielmakis, E. Extreme ultraviolet high-harmonic spectroscopy of solids. *Nature* 2015, 521, 498502.

16. Luu, T. T.; Wrner, H. J. Measurement of the Berry curvature of solids using high-harmonic spectroscopy. *Nature Communications* 2018, 9, 916.

17. Tancogne-Dejean, N.; Mcke, O. D.; Krtner, F. X.; Rubio, A. Ellipticity dependence of high-harmonic generation in solids originating from coupled intraband and interband dynamics. *Nature Communications* 2017, 8, 745.

18. Liu, H.; Li, Y.; You, Y. S.; Ghimire, S.; Heinz, T. F.; Reis, D. A. High-harmonic generation from an atomically thin semiconductor. *Nature Physics* 2017, 13, 262265.

19. Tancogne-Dejean, N.; Rubio, A. Atomic-like high-harmonic generation from two-dimensional materials. *Science Advances* 2018, 4, eaa05207.

20. Cox, J. D.; Marini, A.; de Abajo, F. J. G. Plasmon-assisted high-harmonic generation in graphene. *Nature Communications* 2017, 8, 14380.

21. Mikhailov, S. A. Non-linear electromagnetic response of graphene. *Europhysics Letters* 2007, 79, 27002.
22. Al-Naib, I.; Sipe, J. E.; Dignam, M. M. High harmonic generation in undoped graphene: Interplay of inter- and intraband dynamics. *Physical Review B* **2014**, *90*, 245423.

23. Al-Naib, I.; Sipe, J. E.; Dignam, M. M. Nonperturbative model of harmonic generation in undoped graphene in the terahertz regime. *New Journal of Physics* **2015**, *17*, 113018.

24. Bowlan, P.; Martinez-Moreno, E.; Reimann, K.; Elsaesser, T.; Woerner, M. Ultrafast terahertz response of multilayer graphene in the nonperturbative regime. *Physical Review B* **2014**, *89*, 041408(R).

25. Yoshikawa, N.; Tamaya, T.; Tanaka, K. High-harmonic generation in graphene enhanced by elliptically polarized light excitation. *Science* **2017**, *356*, 736738.

26. Taucer, M.; Hammond, T. J.; Corkum, P. B.; Vampa, G.; Couture, C.; Thir, N.; Schmidt, B. E.; Lgar, F.; Selvi, H.; Unsuree, N. *et al.* Nonperturbative harmonic generation in graphene from intense midinfrared pulsed light. *Physical Review B* **2017**, *96*, 195420.

27. Baudisch, M.; Marini, A.; Cox, J. D.; Zhu, T.; Silva, F.; Teichmann, S.; Massicotte, M.; Koppens, F.; Levitov, L. S.; Garca de Abajo, F. J. *et al.* Ultrafast nonlinear optical response of Dirac fermions in graphene. *Nature Communications* **2018**, *9*, 1018.

28. Runge, E.; Gross, E. K. U. Density-Functional Theory for Time-Dependent Systems. *Physical Review Letters* **1984**, *52*, 997–1000.

29. van Leeuwen, R. Causality and Symmetry in Time-Dependent Density-Functional Theory. *Physical Review Letters* **1998**, *80*, 12801283.

30. Castro, A.; Marques, M.; Alonso, J. A.; Rubio, A. Optical properties of nanostructures from time-dependent density functional theory. *J. Comp. Theoret. Nanoscience* **2004**, *1*, 231–255.
31. Tancogne-Dejean, N.; McKe, O. D.; Krtner, F. X.; Rubio, A. Impact of the Electronic Band Structure in High-Harmonic Generation Spectra of Solids. *Physical Review Letters* **2017**, *118*, 087403.

32. Qin, R.; Chen, Z.-Y. Strain-controlled high harmonic generation with Dirac fermions in silicene. *arXiv preprint* **2018**, arxiv:1805.10773.

33. Roberts, A.; Cormode, D.; Reynolds, C.; Newhouse-Illige, T.; LeRoy, B. J.; Sandhu, A. S. Response of graphene to femtosecond high-intensity laser irradiation. *Appl. Phys. Lett.* **2011**, *99*, 051912.

34. Vampa, G.; Brabec, T. Merge of high harmonic generation from gases and solids and its implications for attosecond science. *Journal of Physics B* **2017**, *50*, 083001.

35. Fleischer, A.; Kfir, O.; Diskin, T.; Sidorenko, P.; Cohen, O. Spin angular momentum and tunable polarization in high-harmonic generation. *Nat. Photonics* **2014**, *8*, 543–549.

36. Pisanty, E.; Sukiasyan, S.; Ivanov, M. Spin conservation in high-order-harmonic generation using bicircular fields. *Phys. Rev. A* **2014**, *90*, 043829.

37. Chen, Z.-Y. Spectral control of high harmonics from relativistic plasmas using bicircular fields. *Phys. Rev. E* **2018**, *97*, 043202.

38. Andrade, X.; Strubbe, D. A.; Giovannini, U. D.; Larsen, A. H.; Oliveira, M. J. T.; Alberdi-Rodriguez, J.; Varas, A.; Theophilou, I.; Helbig, N.; Verstraete, M. *et al.* Real-space grids and the Octopus code as tools for the development of new simulation approaches for electronic systems. *Physical Chemistry Chemical Physics* **2015**, *17*, 31371–31396.

39. Castro, A.; Appel, H.; Oliveira, M.; Rozzi, C.; Andrade, X.; Lorenzen, F.; Marques, M.; Gross, E.; Rubio, A. octopus: a tool for the application of time-dependent density functional theory. *Phys. Stat. Sol. B* **2006**, *243*, 2465–2488.
40. Andrade, X.; Alberdi-Rodriguez, J.; Strubbe, D. A.; Oliveira, M. J. T.; Nogueira, F.; Castro, A.; Muguerza, J.; Arruabarrena, A.; Louie, S. G.; Aspuru-Guzik, A. et al. Time-dependent density-functional theory in massively parallel computer architectures: the octopus project. *J. Phys.: Cond. Matt.* **2012**, **24**, 233202.

41. Marques, M. A. L.; Oliveira, M. J. T.; Burnus, T. Libxc: a library of exchange and correlation functionals for density functional theory. *Comput. Phys. Commun.* **2012**, **183**, 2272–2281.

42. Castro, A.; Marques, M.; Rubio, A. Propagators for the time-dependent Kohn-Sham equations. *J. Chem. Phys.* **2004**, **121**, 3425–3433.

**Acknowledgement**

We acknowledge financial support from the National Natural Science Foundation of China (NSFC) (11705185) and the Presidential Fund of China Academy of Engineering Physics (CAEP) (YZJLX2017002).