Extreme nonlinear strong-field photoemission from carbon nanotubes

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Strong-field photoemission produces attosecond (10^-18 s) electron pulses that are synchronized to the waveform of the incident light. This nonlinear photoemission lies at the heart of current attosecond technologies. Here we report a new nonlinear photoemission behaviour—the nonlinearity in strong-field regime sharply increases (approaching 40th power-law scaling), making use of sub-nanometric carbon nanotubes and 800 nm pulses. As a result, the carrier-envelope phase sensitive photoemission current shows a greatly improved modulation depth of up to 100% (with a total modulation current up to 2 nA). The calculations reveal that the behaviour is an interplay of valence band optical-field emission with charge interaction, and the nonlinear dynamics can be tunable by changing the bandgap of carbon nanotubes. The extreme nonlinear photoemission offers a new means of producing extreme temporal-spatial resolved electron pulses, and provides a new design philosophy for attosecond electronics and photonics.
Strong-field photoemission occurs when the optical-field is sufficiently strong to bend the vacuum barrier at the material surface, and then a purely perturbative description of the emission process in the photon-driven picture is no longer sufficient. In such a regime, electron emission is controlled by carrier waveform of the laser pulse rather than its envelope, and occurs in a fraction of an optical cycle. By employing near-infrared or visible laser pulses, it is possible to generate electron pulses with an attosecond temporal resolution and with a high degree of synchronization to the incident optical waveform. Not only does this advance time-resolved electron characterization into an attosecond time domain, but it also provides attosecond control and measurement methodology. In recent years, the emerging strong-field physics at the nanoscale solids becomes a hot research topic, as it combines attosecond processes with nanoscales. This not only brings a unique and sometimes unexpected strong-field phenomena due to the distinctive electronic structure of nanoscale solids, but is also promising for realizing highly integrated attosecond instruments and devices. In addition, the local field enhancement of nanoscale solids allows to access strong-field regime at a relatively low laser intensity.

As the optical-field strength \( F \) increases, photoemission may transit into a strong-field regime, marked by the Khodysh parameter \( y = \sqrt{2} \frac{m e F}{\epsilon_0} \), where \( \omega \) is optical frequency, \( \Phi \) is work function, \( m \) is the mass of the electron and \( e \) is its charge, and \( \beta \) is the field enhancement. When fully accessing a strong-field regime \( (y < 1) \), the optical-field is strong enough to create a penetrable barrier, and electron tunneling takes place from states within the vicinity of the Fermi level, which is also called as a penetrable barrier, and electron tunneling takes place from states above the Fermi level. This will conceal the intrinsic OFE behavior of the CK edge can be comparable to or even larger than that from the CB (Fig. 1c). Therefore, the transition into VB tunneling emission may depart from CB tunneling emission, and behave as an upward bending of the \( I - F \) curve alongside with an extremely high \( K \), as shown in Fig. 1d. The sharpness of the bending, referred to as the \( K \) of the \( I - F \) curve, should be proportional to the bandgap. The behavior has been observed in static-field emission from semiconductors, which is expected to be observed in OFE in principle.

Indeed, we observe that the \( I - F \) curve bends up dramatically from the conventional OFE regime, with a greatly enhanced high nonlinearity \( (K = 40) \). Then, we obtain a high CEP modulation depth up to 100%, with a high modulation current up to 2 nA, simply by using a few-cycle ultrafast oscillator and a source meter. The underlying mechanism of the behavior is believed to be an interplay of VB-OFE together with charge interaction, which is supported by quantum-mechanical time-dependent density functional theory (TDDFT) calculations and classical two-step Simplemmer model calculations. Our measurements are informative for designs of future ultrafast, ultrabright nanostructured photocathodes, as well as extreme sensitive CEP detectors. From a more general perspective, our work takes a step toward improving temporal resolution of strong-field-driven, attosecond science and technology.

Results
Achieving semiconducting CNT cluster emitter. A single-wall CNT cluster, grown by chemical vapor deposition method, is employed as the emitter (see the “Methods” section for materials synthesis). The diameter of the cluster is 2 μm. Each CNT in the cluster has a sub-nanometric tip. By assuming a random distribution of CNT chiralities, one-third of CNTs in the cluster is metallic tubes, while others are semiconducting tubes. Compared with semiconducting CNTs, the metallic ones have a superior OFE current, due to the higher electron density at their Fermi level. This will conceal the intrinsic OFE behavior of semiconducting CNTs. Therefore, to reveal the OFE behavior of semiconducting CNTs, the metallic ones must be removed from the cluster. In the present experiments, we applied an aging process—illuminate the emitter by a strong enough aging laser pulse to reach a current level beyond the threshold (saturation current), and then the metallic tubes will be removed due to overload, while the semiconducting tubes survive. A similar method has been successfully employed to remove metallic CNTs from CVD-grown horizontal CNT films for a semiconducting CNT transistor. In the present work, the aging process opens the bandgap of the entire CNT cluster.

Extremely nonlinear \( I - F \) curve. Typically, the \( I - F \) curves obtained by using 100-fs laser pulses with a central wavelength of 820 nm (see Methods for experiments), before and after applying an aging laser pulse with 1.4 V nm\(^{-1}\) optical-field strength, are shown in Fig. 2a, b. Before aging, the photoemission is believed to be dominant by metallic tubes, through which the \( I - F \) curve is shown in Fig. 2a. The inset shows the scanning electron microscopy (SEM) image of the as-grown CNT cluster. The low-field section of the curve can be fitted to multiphoton photoemission formalism, \( I \propto F^N \). We find \( N = 6 \) for the as-grown CNT cluster (with a photon energy \( h\nu = 1.55 \text{ eV} \)). However, as the work function of CNT \( \Phi_{\text{CNT}} \approx 4.4 \text{ eV} \), we expect \( N = 3 \). The previous experiment on gold nanotips has identified the similar increases, which were speculated to be attributed to either geometry effect or deeper energy band contribution. With \( F \) increasing, the
**Fig. 1** Operation principle of extreme nonlinear OFE. 

**a** Diagram of OFE from CNT. Electrons (blue balls) are emitted from semiconducting CNT, driven by a negative half-cycled (red line) strong electromagnetic field of a femtosecond laser. 

**b** Diagram of CB-dominated OFE (CB-OFE) that occurs at a relatively low optical-field strength. The electron-filling states (orange) in allowed bands (purple lines) follow the Fermi–Dirac distribution near Fermi level ($E_F$). Red and blue lines represent the periodical vacuum level driven by a strong optical-field in negative and positive cycles, respectively, with a circular frequency of $\omega$. Purple balls present the tunneling electrons. 

**c** Diagram of transition into VB-dominated OFE (VB-OFE) that occurs when the optical-field strength is increasing. 

**d** Illustration of the nonlinear photoemission $I$–$F$ curve in log–log plot. The upward bending of the curve is a result of transition from CB-OFE (green line) to VB-OFE (red line). Both CB-OFE and VB-OFE follow the FN form ($\gamma < 1$). The difference in emission rates is induced by different electron amounts in CB and VB. Multiphoton photoemission occurs at a low driving field limit ($\gamma > 1$)

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**Fig. 2** Extreme nonlinear OFE current. 

**a** Experimentally obtained log–log plot of optical-field ($F$) dependent total photoemission current ($I$) for a CNT cluster before aging, driven by 100-fs laser pulses with a central wavelength of 820 nm. Two linear behaviors are observed, as shown by different colors: multiphoton photoemission (MPP) (gray pentagonal dots); OFE (green square dots). The inset shows the scanning electron microscopy (SEM) image of the emitter. Scale bar is 2 $\mu$m. 

**b** $I$–$F$ curve of aged CNT cluster in which the metallic tubes have been removed. Three linear behaviors are observed: MPP (gray pentagonal dots); CB-OFE (green square dots); VB-OFE (purple circular dots). An extremely high slope of $K =$ 40 (dashed line) was observed. The inset shows the SEM image of the emitter. Scale bar is 2 $\mu$m. 

**c** CEP-stabilized measurement of the $I$–$F$ curve of the same emitter, by using 7-fs few-cycle laser pulses centered around 800 nm. A slope of $K =$ 40 is obtained as well. 

**d** The CEP-dependent photoemission current at a fixed laser intensity with a peak $F =$ 1.3 V nm$^{-1}$ with a cosine fit (solid line)
The $I$–$F$ curve of the aged CNT cluster emitter reveals a totally different photoemission behavior (Fig. 2b). The inset shows the SEM image of the aged CNT cluster, which shows a great shrink of the apex due to the laser annealing and removing of metallic tubes. At this stage, the photoemission is believed to be dominated by semiconducting tubes. Therefore, photoemission current is greatly reduced at the same optical-field strength, due to the greatly reduced electron density of states (DOS) near Fermi level. The $I$–$F$ curve behaves as a conventional strong-field photoemission at low-field section ($F < 1.1$ V nm$^{-1}$), with a transition from the multiphoton regime to a strong-field regime at $F > 1.3$ V nm$^{-1}$ (corresponding to $\gamma > 0.7$), where the curve departs from the conventional OFE regime and bends up sharply. This behavior is believed to be the OFE from VB states of semiconducting tube. In this unique OFE process, an ultrahigh photoemission nonlinearity is observed—the $I$–$F$ curve shows extremely high $K=40$, which is much higher than all previous findings.$^{25,26,29,30}$

**Highly CEP-sensitive photoemission.** Having observed the extreme strong-field photoemission behavior, we next undertake the CEP-dependent photoemission measurements.$^{26,27}$ Ultra-short laser pulses of around three optical cycles (7-fs pulse duration) with an 800-nm central wavelength are used (see Methods for experiment details). The CEP-stabilized measurement of an $I$–$F$ curve is shown in Fig. 2c. In this measurement, the total photoemission current is greatly reduced compared with the 100-fs case (Fig. 2b), due to a greatly reduced pulse width. Therefore, only the third region (VB-OFE regime) at the high $F$ section in the $I$–$F$ curve is clearly observed, in which $I$ is above the noise current level (10$^{-11}$ A). In the high $F$ section (corresponding to $\gamma < 0.66$), a similarly high nonlinearity ($K = 40$) is observed. Then, we fixed the laser intensity ($F = 1.3$ V nm$^{-1}$), and controlled the CEP ($\Delta \Phi_{\text{CEP}}$) for photoemission measurements, as presented in Fig. 2d (see Supplementary Fig. 2 for more typical curves). As expected, in the extreme nonlinear VB-OFE regime, $I$ is modulated effectively by changing the CEP.$^{27}$ By tuning CEP for $6\pi$, the measured data points can be fitted to a Cosine curve quite well, providing solid evidence of a strong-field photoemission mechanism.$^{8}$ The modulation depth reaches up to 100%, which is around twice as high as previously reported values obtained by using metallic tips.$^{27}$ The total modulation current reached up to 2 nA, which is beyond the state-of-the-art techniques (around 3 pA)$^{26}$. This result clearly shows that full access to the VB-OFE regime can offer more sensitive control of the photoemission process with CEP, which shows promise for a sensitive CEP detector simply by using a source meter, and then further improvement of the temporal precision of attosecond measurements and control.$^{11}$

**Calculated electron dynamics by using TDDFT.** After the demonstration of such extreme nonlinear strong-field photoemission behavior, we then theoretically depict the difference in photoemission behaviors from the metallic tube and semiconducting tubes. We calculate the photoemission process by using the framework of TDDFT, which covers both the photon (weak) and field (strong) regimes in a single description.$^{40,41}$ Calculations are performed for two single-walled CNT models—zigzag (10,0) semiconducting tube and armchair (6,6) metallic tube (see Supplementary Fig. 3a, b for DOS). The diameter of both models is smaller than 1 nm, which is within the range of tube diameters used in the experiments (see Supplementary Fig. 4c for Raman). An incident Gaussian light pulse with an 800-nm central wavelength and a full width at half maximum of 7 fs is used in our calculations. The photoemission current at the tips is calculated (see Methods). The calculated $I$–$F$ curves of the two models are shown in Fig. 3a, b. We observe the expected photoemission behaviors for both metallic and semiconducting models. As shown in Fig. 3a, the curve can be fitted to a power-law scaling, which indicates a multiphoton photoemission regime. The curve bends down at high $F$ section, which is an evidence of accessing the OFE regime. No curve bending up is observed in metallic models, which is consistent with all the findings in this work and literatures. As shown in Fig. 3b, the simulated curve of semiconducting model clearly shows an upward bending and deviation from conventional OFE scaling, which is consistent with the experimental observation in Fig. 2b.

Compared with the experimental results, the second part of the curve (CB-OFE regime) is much less prominent—the photoemission entered VB-OFE directly from photon-driven photoemission. The present model cannot reproduce the behavior of CB-OFE mainly because the CB is almost empty at low temperature. The laser heating effect may be involved in the experiments; however, this cannot be reproduced as only one laser pulse is simulated. In addition, it should also be noticed that the curve slope is much lower than the experimental results, which is because of a much smaller distance of the current-collection plane (only 0.2 nm, see Supplementary Fig. 3c) in the present model. The charge interaction, which is intrinsically considered in TDDFT, may greatly affect the calculated photoemission current. Due to the strong charge interaction at near field, the propagation of low kinetic energy electrons may be greatly suppressed. Therefore, at far field, the calculated results should be close to the experimental results. To confirm such a reason, we calculated the current at different plane distances, as shown in Supplementary Fig. 3d, which shows that the slope of the curve is exponentially increasing with the plane distance increasing. Further increasing the distance, the value of the slope may saturate to a constant that approaches the experimental result. However, this will cost a lot more calculation resources, and is impractical based on the current calculation ability. Besides, the realistic micrometer-long CNT contains much more electrons than the simulated model, which have more electrons accumulated at the tip area due to the “lightning rod effect”. This induces a much higher field enhancement factor, and thus contributes to the extreme-large slope observed in the experiment as well. As complements, we state three other methods to count the emitted electrons (see Supplementary discussion of the TDDFT simulation results and Supplementary Figs. 5–7).

As speculated above, the curve bending up is due to the electron tunneling from VB states. To examine this speculation, we calculated the excitation behaviors by tracking the changes of electrons in different energy levels at different $F$ in three different regimes pointed by arrows in Fig. 3b (see Methods). With a lower optical-field ($F = 1$ V nm$^{-1}$, Fig. 3c), the electrons are mainly excited from the states around an energy level of $-1.5$ eV, which is far from the valence band maximum (VBM) at $-0.5$ eV. This difference indicates a photon-driven regime, which occurs to satisfy the momentum conservation$^{42,43}$. As the optical-field increases ($F = 3$ V nm$^{-1}$, Fig. 3d), the number of photon-driven electrons increased greatly (almost eight times) with unchanged peak position ($-1.5$ eV). This suggests that excitation is still dominated by photon-driven regime. However, it is noticed that the energy spread of the excited electron broadens a little, which suggests that the strong-field effect starts to affect the excitation.
With the higher optical-field ($F = 5 \text{ V nm}^{-1}$, Fig. 3c), the excitation shows a totally different behavior. The increasing of photon-driven electrons is largely suppressed, while the excitation peak moves to the energy level ($-0.9 \text{ eV}$) near VBM, with excitation number reducing greatly when the energy level goes deeper. This clearly indicates that the excitation is dominated by the field-driven tunneling. In the field-driven tunneling emission regime, the tunneling (excitation) probability of electrons is far less dependent on the photon energy; rather it mainly relies on both the initial energy level and its DOS. The higher energy level, the larger tunneling probability, as it faces a narrower tunneling barrier. This is why the peak moves toward the VBM. However, tunneling probability is also limited by the DOS. This is why the excitation peak is not located exactly at the VBM. These results confirm that the observed $I$-$F$ curve bending up in the present work is a result of strong optical-field-driven electron tunneling from the VB of semiconductors.

**Calculated electronic structure-dependent photoemission.** The repeatability of the strong-field photoemission behavior is confirmed by investigating tens of CNT cluster emitters (see Supplementary Fig. 8 for more typical curves). However, we noticed that the slope of the third regime (VB-OFE) varies from sample to sample ($24 < K \leq 40$ in the present work). As speculated above, the sharpness of the curve bending, referred to as $K$, is proportional to the bandgap. Thus, we believe that the $K$ variation is due to the difference in the bandgap of the entire CNT cluster after aging process. To illustrate this variation, we compute the OFE current by using the extended two-step Simpleman model\(^1\) (see Methods). In the first step—electron tunneling, the computation is based on the integration of instantaneous Fowler–Nordheim (FN) tunneling current and considers all potential emissions from the occupied states near the Fermi level. In the second step—electron acceleration, the photoelectron starts with zero velocity at the position of the tunnel exit in the space-dependent (exponentially decays from the tip) ponderomotive potentials\(^8\). The deeper energy-level electron tunneling covers a longer distance and then gains less kinetic energy. In the present model, we set an energy threshold ($E_{\text{th}}$) that the emitted electrons with kinetic energy smaller than $E_{\text{th}}$ cannot be collected. The validity of this condition is evidenced by bias voltage-dependent photoemission measurement and kinetic energy spectra (see Supplementary Methods and Supplementary Fig. 9). There is a sharp increase in photoemission current upon increasing the bias from 25 to 90 V (Supplementary Fig. 9a). The fact suggests that part of the emitted electrons with the lowest kinetic energy cannot be collected (be driven back to the surface by Coulomb repulsion\(^30\), see Supplementary Discussion of charge interaction) at such low bias. The effect may vanish by increasing the bias voltage. However, this leads to a damage of CNT due to current overload. The value of $E_{\text{th}}$ can be estimated by the electron kinetic energy spectra. In the spectra, the number of electrons with kinetic energy smaller than $E_{\text{th}}$ should be greatly suppressed. As shown in Supplementary Fig. 9b, the cutoff energy at the low-energy side is around 1.5 eV, which suggests $E_{\text{th}} \approx 1.5 \text{ eV}$.

Based on this model, the OFE behaves in three regimes, as shown in Fig. 4a—the contour plot of the $F$-dependent number of emitted electrons from different energy levels. The $I$-$F$ curve is also plotted in the same figure. In Regime 1—low driving field...
Fig. 4 Illustration of bandgap dependency by Simpleman model calculation. a Contour plot of the $F$-dependent number ($G$, normalized at each $F$ point) of emitted electrons from different energy levels, for a CNT model with a bandgap of -1.0 eV. $I$-$F$ curve (solid yellow line) is plotted. Transition points between different regimes are marked by red points. A transition point at $F = 1.1$ V nm$^{-1}$ is noted, before which the electrons mainly emit from CB states (above zero energy level), after which the electrons mainly emit from VB states (below zero energy level). At the same point, an upward bending of the $I$-$F$ curve occurs. b $I$-$F$ curves of three CNT models with different bandgaps: left (cyan) $\approx 0.5$ eV, middle (gray) $-1.0$ eV, and right (purple) $-1.5$ eV. Higher bandgap is associated with greater nonlinearity. Note that the FN model-based simulation is only valid when $F$ exceeds $1$ V nm$^{-1}$.

In conclusion, an extreme nonlinear strong-field photoemission can be further explored in a platform of individual CNT device with controlled nanoscale tunneling gap (<10 nm). We predict that such highly sensitive optical-field control of the electron motion in nanostructures is a promising platform for the design of quantum electronics, and may pave the way for the generation, measurement, and application of attosecond electronics and optics.

**Methods**

**Growth and characterization of CNT emitters.** Vertically aligned single-walled CNT cluster arrays were grown on a highly doped n-type silicon chip by chemical vapor deposition (CVD). The silicon substrate was first coated with an Al (10 nm)/Fe (1 nm) multilayer catalyst, patterned by photo-lithography and deposited by sputtering. The substrate was then heated to 900 °C, at 10$^{-2}$ mbar. During heating, gaseous ammonia was introduced to etch the surface of the catalyst and stimulate the formation of nanoslands. Acetylene was chosen as the carbon feedstock, and introduced to the deposition chamber once the temperature reached 900 °C. The growth process lasted for 1 minute; resulting in 10-μm-tall CNT clusters of defined areal patterns. Following the growth process, the samples were annealed in hydrogen at 1000 °C for 2 h to remove amorphous carbon deposits along with other remaining impurities and adsorbates. SEM image of the as-grown CNT cluster array is shown in Supplementary Fig. 4a. The high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F20) result is shown in Supplementary Fig. 4b. The diameters of the CNTs were assessed from their radial breathing mode frequency ($\nu_{RBM} = 248$ cm$^{-1}$) through Raman spectrum, as shown in Supplementary Fig. 4c. The pristine SWNTs were dispersed in absolute alcohol via ultrasonification and transferred onto a SiO$_2$/Si substrate. Raman spectra were acquired by using He–Ne laser (632.8 nm) excitation, with data recorded by using a confocal micro-Raman spectrometer (HORIBA JobinYvon, LabRam HR 800) with a 0.35 cm$^{-1}$ resolution by using 1800 mm$^{-1}$ grating. The system had a 1-μm optical probe diameter by using a 100 x (N.A. = 0.9) Nikon objective.

**Measurements by using 100-fs laser system.** Refer to ref. 34 for the experimental setup. Photoelectron emission from CNT arrays was triggered with 100-fs laser pulses, with a central wavelength of 820 nm, at an 80-MHz repetition rate from a Ti:Sapphire ultrafast laser (Spectra-Physics, Mai Tai-Series, SHG). A standard Si photodiode power sensor (Thorlabs S130C) was used to measure the laser power. White light and a charge-coupled device (CCD) were employed to monitor the sample position and the laser spot profile. The laser was linearly polarized with its polarization angle being controlled via a polarizer and a half-wave plate, as required. The laser was normally incident on the emitter via front illumination, which was focused to a 2.50-μm-diameter spot at the CNT cluster apex. To confirm that the CNTs are in the focus, we first check it by microscopy to move the CNT cluster to the center of the laser spot. Then, we carefully tune the laser power to obtain a moderate emission current. After that, we slightly scan the position of the CNT sample on the piezo stage (with 10 nm resolution) to obtain position with a maximum emission...
current, which we believe is the main photoemission site giving the extremely high field enhancement. These photocathode samples were mounted in a high-vacuum chamber (10⁻⁷ Torr). The anode was isolated with the photocathode by using a thick mica-insulating spacer. The anode, together with the insulating separator, was placed directly on the surface of the photocathode with the CNT arrays centrally aligned. A Keithley 6430 source measurement unit was used to bias the anode with voltages of up to 50 V, with the anode current measured. Such a small static voltage generates a negligible effect on electron emission. All experiments were carried out in a high-vacuum chamber. Unless otherwise stated, the current measurements presented in this paper are those recorded at the anode. Every current data, collected by source meter, were acquired from an arithmetic average of 100 repeated measurements.

**Measurements by using 7-fs laser system.** The setup is shown in Supplementary Fig. 16. A laser oscillator (Femtolaser CEPA) with a repetition rate of 75 MHz, centered at ~800 nm, a Fourier-limited pulse duration of <7 fs (Supplementary Note 2). The spectral dispersion is managed with chirped mirrors and thickness of the materials in the beam path. The laser pulses are focused on the apex of the CNT clusters by an off-axis spherical mirror to an ~10-μm-diameter spot (Supplementary Fig. 15c), which can easily cover the apex of our CNT cluster, with an incident angle of ~45°. The laser spot was centered by measuring the position-dependent photocurrent. In this setup, the photocurrent emission is proportional to the peak optical-field that is inversely proportional to the pulse width. Thus, to confirm that the pulse duration is almost the shortest at the sample, we measured the photocurrent at different thickness of the glass sheet. The pulse width is the shortest when the photocurrent emission is centered in the CNT. The carrier-envelope offset of the laser pulse is stabilized with an F-2/F interferometer. Long-term drifts in the CEP are corrected by using an out-of-loop F-2/F interferometer. The optical-field induced photocurrent from the CNT cluster is measured by a Keithley 6430 source measurement unit with current preamplifier unit, which has a high-amount preampli- cation. The CEP of those pulses was controlled with a pair of fused silica wedges. Every current data, collected by the source meter, were acquired from an arithmetic average of 100 repeated measurements. All the data points of the I-F curves are obtained at a very stable situation (see Supplementary Fig. 17), which avoids the materials damage-induced photoemission current degradation.

**TDDFT computation method.** The TDDFT simulations are done in two main steps. First, ground-state information of the CNT model is obtained based on density functional theory (DFT) calculations, including the optimized atomic structure. The TDDFT simulations are done in two main steps. First, ground-state information of the CNT model is obtained based on density functional theory (DFT) calculations, including the optimized atomic structure. Both of them describe the laser-matter interactions via solving the time-dependent Kohn–Sham (TDDKS) equation:

\[
\frac{\partial}{\partial t} \psi_0(r,t) = \left[ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(t) + V_{\text{ion}}[\psi_0(t), \psi]^2 \right] \psi_0(r,t) 
\]

(1)

Here, \( \psi_0(t) \) are the single-particle Kohn–Sham states (also called KS orbitals), \( V_{\text{ext}}(t) \) is the time-dependent external potential that is generated by a optical-field, \( V_{\text{ion}}[\psi_0(t), \psi] \) is the Hartree potential that describes the classical mean-field interaction of the electron distribution, \( V_{\text{ion}}[\psi_0(t), \psi] \) is the exchange–correlation (xc) potential that includes all nontrivial many-body contributions, and \( n(r,t) \) is the many-body electronic density. Note that when the external field \( V_{\text{ext}}(t) \) is zero, the TDDKS equations would reduce to the ground-state Kohn equation. In our simulations, we use the length gauge to describe the interactions between the optical-field and 1D single-wall CNTs, where the vector and scalar potential of the field \( E(t) = \mathbf{A}(t) - \mathbf{v}_0 \times \mathbf{r} \), and the laser reaches the maximum intensity \( F \) at the time \( t_0 = 15 fs \). OCTOPUS uses a real-space grid discretization to represent fields such as the Kohn–Sham states and the electronic density. Each function is represented by its value over an array of points distributed in real space. Differential operators are approximated by high-order finite-difference methods, while integration is performed by a simple sum over the grid points. The carrier-envelope offset of the real-space grid approach is that the discretization of the Kohn–Sham states \( \psi_0(r,t) \) is more visually intuitive than any other basis such as plane-wave or atomic-orbital basis sets. The quality of the discretization can be increased by reducing the spacing and increasing the size of the simulation box, at the cost of an increased computational cost. In our calculations, the simulation grid is defined by assigning a spherical zone around each atom with a radius of 6.0 Å and a spacing of 0.2 Å. The selected simulation parameters can make a good balance between the calculation precision and cost. Meanwhile, the adiabatic local density approximation (ALDA) is used for the exchange–correlation functional, and Trouiller-Martins pseudopotentials are used to represent the interaction between valence electrons and the atomic core. In our model, the photoemission is described by propagating electron wave packets \( \psi_0(r,t) \) under excitations for 28,000 steps, with a time step of 0.002 fs (Eq (1)). During the simulation, a \( S \) imaginary potential is added at the boundaries to improve the quality of the spectra by avoiding the formation of standing density waves. Then, the time- and space-dependent microscopic current density

\[
J(x,t) = -\frac{\hbar}{2} \sum_{\alpha=1}^{N_e} \{ \psi_0(x,t) \psi_0^*(x,t) \} \left( \psi_0^*(x,t) \partial_t \psi_0(x,t) + \psi_0(x,t) \partial_t \psi_0^*(x,t) \right) 
\]

(4)

is integrated across a chosen plane that is perpendicular to the \( z \) direction with a distance of 2.0 Å from the cap of the nanotube.

\[
\mathcal{I}(t) = \int J(x,t) \cdot dS 
\]

(5)

The frequency-dependent current across this plane is obtained by taking the Fourier transform \( I(\omega) = \int d\mathbf{t}' I(\mathbf{t}') \exp(i\omega t) \). Then, the maximum intensity \( I(\omega) \) is recorded with the increase in \( F \).

Then we calculate the space- and time-dependent changes in the occupation of KS states. We characterize the overall excitation dynamics through tracking the changes in the number of electrons in different energy levels. This part was performed with the TDAP as implemented in SIESTA47–49. Compared with real-space grids, the adoption of overwhelmingly efficient atomic-orbital basis sets are small in size and fast in performance, which enable simulations of a finite- size system with large vacuum space without heavy calculation cost while maintaining a relatively high accuracy. To understand different behavior of electrons under various field strengths, we present the time–dependence Kohn–Sham states, \( \rho_0(t) \), onto the ground-state (\( t=0 \)) Kohn–Sham states, \( \rho_0 = 0 \), where \( n \) and \( m \) are the state indices labeled by increasing orbital energy

\[
P_{nm} = | \langle \phi_n | S | \phi_m \rangle |^2 
\]

(6)

where \( S \) is the overlap matrix expressed with numerical atomic-centered orbitals. In this scenario, real-time excited state trajectories are achieved with many-electron densities self-consistently propagating at every electronic step, offering a direct microscopic picture on the ultrafast dynamics of electrons upon photoexcitation. The laser waveform is set in the same way as the previous step; however, a much larger time step of 0.05 fs is set to accelerate the computing process. The projection is performed at 27 fs.

**Simulation based on extended Simpleman model.** We adopt the two-step Simpleman model43 to simulate the current density and electron kinetic energy. The diagram of the simulation model is shown in Supplementary Fig. 18a. The first
The kinetic energy spectra of the final electrons are

\[ F(k) \propto \int d\tau \int dE \rho(E,t_0)\delta(\xi(\tau, \phi) - E_{\text{th}} - k^2) \left( \frac{\hbar^2}{2m} \right)^{3/2} e^{-k^2E^2/2m} \]

where \( j \) is the energy resolution.
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