Photoexfoliation of Graphene from Graphite: An *Ab Initio* Study

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We propose to use ultrashort laser pulses to detach intact graphene monolayers from a graphite surface, one at a time. As suggested by a combination of real-time *ab initio* time-dependent density functional calculations for electrons with molecular dynamics simulations for ions, this athermal exfoliation process follows exposure to femtosecond laser pulses with a wavelength of 800 nm and the full width at half maximum (FWHM) of 45 fs. Shorter pulses (FWHM = 10 fs) with the same wavelength and intensity speed up the exfoliation and cause transient contraction in subsurface layers. Photoexfoliation should be capable of producing intact graphene monolayers free of contaminants and defects at a high rate.

Graphene, a monolayer of graphite [1], has emerged as a unique nanostructure that combines high mechanical, thermal and chemical stability with unusually high electron mobility [2]. It may be produced by mechanical [1] or chemical [3–7] exfoliation of graphite, or may form by annealing SiC single crystals [8], or by chemical vapor deposition [9]. Among the production methods, the initial ''scotch tape'' mechanical exfoliation [1] is still unsurpassed in producing the highest quality samples with a minimum of contaminants and defects, which are known to significantly degrade the electronic properties of graphene. Since this method is impractical for high-rate production of graphene, it is imperative to search for sustainable alternative ways to detach graphene monolayers from graphite.

Motivated by the recently observed detachment of charged nanoparticles, including graphene nanoflakes, during laser ablation of graphite [10], we propose to use graphite irradiation by femtosecond laser pulses as a gentle method to detach an entire graphene monolayer from graphite. In contrast to the rather unspecific laser ablation process that locally destroys the surface structure, we find that specifically shaped femtosecond pulses may initiate desired structural changes before thermally exciting the atomic motion. The calculations underlying the proposed method to exfoliate graphite are based on *ab initio* time-dependent density functional theory (TDDFT) [11] for electrons in combination with molecular dynamics (MD) simulations for ions. This approach provides insight into the electron-ion dynamics at a graphite surface exposed to a pulsed laser beam in real time. We observe exfoliation of the topmost graphene layer immediately following a femtosecond laser pulse with the full width at half maximum (FWHM) of 45 fs and a wavelength $\lambda = 800$ nm. Shorter pulses (FWHM = 10 fs) with the same wavelength speed up the exfoliation, and are accompanied by changes in the

interlayer distance in the subsurface region, as recently observed using electron diffraction [12,13]. Much shorter pulses with a FWHM below 10 fs do not cause exfoliation, whereas long pulses are likely to cause detachment of multiple graphene layers at the surface.

Our TDDFT-MD *ab initio* simulations offer an unbiased microscopic insight into the ionic motion initiated by light irradiation, since this formalism treats electron and ion dynamics on the same footing in real time. While computationally much more demanding than more heuristic approaches based on an artificial population of tight-binding electron levels and their subsequent repopulation according to the Boltzmann equation [14], our approach provides much more dependable results since it is free of parameters and specifically addresses nonequilibrium conditions.

We model the surface of hexagonal graphite by a periodic array of infinite slabs containing 10 graphene layers in hexagonal (*AB*) stacking. We use 2×2 2D supercells with respect to the primitive graphene unit cell in the plane of the layers, so that each 3D supercell contains 80 carbon atoms. We represent the irreducible wedge of the Brillouin zone by one *k* point, which corresponds to sampling the full Brillouin zone by 6 *k* points to represent the Bloch wave functions for the momentum-space integration. Our calculations are based on the density functional theory (DFT) within the local density approximation [15] and use the Ceperley-Alder exchange-correlation functional [16] for the uniform electron gas as parameterized by Perdew and Zunger [17]. Interactions between valence electrons and ions are treated by the norm-conserving pseudopotentials [18] with separable nonlocal operators [19]. The electron wave functions are expanded in a plane-wave basis with an energy cutoff of 60 Ry.

We represent the laser irradiation by subjecting our system, initially at $T = 0$ K, to an external alternating electric field (*E* field) polarized normal to the surface, in

agreement with the experimental conditions of Ref. [10]. (In absence of experimental data, we have not tested the response of graphite to an E field polarized parallel to the surface.) The imposed periodic boundary conditions require the corresponding electrostatic potential to follow a sawtooth curve with an abrupt step, associated with polarity inversion, in the middle of the vacuum region in between the slabs. The $E(t)$ pulse is represented by a harmonic carrier modulated by a Gaussian.

Our numerical results during and following the laser pulse are obtained using the FPSEID (First Principles Simulation tool for Electron Ion Dynamics) code [20], which couples the TDDFT [11] for the dynamics of electrons with the dynamics of ions. The force field is described by the Ehrenfest scheme [21], which represents transitions between different potential energy surfaces within the mean-field approximation. We use the Suzuki-Trotter formula [22] to efficiently describe the propagation of electron wave functions in real time. We found that the total energy of the system increased solely by the precise amount absorbed from the time-dependent external electric field during the simulation [23].

Our most striking result is the effect of the laser pulse shape on the structural evolution at the irradiated graphite surface, shown in Figs. 1 and 2. We represented $\lambda = 800$ nm laser pulses by Gaussian wave packets, shown in Fig. 2(d), characterized by the maximum amplitude E_0 of the optical E field and the FWHM. Figure 1 depicts structural changes occurring in a 10-layer graphite slab following exposure to laser pulses with $E_0 = 3.4$ V/Å and FWHM of either 45 fs or 10 fs. Details of the time evolution of the interlayer spacing during the laser irradiation are depicted in Fig. 2. In our geometry, structural changes near the top and near the bottom of the graphite slab are the same.

There are several interesting observations regarding our results. First, as seen in Fig. 1 and still better in Fig. 2(c), only the topmost layer detaches, whereas subsurface layers
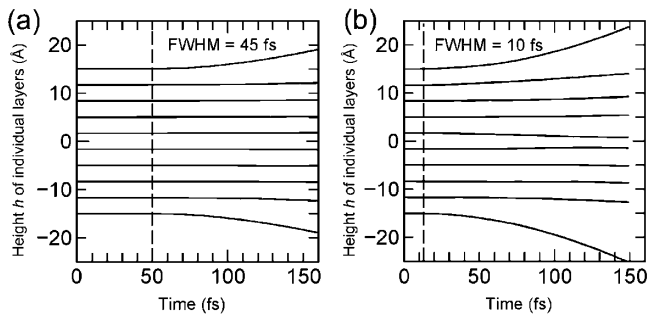
experience much smaller structural changes. This detachment is initiated by both short and longer pulses, which deposit different amounts of energy into the substrate. Our calculations indicate that 20 mJ/cm^2 are deposited in graphite during the FWHM $= 10$ fs pulse, whereas 87.9 mJ/cm^2 are deposited during the FWHM $= 45$ fs pulse. In each case, the exfoliation process started only after the laser pulse had reached its maximum. Consequently, layer detachment occurs earlier when reducing the pulse length at the same amplitude of the optical E field. Our calculations for a still shorter FWHM $= 3$ fs pulse indicate no exfoliation, suggesting that the optimum pulse width should lie near 10 fs. Reducing the optical E-field amplitude of the FWHM $= 45$ fs pulse to $E_0 = 1.4$ V/Å causes a decrease of the energy deposited in the substrate to 25 mJ/cm^2. The exfoliation dynamics in this case slows down by 1 order of magnitude, but still remains

FIG. 1.   Time evolution of the averaged height h of individual layers within a graphite slab containing 10 AB-stacked graphene monolayers. The maximum amplitude of the optical E field in the applied pulse is 3.4 V/Å and occurs at the time indicated by the vertical dashed lines. The full width at half maximum of the pulse is 45 fs in (a) and 10 fs in (b).
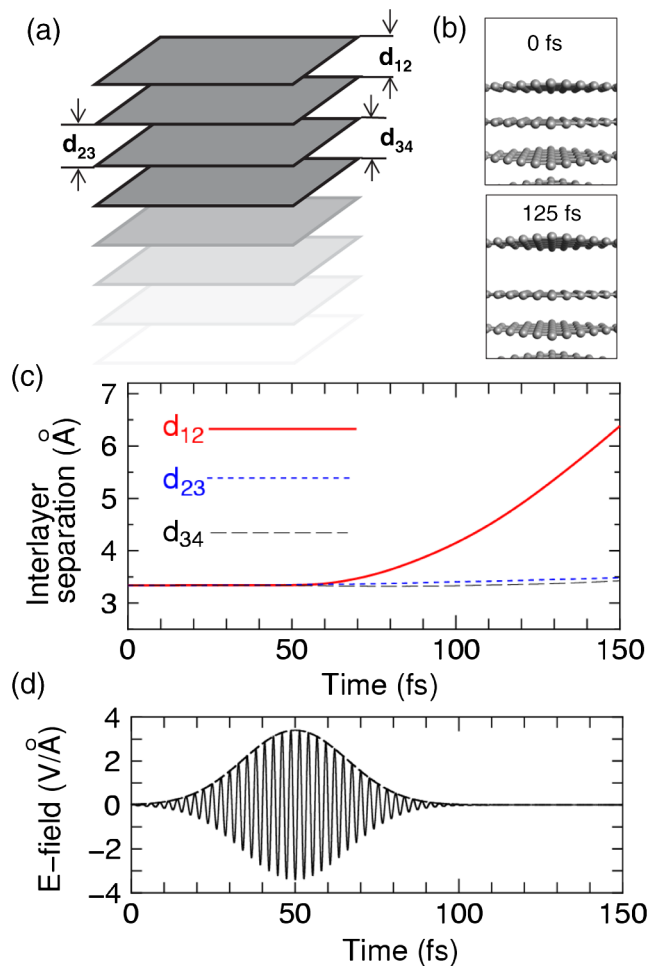

FIG. 2 (color online).   Schematic layer stacking (a) and structural snapshots (b) of the surface of AB-stacked graphite during exposure to a FWHM $= 45$ fs laser pulse. (c) Time evolution of the interlayer distances. (d) Time-dependence of the optical electric field E characterizing the laser pulse.

qualitatively the same, resulting in the detachment of the topmost graphene monolayer only.

Not visible on the vertical scale of Fig. 1 is the very small difference in the out-of-plane motion of the two inequivalent sites in the layers of AB-stacked graphite. Only during the shorter 10 fs pulse, we observe a compression in the middle of the slab, at $h \approx 0$ Å in Fig. 1(b). Computational limitations do not allow us to verify independently that this compression is a transient state, as suggested by recent experimental data [12,13]. Also, our approach does not allow us to describe in-plane lattice deformations such as Kekule distortions, Stone-Wales and vacancy defects, which provide additional energy absorption channels that should slow down or suppress the exfoliation process.

As our key result, we find that exposing the graphite surface to a laser pulse causes detachment of the topmost layer with a kinetic energy exceeding 1 eV/atom. This energy is orders of magnitude larger than the weak interlayer interaction energy in graphite [15,24]. Consequently, our results should not depend on the choice of the exchange-correlation functional used in the DFT description of the ground-state equilibrium structure. Most important, the vertical detachment speed of the topmost layer of 6×10^3 m/s is sufficiently large to allow efficient transfer of the graphene monolayer onto a nearby substrate.

To better understand the reason for the photoexfoliation of graphite postulated here, we should first recall that the energy of the incident photons, $h\nu = 1.6$ eV, is not sufficient to cause ionization or to excite any plasmon modes in graphene. In this case, we might naively expect a quasi-static screening of the applied electric field in the bulk of the slab by charge accumulation at the surface, which would explain the singular behavior of only the top and bottom layers, shown in Fig. 1. To explore this scenario, we inspected the total potential V_{tot} in the slab, consisting of the intrinsic self-consistent potential plus the sawtooth potential associated with the applied optical E field, at different points in time. For the sake of easy interpretation, we averaged the potential across planes parallel to the surface. In Fig. 3 we depict changes in $V_{tot}(h)$ along the surface normal direction h during a FWHM $= 45$ fs laser pulse, shown in Fig. 2(d). Contrary to our initial suspicion, the calculated $V_{tot}(h)$ near the pulse maximum, at $t = 52.64$ fs, follows closely the electrostatic potential of the applied field, with very little screening. In retrospect, this result is in agreement with the observation that $\lambda = 800$ nm photons should penetrate the surface of graphite significantly deeper than our slab thickness of 15 nm. The calculated behavior of $V_{tot}(h)$ at $t = 144.84$ fs, during exfoliation depicted in Fig. 2(c), only reflects the fact that the optical E field across the slab nearly vanishes well after the pulse.

The true origin of the laser-driven detachment of only the topmost layer lies in the microscopic process, by which
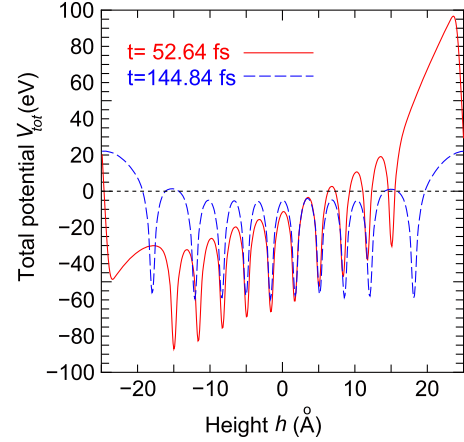

FIG. 3 (color online).   Self-consistent total potential V_{tot} within the graphite slab along the surface normal direction h, averaged across planes parallel to the surface. Snapshots of $V_{tot}(h)$ during a FWHM $= 45$ fs pulse, shown in Fig. 2(d), represent $V_{tot}(h)$ near the pulse maximum ($t = 52.64$ fs, solid line) and well after the pulse, during exfoliation ($t = 144.84$ fs, dashed line).

the laser beam transfers energy to the substrate. The incident laser pulse creates a nonequilibrium situation by heating up the electron gas first to temperatures up to 20 000 K [25]. The onset of equilibration between the ionic and electronic degrees of freedom in the slab is delayed significantly and occurs $\approx 2 \times 10^2$ fs after the laser pulse [26]. Consequently, all graphene layers are vibrationally cold at the time of detachment at $t \approx 100$ fs. In the meantime, however, the hot electron gas was able to expand even beyond the volume of the graphite slab. This can be best seen by inspecting the net charge flow between separate volume regions. At $t = 0$, prior to a FWHM $= 10$ fs pulse, we found all graphene layers within the slab to be charge neutral. Inspecting the same volume region at $t = 30.85$ fs, when exfoliation starts after the laser pulse had decayed, we observe an electron spillout characterized by a significant excess charge of 1.0 electrons in the volume outside the slab. The electron-deficient slab displays a damped oscillatory profile of hole and electron doping normal to the layers, dominated by 0.7 holes per 8-atom slab unit in the top and bottom layers, and 0.1 holes in the same unit of the second layers from the top and bottom. The third layer accumulates a net negative charge of 0.3 electrons and the fourth layer 0.1 electrons, preventing detachment of the subsurface layers due to Coulomb attraction.

We thus conclude that the process underlying the exfoliation occurs in the nonequilibrium situation, when the laser pulse rapidly heats up the electron gas and causes it to spill out of the surface. The force field within graphite is modified first by the electronic excitations, which reduce the interlayer interactions, and—more importantly—by the Coulomb interaction among the charged graphene monolayers. This Coulomb repulsion eventually ejects the

strongly hole-doped top and bottom graphene layers, whereas the weakly hole-doped subsurface layers are held back by electron-doped layers below. The ejection of the surface graphene monolayers occured well before the expanded electron gas had a chance to cool down by heating up the lattice.

In summary, we propose to use femtosecond laser pulses with specific shapes to detach graphene monolayers intact from a graphite surface, one at a time. This athermal process differs fundamentally from conventional laser ablation, which is a thermal process and destroys the desorbed structure. Unlike chemical exfoliation or chemical vapor deposition synthesis techniques, which generally produce defective or chemically contaminated graphene, photoexfoliation appears capable of producing high-quality graphene monolayers in large quantities. Our proposal is supported by a combination of real-time *ab initio* time-dependent density functional calculations for electrons with molecular dynamics simulations for ions. Our results show that femtosecond laser pulses create a non-equilibrium charge distribution in a vibrationally cold sample. Laser pulses within the realm of current experiments, with the wavelength of 800 nm, maximum optical *E*-field amplitude of 3.4 V/Å and a FWHM between 10 fs and 45 fs, are optimally suited to detach the topmost monolayer from graphite and transfer it to a nearby substrate. Shorter pulses do not cause exfoliation, whereas longer pulses are likely to cause detachment of multiple graphene layers at the surface. We find our computational technique to be well suited to describe and optimize the shape of ultrashort laser pulses not only for the exfoliation of graphite, but more generally as a powerful tool to achieve targeted structural changes in materials.

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