

Can photo excitations heal defects in carbon nanotubes?

Yoshiyuki Miyamoto ^{a,*}, Savas Berber ^b, Mina Yoon ^b,
Angel Rubio ^c, David Tománek ^{b,*}

^a *Fundamental and Environmental Research Laboratories, Nanotube Technology Center, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan*

^b *Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824-2320, USA*

^c *Dpto. Física de Materiales, Facultad de Químicas, Universidad del País Vasco, Centro Mixto CSIC-UPV/EHU and Donostia International Physics Center (DIPC), 20018 San Sebastián, Spain*

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Abstract

We extend the time-dependent density functional formalism to study the microscopic response of defective nanotubes to electronic excitations. We find the lifetime of electronic excitations in these nanostructures to be several orders of magnitude longer than in solids, necessitating the use of excited-state molecular dynamics to correctly describe the atomic motion. We find that electronically excited nanotubes with monatomic vacancies show an unexpected self-healing ability, which is intimately linked to their nanometer size.

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1. Introduction

The continuing trend towards miniaturization, rapidly approaching the atomic scale [1], raises serious concerns about the required degree of perfection and defect tolerance of nanoscale devices. Carbon nanotubes [2], considered as functional building blocks [3] of such devices, can sustain very large current densities [3,4] of 10^9 A/cm², and show an unusually high thermal and mechanical stability [5]. Nanotube-based transistors out-perform state-of-the-art silicon-based elements in terms of speed, on/off ratio, and the maximum current [4,6].

However, substantial defect densities in currently available nanotubes raise a concern about the performance and reliability of nanotube-based devices. Theoretical studies showed that even individual vacancies change transport properties of these quasi one-dimensional systems significantly [7,8]. At particular bias voltages, drastic conductance reduction in nanotubes

results from perturbing the π electron system and from the presence of dangling bonds [8]. Another point of concern is, whether defects may trigger failure earlier in nanoscale devices than in current Si-based devices. This concern is based on the fact that a ‘ten-nine’ purity requirement is currently being placed on silicon wafers in order to avoid device failure, which appears to be initiated by processes occurring at defect sites in the electronically excited state [9,10]. So far, little is known about possible microscopic processes that could lead to failure of defective nanotubes.

Here we study the defect tolerance of nanotube components by monitoring the response of carbon nanotubes with atomic vacancies to electronic excitations. Such excitations may be induced by interaction with electromagnetic radiation, or by electron–electron scattering in current-carrying nanotubes. Since nanostructures appear to be more susceptible to defects than bulk systems, we intuitively expect them to fail earlier. The major result of our theoretical study attests to the contrary. Rather than showing signs of premature failure, we find that nanotubes containing vacancies exhibit a unique self-healing mechanism, associated with the possibility to form new bonds bridging the vacancy site.

* Corresponding authors. Fax: +1-517-353-4500 (D. Tománek).

E-mail addresses: y-miyamoto@ce.jp.nec.com (Y. Miyamoto), tomanek@pa.msu.edu (D. Tománek).

Such a self-healing process does not occur in submicron-scale Si-based devices, and is intimately linked to the nanometer size of our system.

2. Theoretical approach

Since atomic-scale processes leading to device failure in the electronic excited state occur on the sub-picosecond to picosecond time scale, they are very hard to track experimentally. As a viable alternative, which should provide microscopic information about atomic-scale processes occurring during failure, we propose the use of molecular dynamics (MD) simulations of defective carbon nanotubes subject to electronic excitations. This type of computational approach turns out to be particularly challenging, since the study precludes the solution of the time-dependent Schrödinger equation for the time evolution of the electronic wave functions in the presence of ionic motion, caused by the changing charge distribution. This computer intensive calculation has been performed using the recently developed first-principles simulation tool for electron–ion dynamics (FPSEID) [11,12].

Since we suspect intrinsically strained narrow nanotubes to be most susceptible to failure, we focus in our study on the (3,3) nanotube with a monatomic vacancy as a test case. With only 0.4 nm in diameter, this is one of the narrowest nanotubes observed [13,14]. To distinguish nanotube-specific intrinsic behavior from effects caused by the nanotube environment in the experimental situation [14], we consider an isolated nanotube in vacuum. We use periodic boundary conditions throughout our simulations, also implying a periodic arrangement of vacancies with an axial separation of four to six primitive unit cell sizes of the defect-free nanotube. Consequently, the unit cells used in our calculation hold between 47 and 71 atoms.

We considered the relaxed monatomic vacancy structure in a (3,3) carbon nanotube, depicted in the left panel of Fig. 1a, as the starting point to investigate structural changes that may be induced by electronic excitations. The study was performed within the *ab initio* time-dependent density functional formalism coupled to molecular dynamics simulations (TDDFT-MD) [11,12]. We used the local density approximation (LDA) to the density functional theory (DFT) [15,16]. Valence electron states were described using Troullier–Martins type pseudopotentials [17] and a plane wave basis with the kinetic energy cutoff of 40 Ry. Due to the large size of the unit cell representing the defective tube, we limited our sampling of the momentum space to the Γ point. Comparison with density functional calculations for systems with a larger unit cell justifies the use of the Γ point approximation, which was also necessitated by the extremely high demand on computational resources.

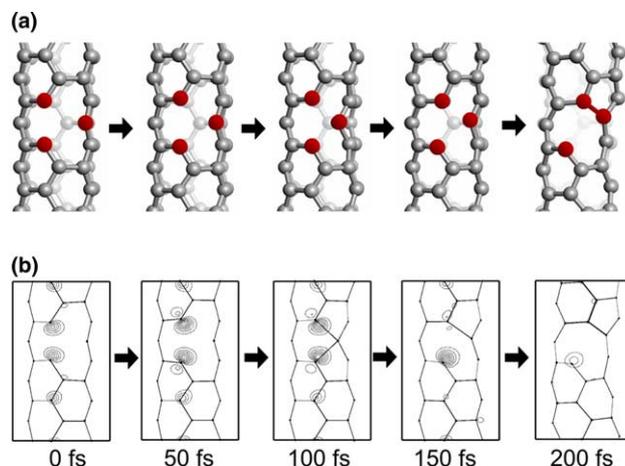


Fig. 1. (color online) Self-healing process within a (3,3) nanotube with a monatomic vacancy, induced by illumination. (a) Time evolution of the geometry. The three atoms adjacent to the vacancy and the new C–C bond, which forms ≈ 200 fs after the electronic excitation, are emphasized by color and shading. (b) Time evolution of the partial charge density associated with the excited electron state. The lowest contour lines are common to the three panels.

3. Results

In our excited-state dynamics simulation, we selected among the many possible excitations the particle-hole state localized at the vacancy site, which yields strong Hellmann–Feynman forces with a tendency to expand the vacancy site and thus to destroy the nanotube. We found this to be the case by promoting an electron from the highest occupied state to the second lowest unoccupied state. Following this optically allowed excitation, we noticed an energy reordering of the highest and second highest occupied states [18]. The energy of 0.9 eV, associated with this excitation, was determined from the total energy difference between the excited state and the ground state in a (3,3) nanotube with a 47-atom unit cell. The subsequent time evolution of the electronic and atomic structure in this Franck–Condon like process was computed within the TDDFT-MD formalism, by maintaining self-consistency between the wave function and potential, which both evolve in time [11,12]. We used extremely short time steps of 0.08 a.u., corresponding to 1.94×10^{-3} fs, to accurately describe the electron dynamics. This time step is three orders of magnitude shorter than used in ground state *ab initio* MD simulations, and necessitates very large computer resources to cover the typical time scale of subsequent atomic motion, occurring over $\approx 10^2$ fs.

In the beginning of the simulation, we froze all the atoms in the relaxed ground state geometry and obtained the static solution of the electronically excited state. The ion dynamics induced by this excitation is depicted as a time sequence of geometries in Fig. 1a. We found that the vacancy initially started to open in the

direction of the Hellmann–Feynman forces, suggesting a destructive tendency. 200 fs after the excitation, two of the three atoms adjacent to the vacancy approached each other sufficiently close to form a new bond. We interpret the formation of this new bond as a self-healing process, which is unique and extremely beneficial to this nanostructure.

The newly formed bond was found to bridge the initial gap by providing a new connection between atoms adjacent to the vacancy, thus restoring part of the initial structural rigidity and saturating some of the dangling bonds at the vacancy site. Since dangling bonds have been identified as important scattering centers [8], this reconstruction is expected to improve the conductance of the defective nanotube.

Our density functional calculations suggest that in the electronic excited state, the reconstruction occurs spontaneously, without additional thermal activation, on a time scale of 10^2 fs. This is very different from the ground state behavior, where such a reconstruction is also possible, but requires an initial energy investment of 0.3 eV, followed by a net energy gain of up to 1.76 eV per vacancy. Once the reconstruction is completed and the system returns to the ground state, the probability of reopening the monatomic vacancy at ambient temperatures is extremely small in view of the ≈ 2 eV activation barrier required for the reopening of the bond.

To understand the energy gain associated with this healing process in a broader context, we focussed on the electronic ground state first, and performed structure optimization calculations of monatomic vacancies in various nanotubes. In narrow nanotubes, which are more flexible, the energy gain due to a new bond by far outweighs the strain related to the reconstruction, which can easily be accommodated locally. With 1.76 eV per vacancy, the net energy gain due to re-bonding is the largest in the (3,3) nanotube. With increasing nanotube diameter, the strain extends over an increasing region, making this reconstruction energetically less favorable. This results in the net energy gain decreasing from 1.53 eV in the (5,5) nanotube to 1.23 eV in the (7,7) nanotube. In the even wider (10,10) nanotube, the closure of the monatomic vacancy appears to be energetically unfavorable [8]. Ultimately, in a graphene monolayer, the energy gain due to the formation of new bonds is not sufficient to compensate for the large associated strain in the structure [19]. Thus, this self-healing process is intimately linked to the larger flexibility found in nanostructures.

The time evolution of the electronic states during the ionic motion is presented in Fig. 1b as a series of contour maps depicting the norm of the excited electron wavefunction. As time progresses, we find the excited electron distribution to change from an anti-bonding to a dangling bond characteristic. We should emphasize that in contrast to conventional ab initio MD simula-

tions, we monitor the time evolution of each populated and empty single-electron state during the ionic motion. This approach provides information not only about the charge distribution, but also the lifetime of electronic excitations in presence of ionic motion. An important indication for the onset of a non-adiabatic decay is a sudden increase in the off-diagonal matrix elements of the Kohn–Sham Hamiltonian in the basis of the time evolving eigenstates. Following such a non-adiabatic decay, rapid Rabi oscillations are known to appear in the electronic levels, even if the atomic motion is smooth [20].

With the charge distribution determined by the time-evolving populated states, forces acting on atoms are determined using the Hellmann–Feynman theorem [11,12]. This approach offers a significant advantage over the conventional ab initio MD simulations, where forces acting on atoms are calculated from static solutions of the Kohn–Sham equations at each time step, presuming the population of each Kohn–Sham state is known. Predicting the correct sequence of populated levels is a challenging undertaking especially in case of level alternation, which occurs in the single-electron spectrum following the electronic excitation, as shown in Fig. 2. In our system, we found the character of the hole wave function to differ significantly from the valence band character. Similarly, the character of the excited electron was found to differ from the conduction band states. Thus, the

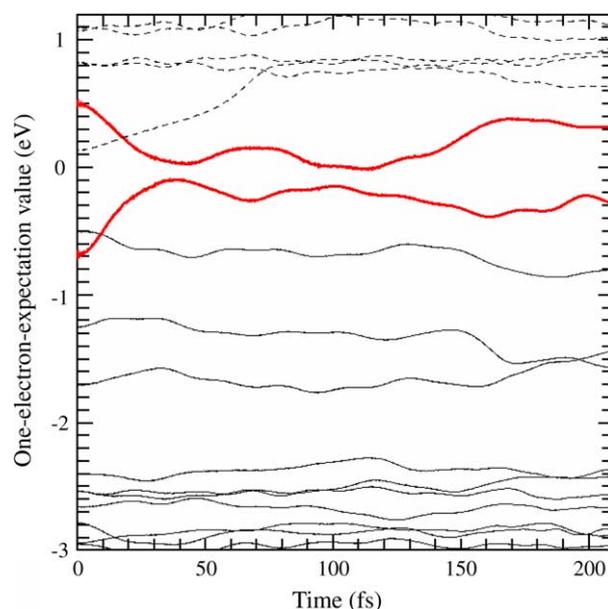


Fig. 2. (color online) Time evolution of the energy spectrum during the atomic motion following the initial electronic excitation. Fully occupied states are denoted by solid black lines, completely empty states by dashed black lines. Time evolution of the electron–hole pair, created by the electronic excitation, is shown by the heavier red solid lines.

level alternation seen in Fig. 2 did not cause a non-adiabatic decay of the excitation, and the system remained on the adiabatic potential energy surface during our simulation.

Unlike in bulk systems, where electron–hole excitations typically decay on a femtosecond time scale, we did not find any indication for such a non-adiabatic decay of the excitation in the defective nanotube during our MD simulation, extending over 200 fs. We find the long lifetime of this excitation intimately linked to new electronic states associated with the vacancy, which do not couple to the valence and conduction bands of the nanotube. Due to the apparent long lifetime of the electronic excitation, a significant fraction of the ion dynamics occurs on the excited state potential energy surface, which differs significantly from the ground state potential energy surface. In defect-free nanotubes, electronic excitations decay much faster, and play only a negligible role in the atomic motion.

An important difference between ground and excited state dynamics concerns the activation barrier, which is absent in the electronically excited state, but has a value of 0.3 eV in the electronic ground state. Consequently, self-healing induced by electronic excitations should occur very fast even at low temperatures. We find it intriguing that even excitations, which initially tend to destroy the structure at the defect site, may induce self-healing. Our most significant finding is that electronic excitations can be tuned to selectively repair defects, while leaving the remaining perfect structure intact, without inducing new defects.

As an alternative to the rapid excited state dynamics, several activated processes could occur in the electronic ground state. In view of the moderate activation barrier of 0.3 eV, a bond bridging the vacancy in a defective (3,3) nanotube may form on the time scale of seconds at ambient temperature. This process occurs even faster at higher temperatures [21], since high-temperature dynamics often mimics on a short time scale the long-time behavior at lower temperatures. At temperatures approaching the melting point, we may expect the nanotube to be destroyed, starting with a pre-melting near the vacancy site.

To obtain a rough insight into processes occurring at high temperatures, we performed Nosé–Hoover molecular dynamics simulations of a nanotube subject to a rapid temperature increase. Our preliminary findings [18] suggest that the defective nanotube remained intact even at temperatures comparable to the melting point of graphite [22]. At these very high temperatures, we observed the formation of bonds bridging the gap created by the monatomic vacancy, similar to those formed during the electronically induced self-healing. Since the system gained energy during this process, the reconstruction persisted after the structure had been cooled down.

4. Summary and conclusions

In summary, we performed time-dependent density functional molecular dynamics simulations of electronically excited defective nanotubes. We have identified a self-healing process of vacancies following an electronic excitation, which induces the formation of a new bond between atoms at the vacancy edge on a very short time scale. The stability and conductivity of narrow nanotubes with monatomic vacancies is expected to improve following the reconstruction. The energy gain associated with this process is intimately linked to the size of these nanostructures and absent in their bulk counterparts. The efficiency of the self-healing process, which may be initiated by photo-excitations, bears promise for future nanotube applications.

We should point out that our simulations correspond to vacuum conditions and that defect–gas interactions cannot be ignored in more realistic situations. We also explored the possibility of healing other imperfections, such as oxygen contamination or Stone–Wales type defects, which may exist in nanotubes. Our results suggest that electronic excitations do not eliminate Stone–Wales defects, but rather induce localized vibrations in their vicinity [23].

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