Stone—Wales defect generation in carbon nanotube being fractured

S. S. Moliver*

State University Ulyanovsk, Tolstoy street 42, Ulyanovsk 432 970 Russia

Abstract: Quantum-chemistry modeling of carbon nanotubes (8,0) and (5,5) has revealed certain properties of the topochemical Stone—Wales defect. The rolling-up of a planar graphene sheet into a small-diameter nanotube leads to approximately 0.6 eV decrease in defect formation energy. The SW-defect localized states are resonant with nanotube energy spectrum. In case of fracture-type deformation, the SW-defect on the compressed side of the tube is energetically favourable. At a fracture angle above critical value – yield point [1.7 degrees for (8,0), 2.7 degrees for (5,5)], SW-defect appearance decreases total energy of the tube. Thus, fracturing deformation of the nanotube turns on a plasticity channel in the form of mechanical generation of the Stone–Wales defect.

Key words: carbon nanotubes, electronic structure, point defects, plasticity.

INTRODUCTION

Native growing point defects of graphene and carbon nanotubes are related to C—C dimer. In elementary semiconductors (diamond, silicon) native point defects are: vacancy, interstitial, impurity, and their complexes; on the contrary, in carbon nanotubes such ones are: a topochemical turn of a C—C bond around its centre (A. J. Stone, D. J. Wales, 1986), and incorporation of C—C dimer into honeycomb carbon net [1-3]. Grafted ad-dimer may be treated as a variant of universal bond-switching Stone—Wales transformation, that appears either as a substitution defect (if rotation of a bond returns lattice to ideal geometry), or an interstitial defect (if the same result is achieved by removal of C—C dimer). Naturally, the return to ideal geometry should also involve the relaxation of neighbour bonds, but not their rapture or switching. Note that this mechanism of defect formation coincides with a topochemical transformation of four adjacent hexagons, according to patterns: 5-7-7-5 for SW defect, and 7-5-5-7 for grafted ad-dimer.

Close relation between topochemical defects and mechanical properties of carbon nanotubes was recognized soon after tubes discovery. However, only recent quantum-chemistry calculations revealed that deformation above yield point can lead to the formation of SW-type defects and their complexes [1-2].

* Address correspondence to S. S. Moliver, State University, Tolstoy street 42, Ulyanovsk 432 970 Russia. E-mail: moliver@sv.uven.ru
The present study was aimed at solving the problem of generation of SW-defect in small-diameter tubes under mechanical fracture-type deformation, when mechanical stress is concentrated in a small area of the tube. In our modeling of tube fracture, the coordination of only two adjacent rings of atoms was changed. Fracture of zigzag (8,0) and armchair (5,5) tubes was considered. Method of all calculations was the restricted Hartree—Fock—Roothaan approximation (RHF), fitted to open- and closed-shell electron configurations, and semi-empirically parametrized (INDO). It has been previously used to describe the electron properties of diamond with vacancy-type defects [4], graphite [5], and fullerenes [6].

The idea was to give a tube an increasing fracture angle and find its critical value, at which the total energy of the tube with SW-defect becomes lower, than of a tube without defect. Thus, it was necessary to compare adiabatic energy curves (total energy vs atomic coordinates) of three models:

— defect-free fractured \((m,n)\) tube;
— fractured \((m,n)\) tube with SW-defect at the compressed side of the fracture;
— the same at the stretched side.

**MODEL AND COMPUTATIONAL METHOD**

Quantum-chemistry RHF method was applied to super-cell model, which imposes periodic boundary conditions on a cluster of several unit cells. Super-cells of the tubes under consideration were:

zigzag \((8,0)\): 192 atoms/super-cell, 24 rings, 8 atoms/ring;
armchair \((5,5)\): 220 atoms/super-cell, 22 rings, 10 atoms/ring.

The model of fractured nanotube was obtained as following: pristine super-cell is subdivided by zero-level plane (fig.1), where one of C—C bonds may be rearranged to make SW-defect. The upper half of a super-cell is than tilted by angle \(\chi\), and the lower half is tilted by the same angle in opposite direction. Thus, we fulfill calculations for tubes with periodically repeated alternating fractures, and with two fractures per super-cell. The SW transformations were: either a 90-degree rotation of the most compressed C—C bond (this case is marked by \(\chi>0\)), or similar rotation of the most stretched bond, we mark such SW-defect by \(\chi<0\).

The classification of nanotubes as possessing metallic or insulating properties in dependence of chiral indices \((m,n)\) is valid for large-diameter tubes only, since it is proven by means of MO LCAO approximation for the plane graphene sheet with chiral boundary conditions. In small-diameter tubes many-electron coulomb and exchange corrections differ from those in plane graphene, this can significantly influence the occupancy of electron states.
Our RHF method makes possible to calculate open-shell electron configurations of a high-symmetry model, as well as the closed-shell ones. By direct comparison of configurations energies, the metallic nature of graphite had been proven [5] before, now it has given a nontrivial result, that both tubes, the zigzag (8,0) and armchair (5,5), are insulating.

Total-energy minimization has provided equilibrium size-parameters. We measure them in $d$ units, which is interatomic distance in corresponding graphene model [5]. Tubes radii are: $R=2.24d$ (8,0); $R=2.40d$ (5,5). Vertical bond length in (8,0) is $d$, zigzag height is $z=0.485d$ (cf. $0.5d$ in graphene). Hexagon height in (5,5) is $a=1.73d$ (cf. $3^{1/2}d$ in graphene). Binding energies, all obtained in frame of the same INDO parametrization for various defect-free carbon materials, are:

- $5.74$ eV/atom for semimetallic graphene (216 atoms, fully symmetric super-cell, open-shell configuration $(K')^2(K'')^2$ [5]);
- $5.62$ eV/atom for fullerene C$_{60}$ [6];
- $5.68$ eV/atom for zigzag (8,0) tube;
- $5.69$ eV/atom for armchair (5,5) tube.

**RESULTS**

The energy of SW-defect formation in graphene was found to be $2.1$ eV. The length of the turned bond is $0.98$ of the normal, while displacements of neighbouring atoms are rather small. Experimental data for formation energy were never reported, the available theoretical estimations use density-functional method and yield $5.0$ eV [8] and $5.1$ eV [9]. A scatter in the results of calculations of the same parameter is quite usual, since the electron structure is modeled so as to reproduce certain combination of material properties; e.g. for the SW formation energy in graphite, two exchange-correlation functionals, being applied to the same model, yielded $5.2$ and $4.8$ eV [10].

The relation of SW formation energies in graphene and nanotube is governed by a wide set of properties, which should be verified using different methods and models. Fig.2 shows plots of total energies of (8,0) tube, including models of fracture and SW-defect, calculated as described above for different angles of fracture. The (8,0):SW formation energy is obtained by subtracting the two curves of fig.2 and dividing the difference by 2 (number of defects per super-cell). At zero angle of fracture (free tube) this value is $1.45$ eV, meaning that rolling-up graphene sheet into (8,0) tube decreases SW formation energy by approximately $0.6$ eV. The same observation for small-diameter tubes (~1-eV decrease) was made by density-functional method [8].

Total energy of fractured (8,0) tube obeys Hook's law, i.e. is proportional to fracture
angle squared. Energies at \( \chi = 1 \) and 2 degrees were calculated without minimization with respect to atomic coordinates. A parabola drawn through these points (fig.2) interpolates well a critical point of SW-defect generation \( \chi = 1.7 \) degree (this will be explained in the following). Let us evaluate a force \( F \), that is necessary to observe critical fracture of (8,0) tube. The elastic energy per super-cell, defined from data of fig.2, is \( U(\chi = 1.7) = 7.46 \text{ eV} \), is accumulated in 2 fractures of super-cell. Transverse displacement of the tube axis per fracture is \( \chi = 2(z + d) \sin \chi = 0.2 \text{ angstrom} \), where \( L = 12(z + d) \) is super-cell length (fig.1). Thus, we obtain an estimate \( F = U/x = 6 \times 10^{-8} \text{ N} \), which is available in atomic-force microscope.

Total energy of fractured (8,0):SW tube is also a parabolic function of the fracture angle, but this curve is not mirror symmetric (fig.2). The SW-defect energy is lower on the compressed side of fracture, than on the stretched side. At \( \chi = +2 \) degree, the nanotube with SW-defect is energetically more favourable, than without defect. Thus, the plasticity of a tube being fractured, may be explained by SW-defect generation. Parabolic interpolation of total energies predicts intersection at \( \chi = +1.7 \) degree, and RHF calculations confirm, that SW transformation at this fracture angle does not change the total energy of (8,0) tube.

Quantum-chemistry calculation gives a molecular-orbital picture of the electronic structure. Energy spectra \( \{ E_a \} \) of molecular orbitals (fig.3) show that it is possible to monitor fracture angle and detect SW-defect generation by measuring density of occupied states. Calculation of this density requires smoothing, since the super-cell model involves only small subset of the k-point manifold of a crystal. We have used smoothing \( \Delta = 0.3 \text{ eV} \), in order to convert molecular-orbital energies \( \{ E_a \} \) into density of states:

\[
\rho(E) = \sum_a \exp\left[-\frac{(E - E_a)^2}{2\Delta^2}\right]
\]

whose behaviour near upper energy edge (fig.3) makes possible to conclude, that SW-defect introduces resonant, rather than discrete, energy levels into electron spectrum of (8,0) tube.

At every fixed fracture angle, equilibrium atomic coordinates of the SW-pair were searched for, as fig.2 shows. Geometry of (8,0):SW is defined by distance \( R_{SW} \) and angle \( \beta_{SW} \) (fig.1). Their variations are reflected by horizontal shifts of total-energy marks from the vertical line of the fixed fracture angle. SW-defect, generated at the compressed side of critical fracture (\( \chi = 1.7 \) degree), was found to be pushed outward the tube surface \( (R_{SW} = R + 0.14d) \), quite alike a material of a continuous-media cylinder under fracture-type deformation.

The sequence of calculations, fulfilled for armchair (5,5) tube's fracture and SW transformation, follows the described above case of zigzag (8,0) tube. It will be sufficient to mention the differences between two cases, which are clear from fig.4. Adiabatic-energy
curves of defect-free tubes support the rule that zigzag tubes are stiffer, than armchair tubes. This could be predicted using simple mechanical ball-and-stick ideas, about a belt of bonds, involved into fracture (fig.1). Lower stiffness of armchair tube, in comparison with zigzag one, changes the response of its SW-defect to the tube fracture. Yield point, i.e. fracture angle of SW-defect generation at the compressed side, is $\chi=2.7$ degree. Energy minimization shows, that defect bond is pushed inward the tube surface ($R_{SW}=R-0.12d$), quite alike stick-and-ball model of armchair tube (fig.1) should do under fracture-type deformation. In armchair tube there is also a channel of SW transformation at the stretched side of fracture, the yield point is $\chi=-3.6$ degree (fig.1), $R_{SW}=R-0.24d$.

**CONCLUSION**

Quantum-chemistry modeling of carbon nanotubes (8,0) and (5,5) has revealed certain properties of the topochemical Stone—Wales defect. The plasticity of nanotubes in certain mechanical experiment, may be predicted without any empirical assumptions about mechanical properties of chemical bonds and/or their connection.

The rolling-up of a planar graphene sheet into a small-diameter nanotube leads to approximately 0.6 eV decrease in defect formation energy.

The SW-defect localized states are resonant with nanotube energy spectrum. In case of fracture-type deformation, the SW-defect on the compressed side of the nanotube is energetically favourable.

At a fracture angle above critical value – yield point [1.7 degrees for (8,0), 2.7 degrees for (5,5)], SW-defect appearance decreases total energy of the nanotube. Thus, fracturing deformation of the nanotube turns on a plasticity channel in the form of mechanical generation of the Stone–Wales defect.

**Acknowledgments.** This study was supported in part by the Russian Foundation for Basic Research, project 08-03-97000.
REFERENCES


Figure 1. Models of fractured nanotubes (8,0) and (5,5) with SW-defect on the compressed side. Empty circles mean atoms in front, black ones are in the rear. Chemical bonds around SW-defect provide 5-7-7-5 pattern of carbon cycles. Fracture of tube axis is shown on the left. Left panel: zigzag (8,0) tube, fracture angle is 2 degrees, vertical scale is 1/6 of the super-cell height. Right panel: armchair (5,5) tube, fracture angle is 3 degrees, vertical scale is 1/11 of the super-cell height.
Figure 2. Calculated total energies of zigzag (8,0) tube with fracture (circles) and with SW-defect (triangles). Ideal parabolas provide the best fit. Each series of triangles represents calculations at a fixed fracture angle – the same as that for corresponding circle, while the horizontal shift reflects variations of atomic coordinates of the SW-defect.
Figure 3. Densities of occupied states (in relative units) calculated using spectra of molecular orbitals of zigzag (8,0) nanotube. Curves are shifted vertically for the eye convenience. (a) graphene, (b) tube without fracture, (c) tube with SW-defect at the stretched side of the fracture, (d) tube with SW-defect without fracture, (e) tube with SW-defect at the compressed side of the fracture.
Figure 4. Calculated total energies of armchair (5,5) tube with fracture (circles) and with SW-defect (triangles). Ideal parabolas provide the best fit. Each series of triangles represents calculations at a fixed fracture angle – the same as that for corresponding circle, while the horizontal shift reflects variations of atomic coordinates of the SW-defect. Fractured-(8,0)-tube energies (common with fig.2) are shown with the dotted parabola.