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How Evaporating Carbon Nanotubes Retain Their Perfection?

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ABSTRACT

We present a mechanism of high-temperature sublimation of carbon nanotubes that does not destroy their ordered makeup even upon significant loss of mass. The atoms depart to the gas phase from the pentagon–heptagon dislocation cores, while the bond disruption is immediately repaired, and the 5|7 seamlessly propagate through the lattice. This explains a broad class of unsettled phenomena when at high temperature or under radiation the nanotubes do not become amorphous but rather shrink in size nearly flawlessly.

Carbon nanotubes owe their amazing and important properties (electronic, optical, or mechanical) to the unique structure, a honeycomb net seamlessly wrapped into a cylinder. Essentially it renders them crystals with no facets or surface, where each atom has exactly the same environment.[1] How carbon atoms assemble into such tubules through catalytic *growth* turned out to be a daunting problem for theory. Here we discuss a process opposite to growth, a *decomposition* of nanotube into carbon atoms as it occurs at high near-sublimation temperature[2−4] or under electron radiation.[5−7] As the analysis below demonstrates, such seemingly random loss of atoms can proceed in a rather organized fashion with the peculiar self-repair mechanism. It shows that sublimation is inherently coupled with the dislocation dynamics in two-dimensional (2D) crystals: ejection of atoms can create edge dislocation dipoles, and it governs the dislocation climb-glide movements, while the dislocation cores serve as scavengers for possibly emerging point defects. This way, a membrane crystal can lose substantial fraction of its mass while maintaining almost perfect structure: it simply shrinks down in scale without much disorder or amorphization. This also well explains the recent remarkable observation of superplastic nanotubes,[4] where their great elongation in spite of multifold mass reduction must proceed through the sublimation−plasticity relaxation process described below.

Although the discussion can broadly apply to 2D crystals and tubes (single graphene layer,[8] cylindrical micelles,[9] microtubules[10]), carbon nanotubes alone offer an abundant record of experimental study. For example, almost 4-fold reduction of diameter (1.4−0.4 nm) under an electron beam did not disrupt the tubular structure,[5] or a thin single-wall neck formed from multiwall tube irradiated at 600 °C.[6,7] Similarly, irradiation was able to transform a carbon cluster into a well-structured carbon onion.[11,12] Most striking is the recent observation of perfectly preserved structure (besides the few mobile kinks) in the course of plastic stretching of a tube, although most of its body (80% mass loss) expired into gas.[4] This accumulating evidence poses a compelling question of how a graphitic layer can avoid defect buildup and especially larger holes while losing a great fraction of its atoms.

High temperature of the atomic lattice brings significant thermal agitation (often enhanced by an electron beam of the microscope). Carbon atoms can more frequently exchange their positions, e.g., via Stone−Wales (SW) bond rotations,[1] by forming Schottky vacancies, interstitial−vacancy pairs, etc. Furthermore, some of the atoms are increasingly likely to entirely abandon the lattice for the benefit of a more entropic gas state, the essence of sublimation, which results in total mass reduction. Intuitively, the exodus of atoms from the lattice should randomly create a growing number of vacancies, inducing disorder and perhaps amorphization, or aggregating in holes (Figure 1a−c). This notion contrasts with the very clean cylindrical shape preserved in experiments in spite of the big reduction in size.[3−5] How can the vast loss in mass be reconciled with the smooth morphing of an ever-sealed tubule (Figure 1a → d) from its initial to final geometry? Natural propensity of covalent bonds to restore connectivity, to self-heal in a network is important but not sufficient, as a trial simulation illustrates: in the course of *random* removal of atoms, many dangling bonds do pair nicely, but the degree of disorder and size of holes progressively increase (Figure 1e−g). Apparently, nature has a more clever mechanism preserving a nearly perfect 2D lattice in spite of its evaporation.

To understand it, consider more thoroughly possible C breakout from different locations of a tube containing generic

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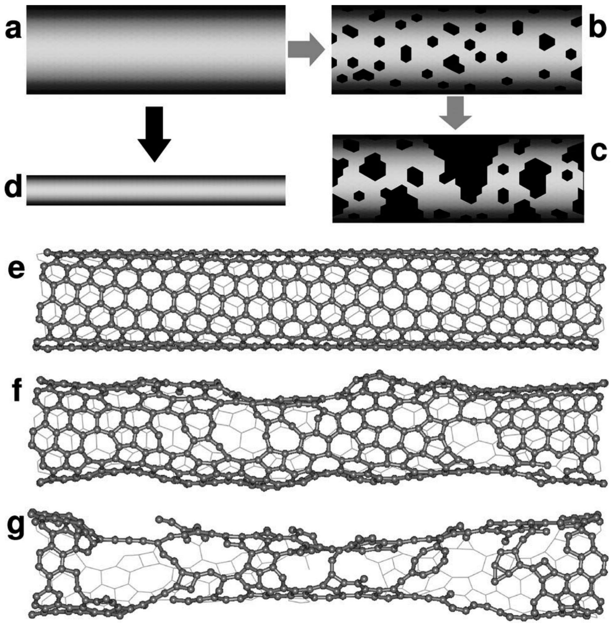

Figure 1. General patterns of material depletion from 2D crystals. Great loss of atoms is expected to create a large concentration of vacancies aggregating into large holes as in a → b → c, or resulting in nanotube amorphization. Random removal of 20% (f) or 55% (g) of atoms from a perfect nanotube (e), shows progressing disorder (simulation was done with classical potential[13]), in contrast to preservation of crystalline integrity in a clean size reduction in experiments, as a → d.

irregularities: a small hole or a vacancy and a 5|7 defect, Figure 2a. Carefully computed energies, required for removing carbon from different sites on the nanotube (into C_2 molecule), *decrease* in the following order, Figure 2b: perfect hexagon-tiled wall, edge of a pre-existing hole or a vacancy, vicinity of a 5|7 defect, and a step on the open end of a tube. (These endothermicities represent accurately the corresponding barriers as well because the reverse processes are barrierless.) The latter means that, in vacuum, a hot tube could undergo a "candle-like" sublimation from the open ends, or its caps could evaporate the C_2 fragments and shrink in a way well-known in fullerene science.[1,14,15] Typically, however, the ends are clamped in the experimental setup.[2−4,6] This suggests a 5|7 defect as the next preferred site for carbon departure. More precisely, comparison of all possibilities in the 5|7 vicinity shows that removing two particular atoms at the side of a pentagon is preferred by almost 2 eV (see Supporting Information Figure S1). This is a significant finding, as it points toward sublimation at the 5|7 rather than randomly or through expansion of multivacancies (holes).

Our next, and surprising, observation is that, upon the deletion of two atoms, the 5|7 defect remains unchanged! Bond reconstruction concurrent with the C_2 removal restores the lattice seamlessly, with the only difference that 5|7 shifts by one lattice parameter (Figure 2c−e). Strikingly, there is no structural change except this simple translation. There is also no violation of mass conservation, as the restoring bonds pull the surrounding lattice inward and ultimately cause the plane shrinkage at infinity, or reduction of tube diameter and length.

It is now important to recall that 5|7 in the lattice of hexagons represents a core of an edge dislocation,[16,17] with Burgers vector **b** (equal to the lattice parameter, $b = \sqrt{3}a$, a being a bond length). The translation described above resembles then the process of climb:[16] reduction of the extra plane upon removal of atoms (or arrival of vacancies, diffusing through the lattice). In the open 2D lattice such pseudoclimb is drastically different than in a "claustrophobic" 3D crystal. The atoms can leave directly into gas with no need and kinetic limitations of slow solid-phase diffusion. Most importantly, pseudoclimb requires no point defects presence near the 5|7 so that the tube can retain its high quality. As atoms are lost to sublimation, the 5|7 zips up

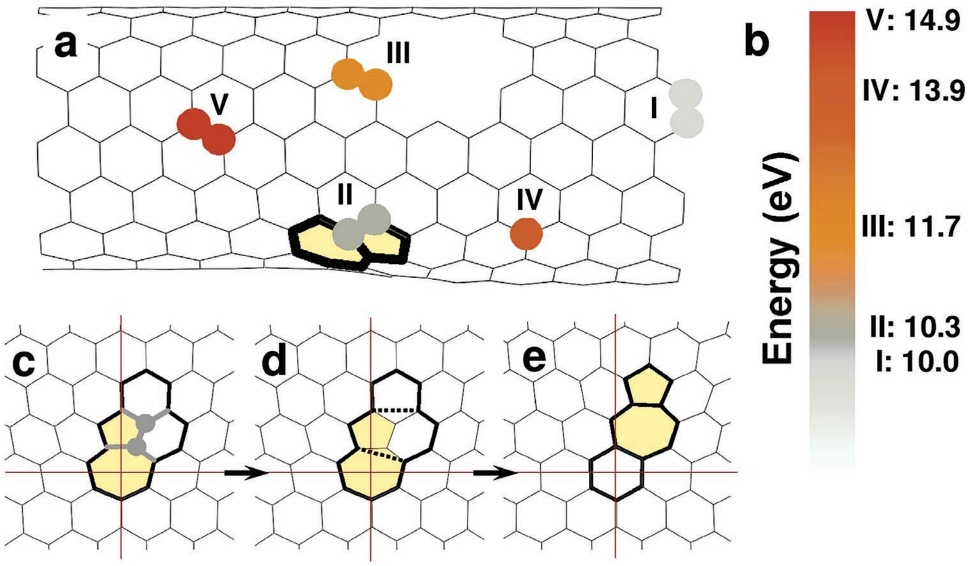

Figure 2. Energy barriers of carbon removal from different sites. (a), at the open tube end I, near the 5|7 dislocation II, from a hole in the tube wall III, or from pristine wall as C_1 atom IV, or a C_2 dimer V. The energy cost is computed (b) and is notably low for the dimer removal from a side of pentagon II because it does not create any new defects or dangling bonds and only moves the 5|7 by one lattice parameter (c → e). Free tube sections of 351 atoms were optimized with the PM3 method.

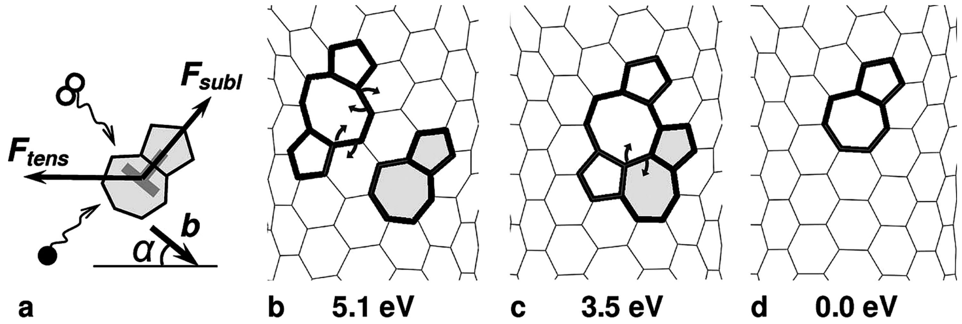

Figure 3. Dynamics of the 5|7 dislocation in the lattice of hexagons. Effective forces on 5|7 (a) are due to elastic tension, F_{tens} (directed circumferentially) or to chemical nonequilibrium that causes sublimation, F_{subl} (perpendicular to the Burgers vector **b**, at angle α to the circumference). 5|7 core can serve as a sink for point defects such as divacancy shown to approach and vanish by a sequence of SW bond rotations, with significant reduction in energy (b → d). Energies were computed with PM3 method on a free-end tube.

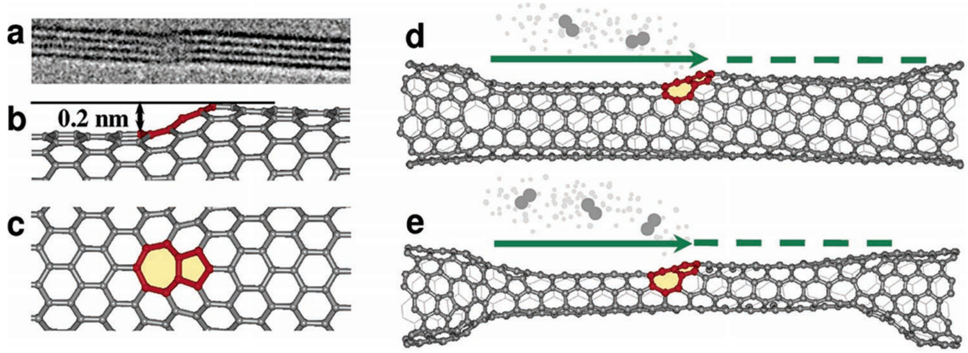

Figure 4. Kink structure and propagation in the course of nanotube sublimation. The pattern and the magnitude (about 0.2 nm tall) of experimentally observed[3] kinks (a) are in qualitative agreement with the relaxed 5|7 core vicinity (b−c) in the nanotube. Simulations (performed with classical potential[13]) show how a perfect nanotube (Figure 1e) shrinks in diameter while the carbon is removed through the lowest energy chanel, and the 5|7 core shuttles along the tube, here at 20% (d) and 55% (e) loss of mass.

the lattice seamlessly. Equiprobable removal of the atoms on the left or right side of the 5|7 moves it in the average direction perpendicular to its Burgers vector, which is conventional for climb. If the chemical potential of carbon is by $\Delta\mu$ lower in gas than in the lattice, and each four-atom departure causes shift by $3a$, the driving force for pseudoclimb is $F_{\mathrm{subl}} = (4/3a)\,\Delta\mu$, directed normal to **b**, toward reduction of the extra plane, from “7” to “5” in Figure 3a.

Complimentary to pseudoclimb, a glide[17,18] of 5|7 core in the ±**b** directions can be achieved by the bond flips, i.e., SW transformations. This mass-conserving movement is obviously indifferent to chemical nonequilibrium but can be guided by the Peach−Kohler force[16] due to elastic tension σ in nanotube wall, $F_{\mathrm{tens}} = \sigma b \sin \alpha$, directed always along the circumference,[17] Figure 3a. (We neglect small force $f_{\mathrm{curv}} \sim 1/d^2$ acting axially, toward the thinner section, due to the elastic energy variation with the diameter change caused by the 5|7.)

In the course of 5|7 migration, they can occasionally recombine with each other or eventually vanish as they reach the sample ends. Now the understanding of the forces applied to a 5|7 allows one to see how these defects can be generated, even in a flawless lattice, through the pair-production processes (remotely similar to those in particle physics). Great tension is known to favor the SW bond rotation,[19] which creates a SW defect, a 5|7/7|5 pair that then can split into individual cores. Concurrently, C_2 removal caused by chemical nonequilibrium in sublimation or induced by irradiation[20] creates divacancy, which is structurally equivalent to a face-to-face 5|7 and 7|5 pair (see Supporting Information Figure S2). To appreciate this equivalence, C_2 removal can be viewed as disruption of a crystal plane, thus creating two extra planes facing each other: 5|7⋯7|5. The important conclusion here is that, in the absence of common Frank−Reed dislocation sources,[16] 5|7 can emerge even among perfect hexagons through either mass-conserving bond flips or via the removal of carbon at sublimation conditions.

Besides serving as the easiest gateway to the gas phase for carbon, 5|7s are also able to interact with the lattice point defects in an important way: vacancies (or interstitials) can be absorbed by a dislocation core, with significant reduction in total energy, as point defects vanish while 5|7 simply shifts its position in accord with the loss (or accretion) of atoms. Figure 3b−d displays the example topology of divacancy merging to the 5|7. Similarly, 5|7 serves as a scavenger for monovacancies, interstitials, adatoms, and addimers that high temperatures or radiation might create.

On the basis of the key mechanisms described above, the emerging picture of sublimation and plasticity is following. Sublimation preferably occurs through C_2 emission from the 5|7 as gateways, causing their stepwise moves. Concurrently, tension can induce their glide via SW bond flips. If the 5|7 dislocation cores were absent or vanished, their fresh pairs in the form of primary 5|7/7|5 defects can be nucleated through either C_2 breakout from a perfect lattice or by SW rotations. The trajectory of 5|7 is controlled by the balance of forces in the "free body diagram" of Figure 3a. For example, in the case of clamped-end sublimation, as the tube tends to shrink, its tension σ and accordingly the force F_{tens} increase, until the generic helical trajectory (climb and glide) turns to mostly an axial direction so that movement of the 5|7 causes no further reduction in length. This should represent the stationary steady state, and this is what computer simulations show (in agreement with the recent experimental observations[4,21]).

Similarity in the qualitative pattern and the magnitude of the observed kink[3,4,22] and computed relaxed structure near the 5|7 supports their identity, Figure 4a−c. Dynamic simulations show how a nanotube can be significantly reduced in size through sublimation while maintaining nearly perfect structure. The key mechanism is the pseudoclimb of the 5|7 core (or a few of them) shuttling back and forth the length of the tube, while emitting a "steam" of carbon, in the form of molecular C_2, Figure 4d,e. Although the combination of climb and glide generally corresponds to a helical path, the tension on the tube reaches the level where the stationary trajectory becomes predominantly axial with no further tension buildup.

The analysis above and the associated simulations clearly demonstrate how a nanotube (or other 2D lattice) can maintain nearly perfect structure while undergoing complete sublimation, possibly accompanied by plastic stretching. This also well explains the recent observation of superplastic nanotubes,[4] where their great elongation in spite of multifold mass reduction must proceed through the sublimation−plasticity process described above. Just near the sublimation conditions, the preferred channel is the removal of atoms from the vicinity of a 5|7 dislocation core, which immediately repairs the damage by healing the bonds seamlessly and propagating through the lattice. The balance of chemical and elastic forces controls the most probable trajectory of the kink. This way, higher energy defects like vacancies or holes can be completely avoided, while the 5|7 plays the role of leading emitter of carbon and maintains the clean nanotube morphology. The described mechanism may further help elucidating topology of thermal healing of larger holes[23] as well as suggest defect-suppressing processes in coalescence and even in growth of nanotubes and fullerenes.

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Supporting Information Available: Description of the methods of energy computations and simulation; the energy cost of removing C_2 from different sites around the 5|7 dislocation; creation of 5|7 pairs by a SW bond flip or by removing carbon from a perfect lattice. This material is available free of charge via the Internet at http://pubs.acs.org.

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