

## Enhanced Ductile Behavior of Tensile-Elongated Individual Double-Walled and Triple-Walled Carbon Nanotubes at High Temperatures

J. Y. Huang,<sup>1,2,\*</sup> S. Chen,<sup>1,3</sup> Z. F. Ren,<sup>1</sup> Z. Wang,<sup>1</sup> K. Kempa,<sup>1</sup> M. J. Naughton,<sup>1</sup> G. Chen,<sup>3</sup> and M. S. Dresselhaus<sup>4</sup>

<sup>1</sup>*Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467, USA*

<sup>2</sup>*Center for Integrated Nanotechnologies (CINT), Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

<sup>3</sup>*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

<sup>4</sup>*Department of Physics, and Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

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We report exceptional ductile behavior in individual double-walled and triple-walled carbon nanotubes at temperatures above 2000 °C, with tensile elongation of 190% and diameter reduction of 90%, during *in situ* tensile-loading experiments conducted inside a high-resolution transmission electron microscope. Concurrent atomic-scale microstructure observations reveal that the superelongation is attributed to a high temperature creep deformation mechanism mediated by atom or vacancy diffusion, dislocation climb, and kink motion at high temperatures. The superelongation in double-walled and triple-walled carbon nanotubes, the creep deformation mechanism, and dislocation climb in carbon nanotubes are reported here for the first time.

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Carbon nanotubes are perceived as being rather brittle because of the strong C-C  $sp^2$  bonds in the honeycomb lattice [1]. It is postulated that nanotubes accommodate no plastic deformation even beyond the elastic limit or before breakage [2–5]. However, we discovered recently that single-walled carbon nanotubes (SWCNTs) become superplastic and can accommodate extremely large plastic strains with a total elongation of 280% when being tensile loaded at high temperatures [6]. Questions pertinent to the superplastic SWCNTs include the following: Does superplasticity prevail in double-walled, triple-walled, and other multiwalled carbon nanotubes (MWCNTs)? and What is the physics behind the superelongation?

In this Letter, we report exceptional ductile behavior of double-walled carbon nanotubes (DWCNTs) and triple-walled carbon nanotubes (TWCNTs) with an elongation of 190% and a diameter reduction of 90% during tensile loading at high electrical bias or high temperatures. High temperature creep deformation, characterized by atom or vacancy diffusion, dislocation climb, and kink motion, contributes to the superelongation.

The success of our experiments is built upon an advance in technology achieved in our laboratory recently in fabricating dog-bone-shaped nanotube samples, which are ideal for *in situ* tensile-loading experiments inside a high-resolution transmission electron microscope [HRTEM, Fig. 1(a)] [6–10]. We found that individual MWCNTs generally thin and break near the middle under high bias voltages [6–10], resulting in the formation of dog-bone-shaped samples that are well suited for tensile-loading experiments.

Figure 1 shows a 190% elongation of a DWCNT during a tensile-loading experiment conducted at a constant bias of 2.2 V ([11], movie M1). Interestingly, the diameter reduction and the elongation occur uniformly along the

tube axis (Figs. 1(b)–1(e), [11]), which we find remarkable since it involves the diffusion and rearrangement of almost all the carbon atoms in the nanotube. This indicates that atom or vacancy diffusion plays a critical role in the elongation process.

Computer modeling [12–15] indicates that the carbon bonds transverse to the axial tension rotate gradually toward the longitudinal position. Consequently, the chirality of the nanotube changes correspondingly, say from a starting armchair tube to a final nearly zigzag tube during the tensile-elongation process. Regardless of the starting chirality of the tube, the overall trend of the chirality changes toward the final zigzag configuration. Once the zigzag configuration is reached, the chirality changes little upon further stressing. Note that the overall elongation is mainly attributed to the rearrangement of carbon atoms induced by kink motion and atom or vacancy diffusion, which leads to a reduction of the diameter of the nanotube, not due to the bond stretching. In fact, computer modeling indicates that the total C-C bond length change is less than 3% during the whole elongation process. Very recent theoretical modeling [14] has confirmed remarkably our previous discovery [6] that superelongation in SWCNTs can be achieved by kink motion and atom or vacancy diffusion in the nanotubes. Similar theoretical modeling in the superelongation of DWCNTs or TWCNTs is not available, but we expect a mechanism similar to that in a SWCNT operating in the superelongation of DWCNTs or TWCNTs.

Note that the DWCNT breaks near the middle, ruling out the possibility of wall sliding. Under a constant bias of 2.2 V, the current decreases substantially from over 200 to 50  $\mu$ A with increasing length and reducing diameter [Fig. 1(f)].

Figure 2 shows a 130% elongation of a TWCNT at a constant bias of about 2.3 V ([11], movie M2). Initial elec-

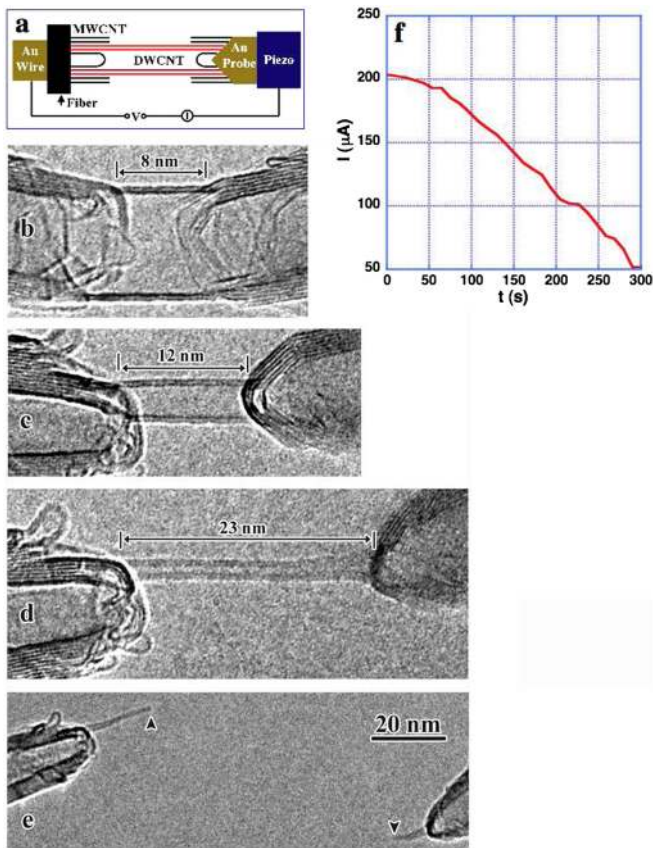


FIG. 1 (color online). Tensile elongation (190%) of a DWCNT at a constant bias voltage of 2.2 V ([11], movie M1). (a) Experimental setup. A dog-bone-shaped sample was produced by electric breakdown of a MWCNT. (b)–(e) Sequential HRTEM images showing the tensile elongation of a DWCNT. In (e) the nanotube is broken near the middle (pointed out by two arrowheads), (f) Current ( $I$ ) versus time ( $t$ ) plot for the same DWCNT [(b)–(d)].

trical breakdown produced a TWCNT inside a DWCNT [Fig. 2(a)]. The outer DWCNT may be too defective and breaks first upon pulling [Fig. 2(b)], causing a current drop of  $224 \mu\text{A}$  [Fig. 2(e)]. The TWCNT elongates uniformly along the tube axis upon pulling, and then the innermost wall breaks [see the arrowhead in Fig. 2(c)], causing a current drop of  $11 \mu\text{A}$  [Fig. 2(e)]. Further pulling breaks the remaining DWCNT [Fig. 2(d)].

The 190% elongation of the DWCNT (Fig. 1) and the 130% elongation of the TWCNT (Fig. 2) at high temperatures are far beyond those of previous experimental results at room temperature [16–18]. Tensile deformation on individual and ropes of SWCNTs by atomic force microscopy showed a much lower breaking strain of less than 6% at room temperature [16], while on individual MWCNTs, a sword-in-sheath failure mechanism with a maximum breaking strain of 12% for the outmost layer at room temperature was reported [17]. The superelongation is apparently due to the ductile nature of nanotubes at high temperatures [12–15, 19–23].

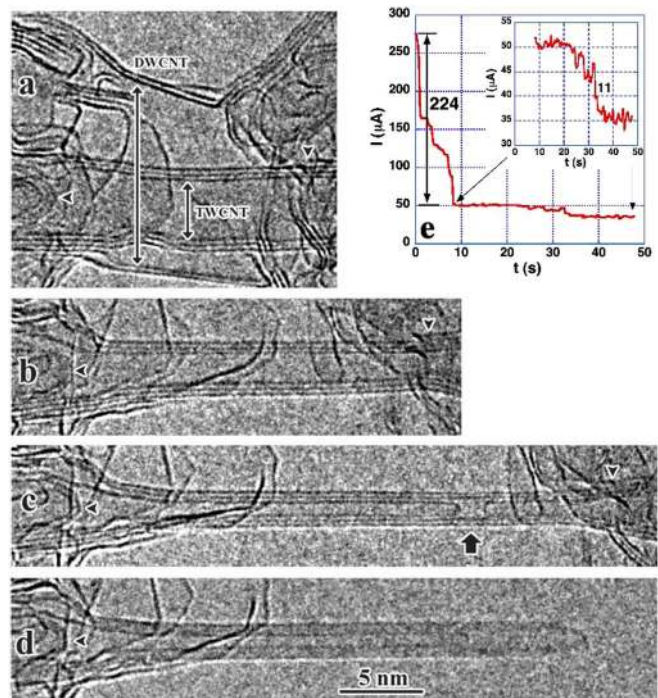


FIG. 2 (color online). Tensile elongation (130%) of a TWCNT at a constant bias of 2.3 V ([11], movie M2). (a) Electric breakdown produced a double-hollow tube with a TWCNT inside a DWCNT with a length of about 15 nm. (b) The outer DWCNT breaks upon pulling, (c) the innermost wall breaks (pointed out by an arrowhead) upon further tensile-loading, (d) the nanotube breaks entirely at a length of about 34 nm. (e)  $I$ - $t$  curves of the nanotube during the elongation. Inset is magnified  $I$ - $t$  curves showing a current drop of  $11 \mu\text{A}$  when the innermost wall is broken.

We have found that superelongation is never observed when nanotubes are pulled at room temperature. Figure 3 shows the tensile elongation of a DWCNT at room temperature ([11], movie M3). The total elongation is 7%, and the diameter reduction is 2%, which are much less than that in the nanotubes pulled at high temperatures.

We pulled about 50 nanotubes, including SWCNTs, DWCNTs, and MWCNTs, either at room temperature (without bias voltage) or at high temperatures (with a bias voltage of above 2 V). The elongation is usually larger than 50% for the nanotubes pulled at high temperatures. The limiting factor to the elongation is that the nanotubes generally experience electrical breakdown very easily and/or undergo wall sliding before substantial elongation. The elongation is generally less than 10% when the nanotubes are pulled at room temperature, which is about five or more times lower than that for the nanotubes pulled at high temperatures. Therefore, it is evident that high temperature plays a key role in the superelongation of the nanotubes.

Our previous experiments showed that individual nanotubes are resistively heated to temperatures above  $2000^\circ\text{C}$  at similar high bias voltages [6–10]. At such high tempera-

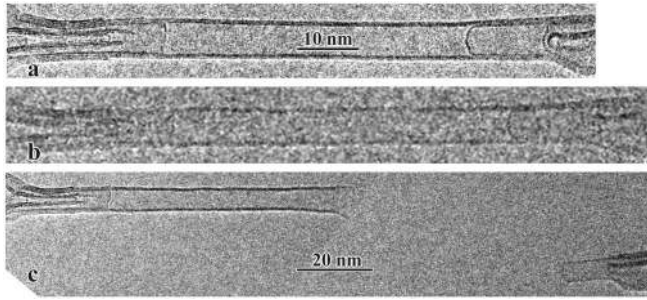


FIG. 3. Tensile elongation of a DWCNT without applying a bias voltage. Electric breakdown produces a DWCNT section with an initial length of 72 nm and diameter of 4.8 nm (a), and it is elongated to a length of 77 nm and a diameter of 4.7 nm (b) before it breaks (c).

tures, defects and diffusion are fully activated, leading to plastic flow in the nanotube. Indeed, during the tensile-loading experiments, kinks frequently emerge, propagate, and then disappear along the nanotube walls [6,9]. The kink motion in carbon nanotubes proves conclusively that nanotubes are extremely ductile at high temperatures. In addition to kink motion, we show below that vacancy or atom diffusion and dislocation climb also play significant roles in the elongation. Theory [15,22] shows that the energy barrier for diffusion decreases almost linearly with strain; therefore, diffusion is favored at high temperature and under high strain. Diffusion helps to heal the defects and prevent the generation of large holes on the nanotube walls during the elongation process.

We show here convincing evidence that point defects such as vacancies and interstitials are highly active at high temperatures. Figure 4 shows the climbing of a Frank dislocation dipole with Burgers vectors being  $\pm 1/2[0001]$  (along the radial direction). The dislocation dipole is produced by electric breakdown of an intermediate nanotube wall. As the dislocations climb, a nanocrack is created on the left wall (marked by stars). However, the crack on the right walls disappears immediately after the dislocation passes by. The velocities of the upper and the lower dislocations are 5 and 24 nm/min, respectively. The reason for the different migration velocities of the dislocations is unclear. It should be noted that a Frank dislocation with a Burgers vector of  $1/2\langle 0001 \rangle$  in a graphite lattice generally cannot glide along the slip planes at room temperature because it is not activated. The only way for a Frank dislocation to move is through dislocation climb, which requires diffusion of vacancies and interstitials. Indeed the dislocation motion in Fig. 4 is caused by dislocation climb, since its motion is along the dislocation plane [the plane wherein the dislocation line resides, which is the (0002) plane]. The dislocation climb observed here is caused by vacancy diffusion and condensation. Dislocation climb in graphite occurs only at temperatures above 2000 °C [24–26]. The activation of dislocation climb provides solid evidence that the nanotube is heated to tem-

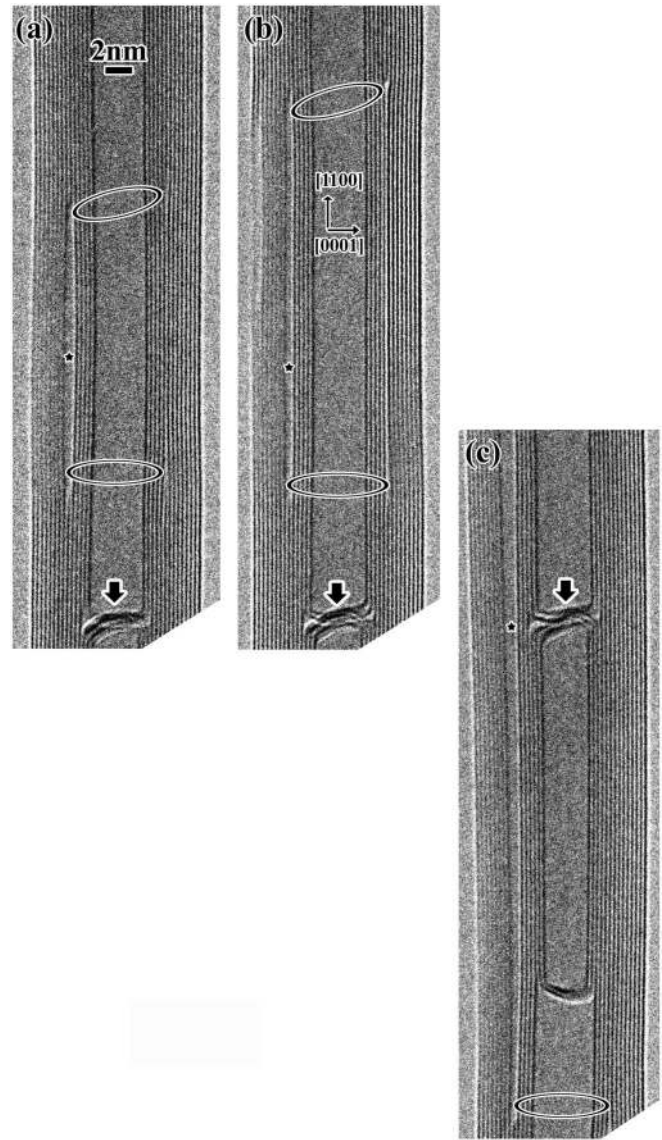


FIG. 4. Sequential HRTEM images showing dislocation climb in a MWCNT at a bias voltage of 1.7 V. The cores of the dislocations are marked by ellipses. The arrowheads mark a feature that is not changed. Stars mark cracks. The upper dislocation in (a) and (b) has moved out of the field of view in (c).

peratures higher than 2000 °C, and that vacancies and interstitials are very active at high temperatures [6–10,23].

The superelongation phenomenon reported here is essentially related to the creep deformation of carbon nanotubes, which is an important high temperature deformation mechanism that has not been explored thus far. When a material is deformed at a temperature above  $0.5T_m$  (where  $T_m$  is the melting temperature), it usually involves the creep deformation mechanism [27–30]. The temperature in our experiments is estimated to be higher than 2000 °C, which is the temperature range where graphite exhibits predominantly plastic behavior, i.e., creep. The observation of vacancy or interstitial mediated kink motion [6,9]

and dislocation climb indicates that creep in carbon nanotubes is dominated by dislocation climb and vacancy diffusion. Our report here calls for further quantitative experiments, such as measurements of the strain rate and temperature effect, and extensive theoretical modeling on the creep behavior of carbon nanotubes. We were unable to measure the applied force during the tensile-elongation process in our platform. Such studies should clarify whether or not carbon nanotubes continue to possess high strength at such elevated temperatures. It might be possible that carbon nanotubes may possess even higher strength at high temperatures than that at room temperature, considering the fact that the tensile strength of graphite nearly doubles as the temperature is increased from room temperature to 2500 °C [24–26]. We have no doubt that further studies in this regard should lead to a deeper understanding of the high temperature mechanical properties of carbon nanotubes, and eventually pave the way for high temperature structural applications, such as aerospace, electrical, and sensor applications. Such studies should also shed light on the mysterious strength increase with increasing temperature in graphite [24–26].

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\*Corresponding author.

Current address: Sandia National Laboratories, Albuquerque, NM 87185, USA.

Electronic address: jhuang@sandia.gov

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