Axial buckling and compressive behavior of nickel-encapsulated multiwalled carbon nanotubes


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In a recent report [Sun et al., Science 312, 1119 (2006)], the partially filled material inside multiwalled carbon nanotubes (MWNTs) was shown to have shrunk and deformed in the axial direction under 300 kV electron irradiation. In this experiment, 100 MeV Au ion irradiation was performed to study the deformation and defects in uniformly nickel filled MWNTs with high-resolution transmission electron microscopy and Raman spectroscopy. We propose that high-pressure induced torsion in confined nickel could possibly result in successive compressions and expansions of the tubes, leading to axial buckling of MWNTs. The tangential Raman G band systematically upshifts as the ion fluence increases, attributed to the torsional strain. In contrast to a square root dependence of the buckling wavelength (λ) on the radius (r) and thickness (t) of the tubes [λ=3.5(r/t)1/2], as predicted by theoretical models, the exponential fit of the data that assumes λ∼e(3/2r) also produces an excellent fit.

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I. INTRODUCTION

The buckling of the single walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) has been a topic of intense research, as is evident from a number of papers published recently. Initial interest in buckling goes back to Euler who discovered the elastic instability and found that a rod, when compressed longitudinally, would buckle sideways if the strain exceeds a certain critical value. The sp2 carbon bond in the basal plane of the graphite is the stiffest in nature. This provides the SWNTs and MWNTs exceptional hardness and the tubular structure allows the material to be flexible and can undergo large elastic deformation without breaking. Theoretical models have been used to understand the buckling of the SWNTs and MWNTs, most have applied the beam theory and the continuous cell models to generate the buckling in the tube walls by clamping the tube ends. However, the models do not impose the structural constraints of nested nanotube structure and use the value of 0.34 nm for the thickness of the wall of the SWNTs. The models predict a square root dependence of the buckling wavelength (λ) on the radius (r) and thickness (t) of the tubes [λ=3.5(r/t)1/2]. The situation is further compounded by the fact that the experimental data and the actual experiments producing buckled structures of nanotubes are almost nonexistent. Most of the experiments have depended on the bending of the tubes that really does not satisfy the conditions of the models that both ends of the tubes be constrained. A recent study by Ni et al. showed axially compressed buckling of SWNTs filled with C60, CH4, or Ne molecules. Wang et al. assumed the effect of critical radial pressure to explain the compressive stress to understand the axial strain.

Recently, we synthesized the nickel filled MWNTs in our laboratory and reported the excellent crystalline orientation of the nickel nanorods. These nanorods are confined inside the MWNTs of length of 0.29–0.90 μm and would be ideally clamped under the stiff sp2 carbon bonds in the basal plane of graphite structure. The irradiation of these exciting structures with Au ions of 100 MeV would generate high-pressure induced stress between the two lattices, as the electronic energy loss of the ions are different for graphene and nickel lattices and also the losses occur over an extremely short period (10−12 s). We report on this innovative method of generating highly stressed buckling patterns in the nickel filled MWNTs along a length of about 0.90 μm. The irradiated tubes with strained walls are studied in detail by high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. We have measured the wavelength of the buckled structure and fitted it with the existing theoretical models.

II. EXPERIMENT

Nickel-encapsulated MWNTs used in this study were synthesized by microwave plasma chemical vapor deposition apparatus, the details of which are reported elsewhere. The MWNTs were treated with isopropyl alcohol in an ultrasonic bath and were transferred by replica technique onto a carbon coated copper grid for transmission electron microscopy (TEM). The lattice imaging of the MWNTs, as well as of the nickel filling, along with electron diffraction patterns before and after irradiation, is recorded using HRTEM in a JEOL TEM 2010 (UHR model) operated at 200 kV. The micro-grids were irradiated perpendicularly by Au ions with energies of 100 MeV at room temperature using 15UD peltatron at IUAC, New Delhi with the fluences of 1012, 5 × 1012, and 3 × 1013 ions/cm2, respectively. Raman spectra of the pristine and irradiated tubes are recorded in a confocal Jobin-Yvon Raman spectrometer with a 514.5 nm, Ar ion laser (20 mW power) and 100× objective lens.

III. RESULTS

Figure 1(a) shows the TEM image of the nickel-encapsulated nanorods and Figs. 1(b) and 1(c) are the HR-
TEM images showing the lattice fringes of the pristine nickel and tube walls before the ion irradiation. The mean outer diameter of the MWNTs, as determined from TEM images in Fig. 1(a), varies in the range 30–50 nm and that of nickel nanorods is 13–17 nm. The length of the filled tubes varies between 0.29 and 0.90 μm and the nanotubes appear straight before irradiation without any evidence of axial disorder, as is evident from the lattice images in Figs. 1(b) and 1(c); the encapsulated nickel, as well as the tube walls, has a nearly perfect structure without any crystalline defects within the resolution of our HRTEM. The lattice spacing of the crystal-line planes of nickel, estimated to be 0.196±0.004 nm, matches closely to the d spacing of (111) Miller planes (0.203 nm). These planes are inclined at an angle of 39.6° with respect to the tube axis, as already reported in our earlier work.16 The fringes observed on the walls of the MWNTs correspond to (002) graphitic basal planes having separation of 0.322±0.002 nm.

Figures 1(d)–1(h) are the TEM images of the nickel-encapsulated tubes after the irradiation with Au7+ ions of 100 MeV at fluence of 3×10¹³ ions/cm². Figures 1(d)–1(f) are low magnification images of the buckled MWNTs while Figs. 1(g) and 1(h) show the curvature of the tube walls in intimate contact with the nickel and that of the outer walls, respectively. As is evident from Figs. 1(d)–1(h), an axial compression and expansion of the nanorods, as well as of the tube walls, have taken place after the irradiation, clearly showing a wavelike pattern along the length of the tube, the wavelength of which can be easily measured. Figures 1(g) and 1(h) depict the progressive curvature produced in the graphite walls as one moves away from the nickel carbon interface. The curvature of the graphite walls produced due to the heavy ion irradiation is lower in the immediate vicinity of the nickel filling and it increases away from the interface, with the steepest curvature being produced in the walls at some intermediate location. It is clear from the figure that defects on tube walls start propagating from the outer tube walls with sharp curvature while graphite walls near the interface have large curvature. The lattice spacing of the graphite walls in the immediate vicinity of the nickel filling, as shown in Fig. 1(g), is altered to 0.333±0.002 nm, as compared to 0.322±0.002 nm before irradiation. Similarly, the angle between the nickel (111) planes and the tube axis changes to 81.6°, as opposed to 39.6° before irradiation, as shown in Fig. 1(g). It is interesting to note that the buckling of the nickel-encapsulated MWNTs is not observed at fluence lower than 3×10¹³ ions/cm². To further confirm these results, the samples prepared under the same conditions were irradiated with Au7+ ions of 1.5 MeV and fluence of 5×10¹³ ions/cm². No buckling was, however, observed.

Figure 2 shows Raman spectra of the nanotubes irradiated with Au7+ ions of energy of 100 MeV at three fluences, 10¹², 5×10¹², and 3×10¹³ ions/cm², respectively. Our pristine tubes show three major bands in Raman spectra: (i) at 1347 cm⁻¹, D band, which originates from the finite size effects in sp² carbons generally associated with the presence of disordered graphite, (ii) at 1573 cm⁻¹, G band (E₂g symmetry), due to the tangential breathing mode in MWNTs; and (iii) at 1609 cm⁻¹, D' band (A₁g symmetry), associated with the maximum in the two-dimensional phonon density of states of graphene.18 In our samples, the Raman band at 1573 cm⁻¹ downshifts from its original position of 1580 cm⁻¹, perhaps due to the coupling of the phonons in the graphene and nickel lattices. Although there is no buckling observed in tubes irradiated with the fluences of 10¹² and 5×10¹² ions/cm², the Raman G band associated with the E₂g mode shifts to 1578 cm⁻¹ [Fig. 2(b)] in the tubes irradiated with 5×10¹³ ions/cm². We do not observe any significant change in Raman spectra for the tubes irradiated with 10¹³ ions/cm². The position of the G band shifts to 1586 cm⁻¹ in the tubes irradiated with the fluence of 3
$10^{13}$ ions/cm$^2$, as shown in Fig. 2(c). A small shoulder at the left of the $D$ band can be also seen in Fig. 2(c). A probable reason for the origin of this shoulder could be the phonon confinement in disordered graphite. Another interesting observation is the significant broadening of the $G$ band with the irradiation. The details of the Raman analysis are shown in Table I.

IV. DISCUSSION

High energy Au$^{7+}$ ions used in the present case dominantly lose their energy in any lattice via the electronic energy loss $(dE/dx)_e$, the value of which for the case of nickel lattice is 32.5 keV/nm. In contrast, the theoretical simulations have shown that the threshold energy for the creation of defects in the nickel lattice is $\approx 67$ keV/nm.$^{20}$ In a recent publication, we have proposed that the value of $(dE/dx)_e$ in nickel nanorods can increase significantly due to the confinement of the nanorods.$^{21}$ As the energy value crosses the threshold value, according to the thermal spike model, a cylindrical region of nanometer size of highly excited electrons is created in nickel nanorods which transfers energy to the lattice in picoseconds. This may lead to the melting of the nickel nanorods confined inside the MWNTs. As the molten nickel solidifies, the difference in thermal expansion coefficients ($\alpha$) of nickel and carbon generate the required stress to produce buckling. It may be noted that there is a huge difference in the values of $\alpha$; the ratio of $\alpha_{\text{Ni}}/\alpha_{\text{C}}$ as reported in the literature is 16, where $\alpha_{\text{C}}$ is the radial thermal expansion coefficient of the nanotubes. Our preliminary calculations

![Figure 2. Raman spectra of the nanotubes irradiated with Au$^{7+}$ ions of energy of 100 MeV at three fluences, $10^{12}$, $5 \times 10^{12}$, and $3 \times 10^{13}$ ions/cm$^2$, respectively. The inset of the figure shows the shift in the position of the $G$ band as a function of the ion fluence.](image-url)
show that the stress generated at the interface of graphite and nickel is of the order 100 GPa and compares favorably to the recently reported value of 40 GPa by Sun et al.\textsuperscript{22} Thus, the high pressure onto the nickel core resulted from different thermal expansion coefficients between the tube walls and the core and/or interface melting. The resultant shear stress at the interface causes the twisting of the nanorod inside the carbon nanotube and generates torsional buckling along the length of the tube.\textsuperscript{23}

A possible outcome of the shear stress generated during the melting and subsequent cooling can be the formation of the Stone-Wales-type defects\textsuperscript{23} on the tube walls which is accompanied by elongation of the tube structure along the axis connecting the pentagons and shrinking along the perpendicular direction and results in multiple buckling along the axial direction. Earlier experiments by Ajayan et al.\textsuperscript{24} on single walled nanotubes had shown that after electron irradiation, the tube develops several necks along the body due to the generation of such defects. The large blueshift and FWHM noted in the Raman band in the samples irradiated with the fluence of $3 \times 10^{13}$ ions/cm$^2$ are strong evidence for the defects generated due to the irradiation. Wu et al.\textsuperscript{23} have shown that the torsional strain may lead to a significant blue-shift in the Raman $G$ band at 1573 cm$^{-1}$ in single wall carbon nanotubes.

The values of $\lambda$ and $r$ in our case can be easily calculated and we can fit the equation $\lambda = 3.5 (r/L)^{1/2}$; however, in our case, $t = n \times 0.34$ nm. Since the number of walls is particularly large in our experiments, the value of $\sqrt{n}$ will be nearly constant for large values of $n$. Figure 3 shows the plots of $\lambda$ vs $\sqrt{r}$ for the various tubes of various diameters used in the present experiments. We have fitted the data by assuming a linear behavior of $\lambda$ vs $\sqrt{r}$ and, contrary to the theoretical calculations as done by Bower et al.\textsuperscript{25} and Pantano et al.\textsuperscript{26} the linear fit does not appear to be very satisfactory. On the other hand, the exponential fit of the data that assumes $\lambda \propto e^{(0.77)}$ produces an excellent fit, as shown in Fig. 3. We should, however, point out that the exponential fit does not really follow from any physical argument, and thus there must be a simpler explanation for the linear fit. An alternate possibility could be that $\lambda \propto r$ and the $t$ could be used as a parameter dependent upon $r$, leading to a square root law, as described above. This interesting result would then indicate that the thickness of the walls of the tubes should not be taken as 0.34 nm, which is definitely justified for the multi-walled nanotubes. The discussion signifies that the understanding of the elastic properties of the nanotubes on the basis of continuum shell theory may be incomplete and one has to include the other constraints of the structure such as nested lattice and the atomicity of the tubes.

As mentioned earlier, the buckling is observed only in the samples irradiated with 100 MeV Au$^{7+}$ ions and with the fluence of $3 \times 10^{13}$ ions/cm$^2$, although Raman results show the presence of defects even in the samples irradiated with the fluence of $5 \times 10^{12}$ ions/cm$^2$. The Raman $G$ band in the samples irradiated with $5 \times 10^{12}$ ions/cm$^2$ shifts by 5.1 cm$^{-1}$ and FWHM is 50.2 cm$^{-1}$. One possible explanation could be that at lower fluence, i.e., at $5 \times 10^{12}$ ions/cm$^2$, the critical value of the strain required to buckle the tubes has still not been attained. The critical imposed strain of nickel nanorods can be calculated using a formula approximated to a simple rod, $\varepsilon_c = 1/2 (n d/L)^2$, where $d$ and $L$ are the diameter and length, respectively, of the nickel nanorod. For the nickel nanorods in our case having diameter $d = 13$ nm and length $L \sim 450$ nm, the value of $\varepsilon_c$ is calculated to be 0.004, while for MWNTs having outer diameter of 40 nm, it is 0.039, an order of magnitude higher than that for the nanotubes. A lower critical value of strain for nickel nanorods indicate that the onset of the described structural changes takes place in nickel first followed by graphite walls. The value of critical strain for MWNTs calculated in our case is comparatively lower than the simulated values obtained for SWNTs for $L = 6$ nm and $d = 1$ nm by Yakobson et al.\textsuperscript{7} which clearly signifies a low strain structure for MWNTs.

\section{V. CONCLUSION}

In conclusion, an axial buckling behavior in nickel filled
thick walled MWNTs has been observed after 100 MeV Au\textsuperscript{+} ion irradiation. We have explained the results by irradiation induced melting of the confined nickel nanorods. The torsional stress generated at the time of the melting may result in the buckling behavior of the tubes. We find that the buckling wavelength can be fitted with the exponential function \( \lambda \propto e^{\frac{1}{1075}} \) instead of a square root dependence of the buckling wavelength (\( \lambda \)) on the radius (\( r \)) and thickness (\( t \)). One cannot, however, discount the possibility that \( \lambda \propto r \) and the \( \lambda \) could be used as a parameter dependent upon \( r \), leading to a square root law. Our results indicate that the theoretical models must include the other constraints of the structure such as nested lattice and the atomicity of the tubes to explain the buckling and elastic properties of MWNTs.

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