

the normal modes. The appearance of the broad band series between 2700 and 1900 cm^{-1} , the peak at 1200 cm^{-1} and the enhanced absorption in the fingerprint region (968 cm^{-1} peak) are all related to the H to D exchange. On the other hand, the β_{OH} peak of C–OH species disappears, indicating that all the hydrogen atoms are replaced from the structural hydroxyl groups. Consequently, the OH stretching peaks must lack from the spectrum, which is true for the peaks at 3630 and 3490 cm^{-1} . Therefore, deuteration makes possible the distinction between ν_{OH} of structural hydroxyl groups and adsorbed water. The broad band centered at 3210 cm^{-1} retained in the spectrum of D_2O exchanged GO is characteristic for the HDO vibrations [8], clearly indicating that this peak corresponded originally (in air-dry GO) to water molecules. We note here that existence of HDO molecules is quite expectable since, after full exchange of the hydrogen content of anhydrous GO (i.e. H of C–OH and COOH groups and the last traces of adsorbed H_2O molecules), they must be present as HDO instead of H_2O in a high excess of ambient D_2O molecules, due to entropy effects. Fig. 1 inset (curve b) shows the effect of deuteration on the band around 1600 cm^{-1} . In contrast to air-dry and anhydrous GO spectrum, there is no band component at 1616 cm^{-1} . This finding indicates not only that there are no H_2O molecules in D_2O exchanged GO, but also that there are no functional groups (e.g. pyrone moieties; Fig. 2 gr. 7) in the GO structure that could promote IR absorption at this wave number, and originally, in spectrum of air-dry GO, only the water molecules were responsible for the signal. Finally, the hydroxyl β_{OH} to β_{OD} band shift reveals a very sharp peak at 1384 cm^{-1}

covered in spectrum of air-dry GO which has never been reported before. We assign this as a peak originating from organic carbonates [8] (Fig. 2 gr. 9).

In conclusion, we have shown by the IR spectrum of the Na-salt of graphite oxide that ketone functionalities must be present in the GO structure. Deuterium exchange over graphite oxide imposes a shift of all OH related bands, allowing for clear distinction between C–OH and H_2O IR stretching vibrations, for elucidation of the origin of the 1600 cm^{-1} band and uncovers a new band, attributed to organic carbonates, hidden in the spectrum of air-dry GO.

References

- [1] Scholz W, Boehm HP. Betrachtungen zur struktur des graphitoxids. *Z Anorg Allgem Chem* 1969;369:327–40.
- [2] Szabó T, Szeri A, Dékány I. Composite graphitic nanolayers prepared by self-assembly between finely dispersed graphite oxide and a cationic polymer. *Carbon* 2005;43:87–94.
- [3] Cassagneau T, Fendler JH. High density rechargeable lithium-ion batteries self-assembled from graphite oxide nanoplatelets and polyelectrolytes. *Adv Mater* 1998;10:877–81.
- [4] Ruess GL. Graphitic oxide. *Monatsh Chem* 1947;76:381–417.
- [5] He H, Klinowski J, Forster M, Lerf A. A new structural model for graphite oxide. *Chem Phys Lett* 1998;287:53–6.
- [6] Brodie BC. Sur le poids atomique du graphite. *Ann Chim Phys* 1860;59:466–72.
- [7] Fuente E, Menéndez JA, Díez MA, Suárez D, Montes-Morán MA. Infrared spectroscopy of carbon materials: a quantum chemical study of model compounds. *J Phys Chem B* 2003;107:6350–9.
- [8] Nakamoto K. Infrared and raman spectra of inorganic and coordination compounds. 5th ed. New York: Wiley; 1997. 86–170.

Size dependent intrinsic bulk twisting of carbon nanotube ropes

H.Y. Liang^a, M. Upmanyu^{a,b,*}

^a Group for Simulation and Theory of Atomic-scale Material Phenomena (stAMP) and Engineering Division, Colorado School of Mines, Golden, CO 80401, USA

^b Materials Science Program, Colorado School of Mines, Golden, CO 80401, USA

Received 14 March 2005; accepted 27 May 2005

Keywords: Carbon nanotubes; Aggregation; Single crystal; Crystallite size; Modeling

* Corresponding author. Address: Materials Science Program, Colorado School of Mines, Golden, CO 80401, USA. Tel.: +1 303 273 3683; fax: +1 303 273 3602.

E-mail address: mupmanyu@mines.edu (M. Upmanyu).

The past decade has seen an explosion of techniques that have successfully realized assembly of aligned single-walled carbon nanotube ropes (CNTRs) [1–3]. These

crystals exhibit excellent electronic and mechanical properties [4–7], while offering unprecedented structural integrity at the nanoscale [8,9]. This unique combination of structure and properties at the nanoscale implies that CNTRs hold promise for next generation nanoelectronics, chemical sensors, drug delivery and nanocomposites. Current understanding of these crystalline assemblies is based on hexagonally-packed aligned nanotubes, with equilibrium inter-tube distances that have been validated via experiments and in several theoretical analyses [8,10,11]. Twisting is a common degree of freedom in this class of filamentous assemblies, yet it has been ignored in most theoretical analyses of CNTRs. Furthermore, recent characterization studies suggest that these assemblies are intrinsically twisted [12–15]. Owing to the inherent coupling between twisting of these assemblies and their electronic and mechanical properties of ropes, it is important to develop a fundamental understanding of this structural degree of freedom in CNTRs. This is the main focus in the present study.

This study is additionally motivated by the fact that while there are several advantages to forming bulk single crystals of these materials, the assembly of CNTRs has been limited to rope radii less than 30 nm [9,11,16]. While easy inter-tube axial sliding has been implicated [17,18], the mechanistic details still remain unclear. Since sliding invariably involves work against the inter-tube Van der Waals forces, it is energetically unfavorable. Furthermore, experimental observations often report CNTR morphologies with thinner “peeled off” rope sections, as opposed to sliding off of isolated nanotubes [13,14]. Apparently, easy intertube sliding is insufficient to explain the limited assembly of CNTRs. Here, we develop a hybrid atomistic-continuum model to investigate the possibility of this bulk degree of freedom, and also investigate the effect of intrinsic bulk twisting of these ropes on their limited self-assembly.

A twisted CNTR is depicted schematically in Fig. 1. Individual nanotubes are helically coiled around the center of the CNTR. Competition between individual nanotube elastic distortions and crystal cohesive energy determines the equilibrium CNTR pitch length Λ_{eq} , and its stability as a function of CNTR radius R .¹ Elastic energy is spent in order to bend, twist and stretch the nanotubes. For the i th nanotube at a distance r_i from the CNTR axis, its helical path (in cartesian coordinates) along the axis can be written in terms of the distance along the rope axis z , i.e.

$$x_i = r_i \cos(\phi z), \quad \text{and} \quad y_i = r_i \sin(\phi z), \quad (1)$$

¹ Entropic effects can induce symmetry breaking defects and misalignments that result in loss of crystallinity; however they dominate at high temperatures and are therefore ignored.



Fig. 1. Schematic showing a stable twisted carbon nanotube rope.

where ϕ is the bulk twist of the assembly, and is related to the helical pitch defined as $\phi = \pi/\Lambda$.² Note that the inter-tube orientational order is preserved as they do not twist relative to their nearest neighbors [19]. Stretching is negligible due to easy inter-tube axial sliding [17,18]. We further ignore ovalization of the nanotubes, as we expect the pitch length to be significantly greater than nanotube radius, $\Lambda_{\text{eq}} \gg r_t$.

Then, the elastic energy is the bending and twisting of each nanotube summed over all nanotubes. For unit rope length, bending and torsional energies of each nanotube depends on its bending and torsional stiffness EI and GJ , respectively:

$$\mathcal{F}_i^b = \frac{EI}{2} \kappa_i^2 \ell_i, \quad \text{and} \quad \mathcal{F}_i^t = \frac{GJ}{2} \frac{\phi^2}{\ell_i}, \quad (2)$$

where κ_i is the nanotube curvature and ℓ_i its length. The curvature and length of each nanotube are both functions of its distance r_i from the CNTR axis:

$$\kappa_i = \frac{\phi^2 r_i}{1 + \phi^2 r_i^2}, \quad \text{and} \quad \ell_i = \sqrt{1 + \phi^2 r_i^2}. \quad (3)$$

Cohesive energy per nanotube is due to weak Van der Waals interactions with neighboring tubes, summed per nanotube pair [10,20]. The interaction energy per unit length of the nanotubes can be determined by integrating Lennard–Jones (L–J) based interactions between nanotube surface elements,

$$U_{\text{tt}}(R_{\text{tt}}, r_t) = \frac{3\pi\rho^2}{8r_t^3} \left(-AI_1 + \frac{21BI_2}{32r_t^6} \right), \quad (4)$$

where R_{tt} is the distance between tube centers and $\rho (= 4/3\sqrt{3}a_{\text{C-C}}^2)$ is the carbon atom surface density. A ($=15.2 \text{ eV } \text{\AA}^6$) and B ($=24100 \text{ eV } \text{\AA}^{12}$) are the L–J parameters and I_1 and I_2 are surface integrals dependent on the reduced inter-tube distance $R'_{\text{tt}} = R_{\text{tt}}/r_t$ [10]. Then, the total cohesive energy per unit rope length $\mathcal{F}_i^c$ can be calculated using Eq. (4), summed over the lengths of the nearest-neighbor tubes. Since we expect the equilibrium pitch length to be much larger than

² For algebraic convenience, we define the pitch length to be associated with a rotation of π radians, as opposed to the usual 2π radians.

the nanotube radii ($\Lambda_{\text{eq}} \gg r_t$), we ignore the effect of nanotube curvature on the inter-tube cohesive energies. Then, the cohesive energy can be simply expressed as the equilibrium cohesive energy per unit length U_{c}^{eq} (U_{tt} at $R_{\text{tt}} = R_{\text{tt}}^{\text{eq}}$) times net (nearest-neighbor) inter-tube interaction length. Surface energy effects follow from the fact that inner tubes have six nearest neighbors, while the surface tubes on the edges and corners have four and three nearest neighbors, respectively.

The total energy of the twisted rope $\mathcal{F} = \sum_i (\mathcal{F}_i^{\text{b}} + \mathcal{F}_i^{\text{t}} - \mathcal{F}_i^{\text{c}})$ can be expressed as a function of the bulk twist angle, $\mathcal{F}(\phi)$.³ Evidently, the twisting enhances the cohesive energy of the rope by increasing the effective interaction length of the individual nanotubes per unit length of the rope, at the cost elastic distortions of the individual nanotubes. The variational derivative of total free energy (per unit rope length) $\partial \mathcal{F}(\phi, R) / \partial \Lambda$, yields the equilibrium bulk twist ϕ_{eq} ($=\pi / \Lambda_{\text{eq}}$). Fig. 2 shows the rope radius dependence of the equilibrium bulk twist, ϕ_{eq} , for (10,10) achiral nanotube based CNTRs. The elastic moduli of nanotubes used in the calculations are $E = 1.347$ TPa and $G = 0.547$ TPa, and the bending and torsion stiffness are calculated based on a nanotube thickness 0.34 nm [11]. The behavior can be divided into three distinct regimes, as shown in the figure. In regime I, it is energetically unfavorable for the CNTR to be twisted—the nanotubes are necessarily straight. The energetic cost associated with the torsional and bending distortions is too large to be compensated by twist-induced increase in inter-tube interactions. This behavior persists till a critical CNTR radius, $R_1^* \approx 42$ nm, beyond which equilibrium CNTR configuration is intrinsically twisted (regime II).⁴

In regime II, increase in inter-tube interaction area (length) effectively counteracts the elastic distortions and therefore stabilizes the bulk twisted state of the CNTR. The magnitude of the equilibrium bulk twist increases monotonically with CNTR radius, with a maximum twist angle $\phi_{\text{eq}} \approx 2.5^\circ/\text{nm}$ ($\Lambda_{\text{eq}} \approx 72$ nm). The shape of curve is sigmoidal, i.e the twist angle increases rapidly at larger radii. Beyond another critical radius $R > R_2^* \approx 54$ nm, the elastic energy stored in the crystal is too small to offset the enhanced cohesive energy of the CNTR. Ideally, the crystal should continually twist. In practice, as explained later, we predict that the crystal disassembles into smaller radii ropes.

The overall twisting behavior depends on the radius of the constituent nanotubes, r_t . To illustrate, we have calculated the two critical rope radii for five (n, n)

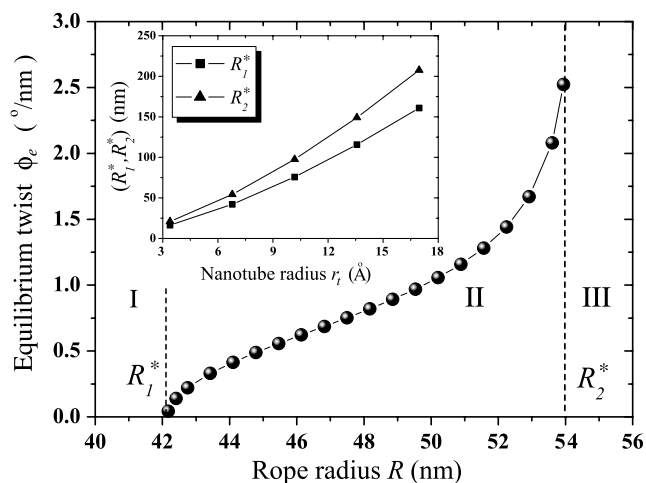


Fig. 2. Variation of the equilibrium twist angle of the rope, ϕ_{eq} with the rope radius R , divided into three regions (separated by dotted lines)—I ($R < R_1^*$, no twist), II ($R_1^* < R < R_2^*$ stable twist), and III ($R > R_2^*$, unabated twist). (inset) The dependence of the critical radii R_1^* and R_2^* on individual nanotube radius, r_t .

achiral nanotube based CNTRs, $5 \leq n \leq 25$ (inset, Fig. 2). The increase in the critical radii is quite dramatic (more so for R_2^*) as the CNTR cohesive energy rapidly decreases due to reduction in overall nanotube surface area, while the circumferential inter-tube separation is relatively insensitive to r_t [8,10]. Also, since the bending and torsional stiffness increase with r_t (mainly increase in the two moments of inertia), the elastic energetic cost also increases. The effect is more pronounced for R_2^* , as it is more sensitive to the cohesive energy of the rope. Therefore, range of rope thickness over which bulk twisting is stabilized increases. Of course, the nanotubes are now prone to ovalize as well. The additional strain energy increases the value of both critical thicknesses.⁵

Is it then possible for sufficiently thick CNTRs to twist unabated? The key to the answer lies in the cross-sectional distribution of strain (elastic) energy stored in twisted crystal (regime II), $\mathcal{F}^{\text{s}} = \sum_i (\mathcal{F}_i^{\text{b}} + \mathcal{F}_i^{\text{t}})$ —it does not increase monotonically away from the CNTR axis. The torsional energy decreases as twisting of nanotubes is distributed over longer lengths, while the bending energy increases as the nanotubes become increasingly curved. Then, the maximum strain energy $\mathcal{F}_{\text{max}}^{\text{s}}$ occurs at an intermediate radial distance, r_{max} . This is confirmed in Fig. 3, a plot of the radial strain energy distribution for rope radii $R = 48$ nm and $R \approx 54$ nm. For $R \approx 48$ nm, the maximum strain energy is closer to the CNTR surface, and quite small— $\mathcal{F}_{\text{max}}^{\text{s}} \approx 0.02$ eV at $r_{\text{max}} \approx 36$ nm. For thicker ropes the strain energy increases while

³ While we have expressed the energy of the twisted rope in continuous form, they can also be expressed in discrete forms. The difference between the two approaches becomes significant only for ropes consisting less than 25 nanotubes.

⁴ In general, finite temperature effects (thermal fluctuations, entropy, etc.) will smooth the transition into between the two regimes.

⁵ Assuming little change in cohesive energy, though this will change as well.

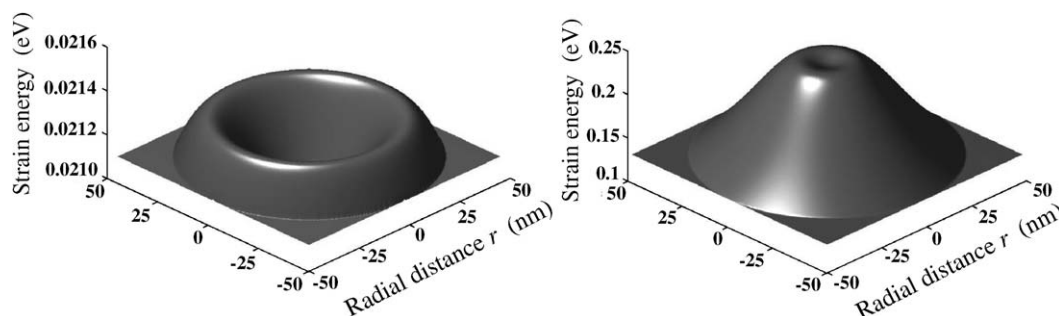


Fig. 3. Strain energy distribution across the rope cross-section, for rope radii $R \approx 48$ nm (left) and $R \approx 54$ nm (right).

the maxima shifts towards the CNTR axis. For $R \approx 54$ nm, the maximum strain energy increases by almost an order of magnitude— $\mathcal{F}_{\max}^s \approx 0.25$ eV at $r_{\max} \approx 12$ nm (Fig. 3).

In effect, as the CNTR radius increases during its assembly, the maximum strain energy increases and its location moves radially inwards. It is most reasonable to expect that strain energy is large enough to locally weaken the inter-tube adhesion on the maximal strain surface, $r = r_{\max}$. Above a critical size, the debonded feature can grow rapidly along the axial direction, quite like the growth of a micro-crack, provided it is favorable for the creation of additional CNTR surfaces (debonded regions) in order to relieve local elastic strain energy [21]. In one scenario, a part of the rope can abruptly peel off the twisted rope, straightening and untwisting as it branches off the parent rope. This is shown schematically in Fig. 4. At high temperatures, entropy aids this process. Since the radius of the parent rope decreases, its bulk twist decreases as well. Alternatively, the CNTR can break up into misoriented polycrystalline bundles [13].

Experimental evidence of twisted CNTRs exist [12–15], but accurate characterization of twisting along macroscopic rope segments still remains a challenge. Bernaerts et al. [12] have reported bulk twisting of laser ablated, 10 nm radius ropes over several hundreds of nanometers. This is in agreement with our predictions, provided we account for finite temperature effects. The strain energy decreases with temperature as it becomes easier to bend and twist individual nanotubes,⁶ while the cohesive energy is relatively unaffected. Therefore, the values of the two critical radii decreases and stable twists can occur in thinner ropes. Entropy effects, albeit small and which we have ignored, become important at these temperatures and will counteract twisting. Overall we expect the sigmoidal curve of Fig. 2 to shift to the

left, i.e. to lower rope radii and a smoother transition between the three regions.

Other studies have reported considerably higher bulk twisting ($\sim 1^\circ/\text{nm}$), but the twist appears to be localized to a small length of the rope [13,14]. Evidently these are frozen-in twists, a consequence of the high temperatures associated with their assembly [19]. On rapid quenching, kinetic constraints prevent the CNTR from untwisting in its entirety. Interestingly, several instances of tree-like branched morphologies of CNTRs have been reported during CNTRs growth in these studies [13,14]. A thinner rope segment abruptly peels off from a much thicker rope. Unfortunately, bulk twisting of the tree “stem” could not be resolved. In self-assembled and annealed CNTRs, super ropes consisting of assembly of smaller CNTRs of radius less than 20 nm have been reported [22,23]. Again, the twisting of the ropes could not be resolved unambiguously. In some cases, micron thick untwisted aligned ropes have been reported, but these consist of multi-walled nanotubes with significantly higher bending and torsional rigidities [16]. Quick calculation suggests that thickness of these untwisted ropes is in agreement with our model predictions.

In conclusion, we show that sufficiently thick CNTRs are naturally twisted. This degree of freedom will modify both electronic and mechanical properties of ropes and their super-assemblies [22,23]. More importantly, we find that it is the bulk twisting of nanotube ropes that limits their thickness, resulting in their disassembly. Note that in catalytic particle-assisted growth, where the root growth mechanism can determine the extent of the assembly, the diameter of the particle can also limit the rope radius [24]. The twist instability can be offset by increasing the energetic cost associated with nanotube distortions, e.g. ropes of multi-walled nanotubes [15,16] or increasing the CNTR surface energy. Alternatively, since the predominant debilitating effect is the easy axial sliding between the nanotubes, effective inter-tube cross-linking can aid bulk synthesis of these crystals [18]. Bulk twisting is rendered difficult as it now entails stretching of the nanotubes, considerably more prohibitive than twisting and bending of nano-

⁶ Temperature decreases the bending and twist persistence lengths ($\ell_p = EI/k_B T$, $\ell_t = GJ/k_B T$), i.e. nanotube lengths at which the energy required to bend or twist is negligible at the system temperature. For single-walled nanotubes, $\ell_p \approx 45$ μm and $\ell_t \approx 100$ μm .

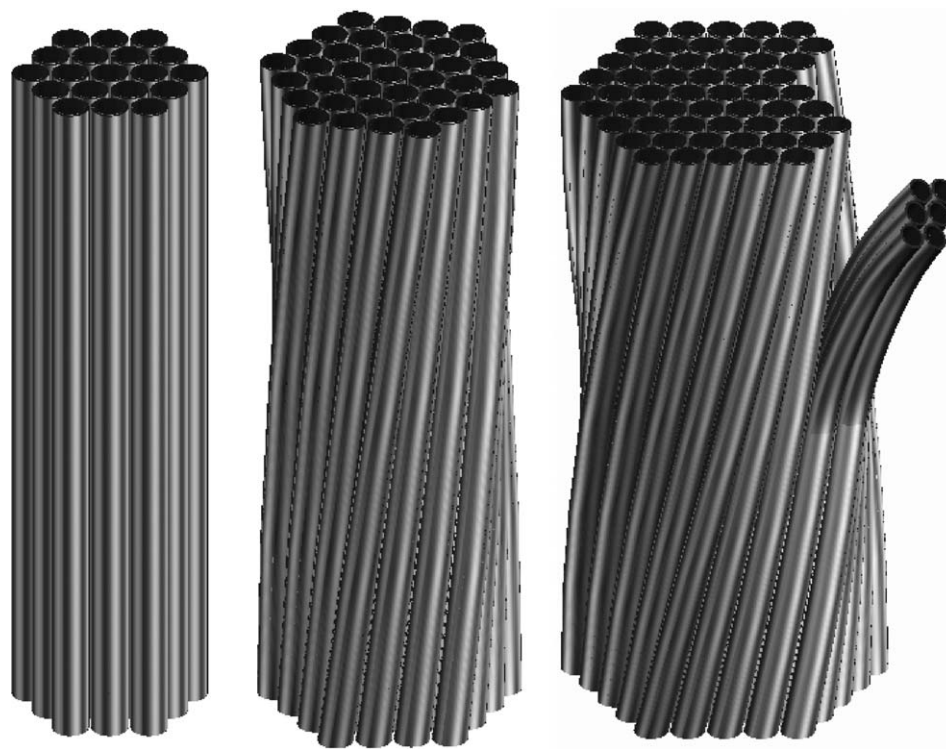


Fig. 4. Schematic illustration of the model predictions of the morphology of CNTRs, as a function of CNTR radius. Stable untwisted ropes (left, regime I), ropes with a stable twist (center, regime II) and the peeling off phenomenon in thicker twisted nanotube ropes (right, regime II), wherein a rope segment spontaneously branches off.

tubes. Ongoing work includes extending this study to cross-linked CNTRs.

Acknowledgements

The authors are grateful to Y. Ni (University of Science and Technology of China) and J.V. Selinger (Naval Research Laboratory) for discussions.

References

- [1] Ajayan PM. Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite. *Science* 1994;265:1212–4.
- [2] Thess A, Lee R, Nikolaev P, Dai HJ, Petit P, Robert J, et al. Crystalline ropes of metallic carbon nanotubes. *Science* 1996;273:483–7.
- [3] Terrones M, Grobert N, Olivares J, Zhang JP, Terrones H, Kordatos K, et al. Controlled production of aligned nanotube bundles. *Nature* 1997;388:52–5.
- [4] Dagani R. Carbon nanotube ropes—moving closer to practical materials. *Chem Eng News* 1996;74:5–6.
- [5] Hone J, Ellwood I, Muno M, Mizel A, Cohen ML, Zettl A, et al. Thermoelectric power of single-walled carbon nanotubes. *Phys Rev Lett* 1998;80:1042–5.
- [6] Lee NS, Chung DS, Han IT. Application of carbon nanotubes to field emission display. *Diam Relat Mater* 2001;10:265–70.
- [7] Gonzalez J. Superconductivity in carbon nanotube ropes. *Phys Rev B* 2003;67:14528–40.
- [8] Tersoff J, Ruoff RS. Structural properties of a carbon-nanotube crystal. *Phys Rev Lett* 1994;73:676–9.
- [9] Qian D, Wagner GJ, Liu WK, Yu M-F, Ruoff RS. Mechanics of carbon nanotubes. *Appl Mech Rev* 2002;55:495–533.
- [10] Girifalco LA, Hodak M, Lee RS. Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential. *Phys Rev B* 2000;62:13104–10.
- [11] Jin Y, Yuan FG. Simulation of elastic properties of single-walled carbon nanotubes. *Compos Sci Technol* 2003;63:1507–15.
- [12] Bernaerts D, Zettl A, Chopra NG, Thess A, Smalley RE. Electron diffraction study of single-wall carbon nanotubes. *Solid State Commun* 1997;105:145–9.
- [13] Henrard L, Loiseau A, Journet C, Bernier P. Study of the symmetry of single-wall nanotubes by electron diffraction. *Solid State Commun* 2000;13:661–9.
- [14] Hamon A-L, Marraud A, Jouffrey B. A geometrical study of single-walled nanotube ropes by transmission electron microscopy. *Phil Mag B* 2001;81:1779–99.
- [15] Colomer J-F, Henrard L, Van Tendeloo G, Lucas A, Lambin P. Study of the packing of double-walled carbon nanotubes into bundles by transmission electron microscopy and electron diffraction. *J Mater Chem* 2004;14:603–6.
- [16] Zhang XF, Cao A, Li Y-H, Xu C-L, Liang J, Wu DH, et al. Self-organized arrays of carbon nanotube ropes. *Chem Phys Lett* 2002;351:183–8.
- [17] Liu JZ, Zheng Q-S, Wang L-F, Jiang Q. Mechanical properties of single-walled carbon nanotube bundles as bulk materials. *J Mech Phys Solids* 2005;53:123–42.
- [18] Kis A, Csanyi G, Salvétat J-P, Lee T-N, Couteau E, Kulik AJ, et al. Reinforcement of single-walled carbon nanotube bundles by intertube bridging. *Nature Mater* 2005;3:153–7.
- [19] Kwon Y-K, Tománek D. Orientational melting in carbon nanotube ropes. *Phys Rev Lett* 2000;84:1483–6.

- [20] Liang HY, Upmanyu M. Elastic self-healing during shear accommodation in crystalline nanotube ropes. *Phys Rev Lett* 2005;94:0655021–4.
- [21] Griffith AA. The phenomena of rupture and flow of solids. *Phil Trans Roy Soc A* 1920;221:163–98.
- [22] Zhu HW, Xu CL, Wu DH, Wei BQ, Vajtai R, Ajayan PM. Direct synthesis of long single-walled carbon nanotube strands. *Science* 2002;296:884–6.
- [23] Ericson LW, Fan H, Peng H, Davis VA, Zhou W, Sulpizio J, et al. Macroscopic, near single-walled carbon nanotube fibers. *Science* 2004;305:1447–50.
- [24] Gavillet J, Loiseau A, Journet C, Willaime F, Ducastelle F, Charlier J-C. Root-growth mechanism for single-wall carbon nanotubes. *Phys Rev Lett* 2001;87:2755041–4.