Stabilization of Individual Carbon Nanotubes in Aqueous Solutions

Rajdip Bandyopadhyaya, Einat Nativ-Roth, Oren Regev,* and Rachel Yerushalmi-Rozen*

Department of Chemical Engineering and The Ilse Katz Center for Meso and Nanoscale Science and Technology, Ben Gurion University of the Negev, 84105 Beer Sheva, Israel

ABSTRACT

Single-wall carbon nanotubes pack into crystalline ropes that aggregate into tangled networks due to strong van der Waals attraction. Aggregation acts as an obstacle to most applications, and diminishes the special properties of the individual tubes. We describe a simple procedure for dispersing as-produced nanotubes powder in aqueous solutions of Gum Arabic. In a single step, a stable dispersion of full-length, well separated, individual tubes is formed, apparently due to physical adsorption of the polymer.

Single-wall carbon nanotubes (SWNT) are expected to exhibit superior mechanical and electrical properties[1–4] as a direct consequence of the nanometric dimensions of the individual tube. Yet, as-produced SWNTs align parallel to each other and pack into crystalline ropes, due to strong intertube van der Waals attraction. Ropes that are typically composed of 100 to 500 tubes pack in a triangular lattice with a lattice constant of $a = 1.7$ nm.[5] The ropes further aggregate into tangled networks. Aggregation was found to act as an obstacle to most applications, diminishing the special mechanical and electrical properties of the individual tubes.[6,7]

The observed reduction in desired properties together with the difficulties in manipulating bundled nanotubes have motivated recent attempts to develop methods that will enable solubilization, dispersion, and separation of SWNTs. Covalent[8,9] and ionic[6,10] modifications resulted in a limited success: dispersion of either SWNT fragments or ropes[10] (rather than individual tubes) in organic media and formation of polymer–nanotube composites[11] were reported. Often, it was observed that the band electronic structure of the native tubes was disrupted by these modifications,[12,13] and in some cases the inherent crystalline structure of the individual tube was severely damaged.[14]

An alternative, which does not involve covalent or ionic interactions, is offered by physical adsorption of long chain polymers.[15,16] In this letter we describe a simple procedure, which relies on nonspecific physical adsorption of a natural polymer, Gum Arabic (GA),[17] for dispersing as-produced
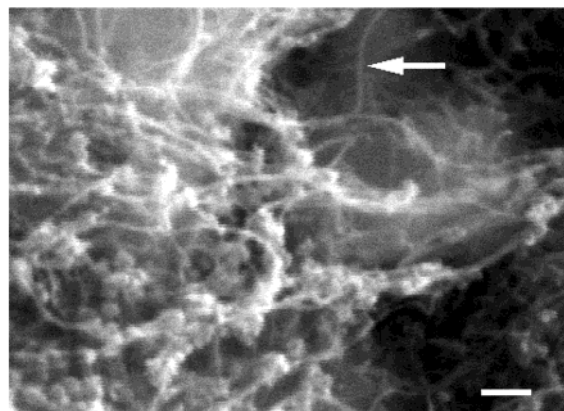
Figure 1. SEM micrograph (Au spattered, JSM-35CF, JEOL, operated at 25kV) of as-produced[20] nanotube powder. The arrow points to a single rope protruding out of the entangled network. Typical rope diameter is in the range of 30–50 nm. Scale bar, 200 nm.

powder of entangled SWNT ropes into individual, well-separated tubes.

In a single step, as-produced SWNT powder is dispersed in an aqueous solution of GA, a water soluble polysaccharide produced by Acacia Senegal trees,[17,18] and a stable dispersion of individual, full-length tubes is formed. The dispersion may then be dried and redispersed at high concentrations of the powder in pure water, resulting in the reformation of a stable dispersion of individual tubes.

The dispersion method is based on an ancient Egyptian recipe, first used 5000 years ago for preparation of carbon-black ink:[19] GA is dissolved in water to form solutions of 0.5 wt % to 15 wt %. A powder of as-produced nanotubes,[20] which contains a bundled network of ropes (Figure 1), is

  * Corresponding authors. E-mail: oregev@bgumail.bgu.ac.il; rachely@bgumail.bgu.ac.il.

Figure 2. Vials containing aqueous dispersions of SWNT (0.05 wt %) after 3 months of incubation at room temperature: (A) 2 wt % GA; (B) 5 wt % GA; (C) 5 wt % SDS; (D) 15 wt % SDS; (E) 5 wt % CTAC; (F) 15 wt % CTAC. Note that a uniform dispersion (indicative of a single phase) is observed in A and B while in the other vials the carbon nanotubes coagulate at the bottom.
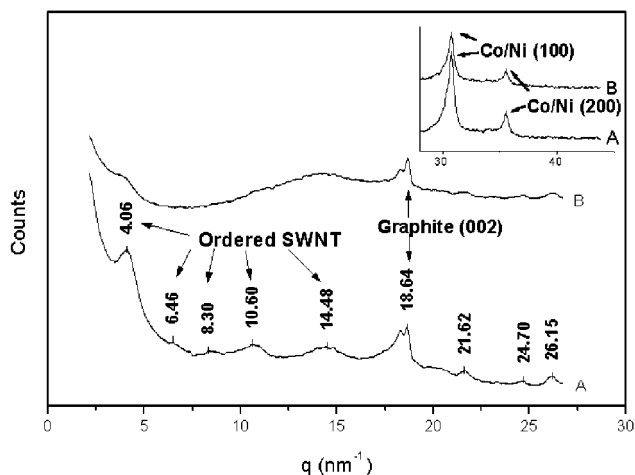

Figure 3. Wide-angle X-ray spectra of (a) as-produced SWNT powder[20] exhibiting a typical rope structure: the peaks at the low-q region indicate a two-dimensional triangular lattice with a lattice constant of 1.8 nm. In addition, multiwall graphitic objects can be seen (at $q = 18.64$ nm^{-1}) in good agreement with previous observations.[5] (b) A powder prepared by drying a dispersion of 3 wt % SWNT in 15 wt % aqueous solution of GA. The intertube reflections have disappeared. The inset presents the reflections of the Co/Ni catalyst used in the synthesis of SWNT.[19] The measurements were carried out by a Philips X-ray powder diffractometer (PW-1050/70) at 40 kV/28 mA with Cu Kα ($\lambda = 0.154$ nm) radiation and graphite monochromator. The scattering vector $q = 4\pi/\lambda \sin \theta$, where θ is the scattering angle.

sonicated at very mild conditions (50 W, 43 kHz) for 15−20 min in the polymeric solutions and a black (of concentrations between 0.2 wt % to 3 wt %), homogeneous ink-like suspension is obtained.

The suspension may then be dried in air, at ambient conditions, and redispersed in pure water in concentrations ranging from 0.5 wt % to 15 wt % (carbon nanotubes powder weight per water weight). The resulting suspensions are stable over few months, and centrifugation (at 4500 rpm for 30 min) does not result in precipitation of the nanotubes. The method is applicable to either SWNT or multiwall nanotubes (MWNT).[1]
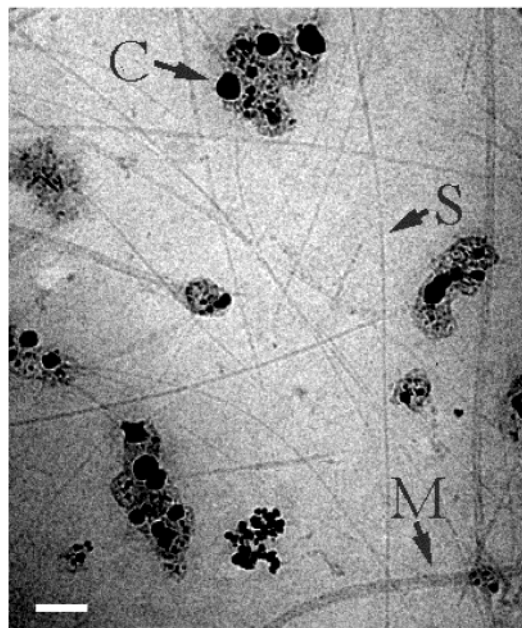
To investigate the origin of the dispersing power of GA solutions on carbon nanotubes, we tested surfactants that vary in charge and molecular weight. Negatively charged sodiumdodecyl sulfate (SDS), positively charged cetyltrimethylammoniumchloride (CTAC) and dodecyltrimethylammoniumbromide (DTAB), nonionic pentaoxoethylenedodecyl ether ($C_{12}E_5$), a polysaccharide (Dextrin), and a long chain synthetic polymer poly(ethylene oxide) (PEO) were compared with GA.[21] We found that none of these materials could act as an efficient dispersing agent for nanotubes in aqueous solutions. In Figure 2 we present an image of some of the dispersions of SWNT in solutions of surfactants and GA. We observe that dispersions of nanotubes in GA are homogeneous, while the other solutions are phase separated with coagulated tubes at the bottom of the vial.

To test the aggregation state of the tubes in the dried powder, we performed X-ray scattering experiments. A typical wide-angle X-ray scattering pattern (WAXS) of as-produced powder[20] is presented in Figure 3a. In Figure 3b we present a WAXS spectrum of SWNT powder following dispersion in GA solution and drying. The peaks that result from intertube packing within the ropes in the as-synthesized SWNT (Figure 3a) have disappeared, leaving only the graphite peaks (most probably MWNT).[1] This observation suggests that the ropes in the dispersed-and-dried powder are well separated into individual tubes of either SWNT or MWNT.

The microscopic structure of the stable, concentrated, redispersed solution of carbon nanotubes was further investigated using cryotransmission electron microscopy (cryo-


Figure 4. Cryo-TEM micrograph of a highly concentrated dispersion of SWNT, prepared by redispersing a dry powder of GA coated SWNT (obtained by drying a solution of 3 wt % SWNT in 15 wt % GA solution) in pure water. The sample was imaged at −170 °C (under focus of 4 μm) using JEOL 1200EXII TEM equipped with a Gatan 626 cold stage. The arrows indicate flexible SWNT (S), the Co/Ni catalyst (C), and most probably MWNT (M). Scale bar, 50 nm.

TEM).[22,23] Figure 4 presents a cryo-TEM image of redispersed nanotubes. Well separated SWNT, of a diameter below 2 nm, are clearly observed, along with some residues,
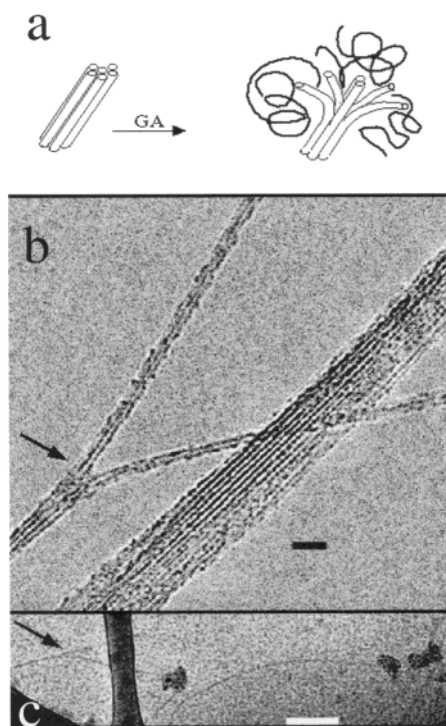
Figure 5. Rope-to-single-tube transition due to adsorption of GA: (a) schematic presentation; (b) high-resolution TEM (JEOL 2010 operated at 200 kV) image of dried solution of 0.05 wt % SWNT in 1 wt % GA (scale bar, 10 nm); (c) cryo-TEM image of 0.05 wt % SWNT in 5 wt % GA (scale bar, 100 nm). Arrows in (b) and (c) show the location of bifurcation.

including the catalyst (note the catalyst scattering pattern in the inset of Figure 3). The length of the SWNT is well above a micron. Similar images were observed in dispersed solutions prior to drying.

These observations demonstrate that adsorption of GA leads to disruption of the intertube interactions in the crystalline ropes, as schematically presented in Figure 5a. The high-resolution TEM image in Figure 5b presents a small bundle during the process of exfoliating. Adjacent to it is either a MWNT or a nonexfoliated bundle. A similar image was observed in the cryo-TEM image presented in Figure 5c. In both figures we observe that the intact structure of full-length SWNT is preserved throughout the process.

The method described above leads to the formation of homogeneous dispersions of individual carbon nanotubes. Drying and re-dispersion of the polymer coated tubes results in highly concentrated dispersions of well-separated tubes.

The spontaneous redispersion of the dried carbon nanotube powder in pure water and the stability of highly concentrated dispersions are signatures of what is known in modern colloid science as steric stabilization.[24] In this mechanism, entropic repulsion among polymeric chains is utilized for stabilization of colloids: In good solvent conditions,[25] polymer chains tend to avoid each other so as not to constrain the conformational space available to each of them. Thus, polymer coated objects experience a repulsive force. In the system described here, GA adsorbs to the aggregated nanotubes, which are of a much smaller dimension than the characteristic radius of the polymeric chains, R_F,[26] and activates a repulsive force at a distance of $2R_F$.[28] At this distance the polymer-induced repulsive force dominates over the vdW attraction[29] between the embedded nanotubes. Consequently, the overall intertube potential becomes repulsive and the nanotube dispersion becomes thermodynamically stable.[24]

An additional consequence of GA adsorption is the exfoliating of ropes into individual tubes. We suggest that the activation of steric repulsion among the polymer coated tubes allows the disassembly of ropes into individual tubes due to a net gain in translational entropy: For a rope that contains about 100 tubes, a 2-fold increase in translational entropy may be achieved.[30]

To conclude, we present a simple method for unbundling as-produced (unmodified, long) carbon nanotubes in aqueous solutions of Gum Arabic. The resulting stable dispersion may be dried into an "instant" ready-for-use powder of individual carbon nanotubes. The unbundling and stabilization of the single tubes in solution is demonstrated unequivocally by a combination of X-ray scattering and cryo-TEM imaging. While the former indicates the loss of intertube ordering, i.e., the disruption of the ropes, the latter provides a direct visualization of the individual SWNT.

The use of GA for stabilization of SWNT dispersions offers a few advantages. Disruption of the interrope packing, leading to dispersion of the tubes, will enable the testing of isolated tube properties and comparison to theoretical predictions. From the practical point of view, the Gum Arabic molecules that adsorb to the carbon nanotubes may act as adhesion promoters leading, to the formation of highly adhesive interfaces between individual tubes and a polymeric matrix.[31]

References

(1) *Science of Fullerens and Carbon Nanotubes*; Dresselhaus, M. S., Dresselhaus, G., Eklund, P. C., Eds.; Academic Press: San Diego, 1996.
(2) Yao, Z.; Dekker, C.; Avouris, Ph. *Top. Appl. Phys.* **2001**, *80*, 147.
(3) Salvetat, J. P. et al. *Phys. Rev. Lett.* **1999**, *85*, 944.
(4) Kociak, M. et al. *Phys. Rev. Lett.* **2001**, *86*, 2416.
(5) Thess, A. et al. *Science* **1996**, *273*, 483.
(6) Vigolo, B. et al. *Science* **2000**, *290*, 1331.
(7) Kwon, Y. K.; Saito, S.; Tomanek, D. *Phys. Rev. B* **1998**, *58*, R13314.
(8) Hamon, M. A. et al. *Adv. Mater.* **1999**, *11*, 834.
(9) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun Y—P. *J. Am. Chem. Soc.* **2000**, *122*, 5879.
(10) Chen, J. et al. *J. Phys. Chem.* **2001**, *105*, 2525.
(11) McCarthy, B. et al. *Synth. Met.* **2001**, *121*, 1225.
(12) Chen, J. et al. *Science* **1998**, *282*, 95.
(13) Boul, P. J. et al. *Chem. Phys. Lett.* **1999**, *310*, 367.
(14) Monthioux, M. et al. *Carbon* **2001**, *39*, 1251.
(15) Coleman, N. et. al. *Adv. Mater.* **2000**, *12*, 213.
(16) Star, A. et. al. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1721.
(17) Gum Arabic (Aldrich Acacia 26,077−0) is a highly branched arabinogalactan polysaccharide. It was found that the material is mainly composed of two components: 70−80% of arabingalactan,

forming a highly branched structure with a hydrodynamic radius, R_h, of about 5 nm and about 20% of an arabingalactan−protein complex with R_h values ranging from 25 to 50 nm. While the composition of the material is known, its conformation has not yet been elucidated, and the origins of its surface activity are not well understood.

(18) Picton, L.; Bataille, I.; Muller, G. *Carbohydr. Polym.* **2000**, *42*, 23.

(19) *Encyclopedia Britannica* 257−259 (William Benton: Chicago, 1966).

(20) Select grade nanotubes (SWNT) were purchased from Carbolex, University of Kentucky, Lexington, Kentucky. The nanotubes were synthesized by arc discharge. According to the specifications by the manufacturer, the powder consists of 85 vol % pure SWNT, graphite, carbon impurities and catalyst (Cobalt and Nickel, ca. 20 nm in diameter).

(21) SDS, CTAC, and DTAB Aldrich, Dextrin (260754 DEXTRIN 60% 9000 g/mole, 30% 3000 g/mol, and the reminder a low molecular weight fraction) were purchased from Sigma-Aldrich. PEO (M_w = 304 600 g/mol) was purchased from Polymer Source Inc., Canada. $C_{12}E_5$ was purchased from Nikko chemicals, Japan. We found that Dextrin and PEO solutions (at similar molar concentrations to 0.5 wt % GA), as well as $C_{12}E_5$ and DTAB solutions at concentrations ranging from 0.05% to a few percent do not stabilize the nanotubes.

(22) In this method, a drop of the solution is placed on a lacey TEM grid and vitrified in liquid ethane.

(23) Bellare, J. R.; Davis, H. T.; Scriven, L. E.; Talmon, Y. J. *Electron. Microsc. Technol.* **1988**, *10*, 87.

(24) *Polymeric Stabilization of Colloidal Dispersions;* Napper, D. H., Eds.; Academic Press: Orlando Florida, 1993.

(25) A solvent in which solvent-chain interactions are preferred over chain−chain interaction, resulting in an extended configuration of the polymeric coil.[24]

(26) R_F is the Flory radius of the polymer.[24] In the relevant experimental conditions it is in the range of 25 to 50 nm.[18]

(27) Aubouy, M.; Raphael, E. *Macromolecules* **1998**, *31*, 4357.

(28) Klein, J.; Luckham, P. *Nature* **1982**, *300*, 429.

(29) *Intermolecular and Surface Forces*; Israelachvili, J., Ed.; Academic Press: San Diego, 1992.

(30) In a model describing a dilute monatomic gas, the entropy, *S*, of *N* independent objects scales as $S \sim Nk_b\ln(A + V/N)$, where *N* is the number of objects, k_b is the Boltzmann constant, A describes the system (see, for example, Hill, T. L. *Statistical Thermodynamics*; Addison-Wesley: Reading Massachusetts, 1960). V is the volume. The quantity in brackets is of order 10^3 or more, but the logarithm is of order unity. Hence $S = O(Nk_b)$, i.e., the entropy increases monotonically with the number of objects.

(31) de-Gennes, P. G. *J. Phys.* **1990**, *68*, 1049.