

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/234886867>

Entropically driven self-assembling of softened multi-walled carbon nanotubes into a reversibly water dispersible coherent solid

ARTICLE *in* JOURNAL OF APPLIED PHYSICS · MAY 2006

Impact Factor: 2.18 · DOI: 10.1063/1.2198937

CITATIONS

6

READS

16

8 AUTHORS, INCLUDING:



Igor Altman

48 PUBLICATIONS 503 CITATIONS

SEE PROFILE



Mansoo Choi

Chungnam National University

125 PUBLICATIONS 2,006 CITATIONS

SEE PROFILE

Entropically driven self-assembling of softened multi-walled carbon nanotubes into a reversibly water dispersible coherent solid

Huaqing Xie, Peter V. Pikhitsa, Young Jeong Kim, Wonjin Youn, Igor S. Altman et al.

Citation: *J. Appl. Phys.* **99**, 104313 (2006); doi: 10.1063/1.2198937

View online: <http://dx.doi.org/10.1063/1.2198937>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v99/i10>

Published by the [American Institute of Physics](#).

Additional information on J. Appl. Phys.

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>

ADVERTISEMENT

**AIPAdvances**

Submit Now

Explore AIP's new open-access journal

- Article-level metrics
now available
- Join the conversation!
Rate & comment on articles

Entropically driven self-assembly of softened multi-walled carbon nanotubes into a reversibly water dispersible coherent solid

Huaqing Xie,^{a)} Peter V. Pikhitsa,^{b)} Young Jeong Kim, Wonjin Youn, Igor S. Altman,^{c)} Jung Gun Nam,^{d)} Seung Jong Lee,^{d)} and Mansoo Choi^{e)}

National CRI Center for Nano Particle Control, Institute of Advanced, Machinery and Design, School of Mechanical and Aerospace Engineering, Seoul National University, Seoul, 151-742, Korea

(Received 17 May 2005; accepted 29 March 2006; published online 30 May 2006)

A bulk multi-walled carbon nanotube pellet has been produced by self-arrangement after drying the aqueous suspension of the carbon nanotubes (CNTs) oxidized by boiling CNTs in concentrated acid. The solid can be re-dispersed in water and self-assembled again. The centimeter order bulk CNT pellet unexpectedly showed compact domains of highly aligned parts of long CNTs which size is much larger than the domain size. Viscosity measurements confirmed that the system in question is completely different from a rigid-rod nematic. We reveal the mechanism of the entropy-driven self-alignment of treated worm-like CNTs in analogy to semiflexible liquid crystalline polymer. The polymer-like behavior of treated CNTs brings the CNTs into a genus of robust polymers. © 2006 American Institute of Physics. [DOI: [10.1063/1.2198937](https://doi.org/10.1063/1.2198937)]

I. INTRODUCTION

Carbon nanotubes (CNTs) have attracted increasing interest since their discovery because of the intriguing properties and the potential for applications.¹ Having an aspect ratio of thousands, CNTs may efficiently wire the macro and micro world. On the other hand, the extremely high aspect ratio of CNTs imposes general topological constraints for filamentous units, which create manipulation problems with disentanglement, individual separation and high packing density alignment in bulk scale. Besides, there are difficulties to disperse CNTs due to their non-reactive surfaces. Also the van der Waals attraction among CNTs often leads to their significant agglomeration.² Appropriate chemical modification of CNT surfaces to add hydrophilic functional groups can dramatically enhance the dispersibility of CNTs in water^{3–5} which is a prelude to their further alignment, achieved in Refs. 6–11 on a micrometer scale. Being oxidized, the CNTs can soften enough to be bent by water surface tension into various “needle eyes” and “nooses”¹² (see also Ref. 13 where drastic weakening of oxidized CNTs was reported). Multi-walled CNTs, being oxidized in oxygen plasma were shown to make a capillary-driven assembly in two-dimensional cellular foams distinguished by large domains of densely aligned CNTs.¹⁴

The distinctive feature of previous works on disentanglement and alignment is that mostly short or shortened CNTs (either by ball-milling or chemical cutting) were used. Short CNTs formed nematic nanotube gels¹⁵ and solid nematic films.¹⁶ In the case of long CNTs a special mechanical trick—flow induced alignment—had to be used to produce

several μm thick ribbons.⁸ While entropically driven self-assembly of long rosette nanotubes showing a domain structure in the alignment of the macromolecule tubes was described in Ref. 17, no analogous structure has been known for long CNTs.

Here we report a self-organization of oxidized long multi-walled CNTs into a centimeter order coherent bulk solid which is reversibly water dispersible. The solid is distinguished by $3\ \mu\text{m}$ domains of highly aligned parts of treated CNTs (TCNTs) with the contour length of $30\ \mu\text{m}$. We suggest that the severe oxidation in nitric acid not only makes the CNTs hydrophilic and self-repelling in water, but also considerably softens the CNTs and eventually brings them into a class of semiflexible polymers. On densification of the CNT suspension during drying, long CNTs undergo an entropically driven self-alignment that we observe, similar to semiflexible polymers. We believe that such softened CNTs can be engineered similar to chain polymer molecules and are capable of substituting polymers for applications at those conditions which a common polymer cannot stand (e.g., temperatures above $1000\ ^\circ\text{C}$ for high-temperature coating or large mechanical tension).

II. EXPERIMENT AND RESULTS

The preparation process involves a concentrated acid treatment of CNTs to add hydrophilic functional groups on CNT surfaces, as described in Ref. 18, TCNTs of $2.5\ \text{g}$ were added into $50\ \text{ml}$ deionized distilled water, and then subjected to intensive sonication to form homogeneous and stable suspensions of individual Brownian-like TCNTs with negligible agglomeration/sedimentation in a several month settlement.¹⁸ On heating in order to remove water out of the concentrated TCNT suspension in a $100\ \text{ml}$ beaker, a hard cylindrical CNT bulk pellet (whose size of $2\ \text{cm}$ is much less than the beaker diameter) formed by self-organization (Fig. 1). For recovering CNTs to their initial non-oxidized state, a part of the pellet was heated at $1200\ ^\circ\text{C}$ under

^{a)}Shanghai Second Polytechnic University, Shanghai, China.

^{b)}On leave from Physics Institute at Odessa National University, Odessa, Ukraine.

^{c)}NanoGram Corporation, San Jose, California.

^{d)}School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea.

^{e)}Electronic address: mchoi@plaza.snu.ac.kr



FIG. 1. (Color online) A photographic image of the self-organized TCNT pellet. Note that the beaker was several times larger than the resulting self-assembled pellet.

vacuum for 1 h to produce a heated TCNT (HCNT) pellet. The density of the pellet was about 0.8 g/cm^3 , which corresponds to packing fraction about 50% for both TCNTs and HCNTs. The TCNT pellet could imbibe water up to 150% of its weight and expand. After drying in air at room temperature the pellet regains its weight in several hours. On immersing into water, the pellet became loose and broken. When subjected to sonication, the TCNTs forming the pellet can be dispersed to form an aqueous suspension of the same stability as before. When the suspension was heated and dehydrated completely, a similar pellet formed once again. This confirms the self-organized and reversibly water dispersible features of the pellet.

Fourier transformation infrared (FTIR) spectra of TCNTs present extra oxygen peaks.^{5,18} HCNTs show the same FTIR characteristics as pristine CNTs (PCNTs) (see Fig. 2), which means that the oxygen containing functional groups are removed during heating. The x-ray diffraction patterns and Raman spectra of the PCNTs, TCNTs,¹⁸ and HCNTs indicated an increase in defect concentration after the chemical treatment and heating. Thermogravimetry coupled with mass spectroscopy also revealed the detachment of the oxygen from TCNTs at temperatures higher than 900°C .

Let us note that in an aqueous suspension the ionization of acidic surface groups of TCNTs increases the electrostatic

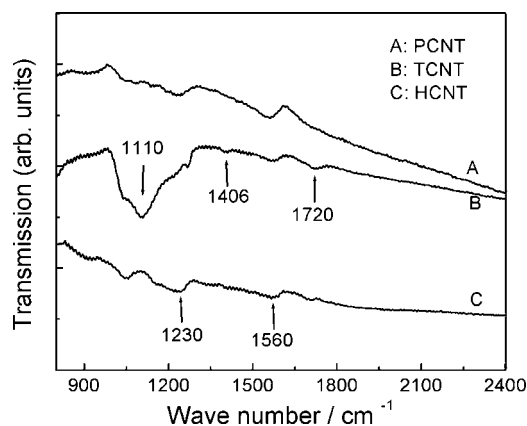


FIG. 2. FTIR spectra of PCNTs, TCNTs, and HCNTs.

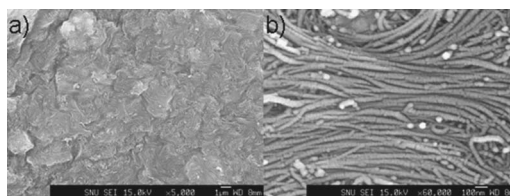


FIG. 3. SEM images of as produced TCNT pellet at different magnification. (a) Surface morphology of the TCNT pellet shows compact domain structure. Note that the contour length of TCNTs of $30 \mu\text{m}$ exceeds the size of the images; that is, each TCNT participates in several domains and domain walls. (b) A higher magnification image shows the alignment in one domain selected. Gold particles, used for the SEM image resolution enhancement of the low conductivity oxidized TCNTs, thicken individual TCNTs.

repulsion among TCNTs, leading to the suspension stability. On removing water, deformation caused by surface tension makes TCNTs come close and contact mutually. The bonding interaction of a surface functional group¹⁹ between TCNTs might act as an additional driving force for the formation of the self-assembled pellet at later stages of their ordering. Heating the pellet to 1200°C under vacuum for 1 h did not make the pellet loose or deformed, thus preserving the same pellet density as for TCNTs. Since any oxygen-containing bonds decompose at this temperature, the original CNTs are recovered, but now are arranged in a dense pure CNT bulk material.

On the first sight, the hydrophilic nature of separated TCNTs is sufficient to make an alignment due to the repulsion of TCNTs in solution. A careful filtering of the suspension below the entanglement threshold indeed leads to some local alignment.⁵ But in our case, the alignment domain size shown in Fig. 3(b) is more than 20 times larger than in Ref. 5. Our TCNTs do not make any entangled gel and thus do not exhibit the entanglement threshold at all. The only difference between our treatment and that of Ref. 5 is that our acid treatment was more violent. The same treatment was used in Ref. 9, but the CNTs were first cut short mechanically, and therefore, the problems with the entanglement were greatly reduced. Cutting alone (without a treatment) cannot lead to ordering.²⁰

III. MODEL AND DISCUSSION

It is logical to assume that our intensive chemical treatment led to a dramatic softening of TCNTs due to many defects to TCNT surface introduced during the oxidation, which reduces their elastic bending^{13,21} $\kappa = E\pi R^4/4$, where E is the Young modulus and $R = d/2$ is the tube radius. We believe that the oxidation occurs for inner shells as well because nitric acid is known to intercalate graphitic structures penetrating through defects into the inner shells and oxidizing them. "Eaten" defective surfaces can be distinguished in transmission electron microscopy (TEM) images (all stages of nitric acid treatment on single-wall CNT structures were extensively studied in Refs. 22 and 23). On contrary, for cellular carbon nanotube foams described in Ref. 14, the oxidation might happen only on outer shells of multi-walled CNTs and they remained insufficiently soft to become semi-flexible and capable of folding.

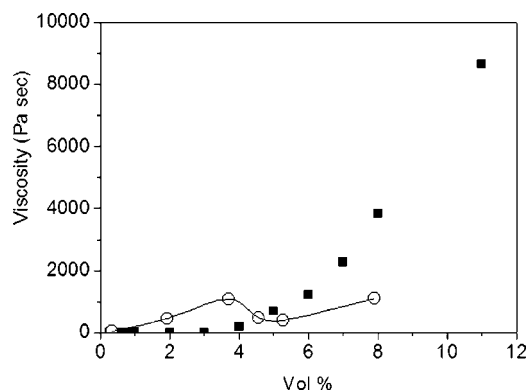


FIG. 4. Viscosity measured at shear rate 0.1 s^{-1} for different volume fractions of CNTs in solution; open circles, averaged viscosity from Ref. 24 for SWNTs; squares, our experiment.

Our key point is that it is the softening of TCNTs that leads to the coherent solid. In other words, TCNTs become similar to worm-like polymer molecules after severe acid treatment and then being placed in water. Indeed, the TCNTs should yield water surface tension compression to come close to each other along their contour length. It can be possible only for sufficiently soft CNTs because the softening destroys the topologically constrained elastic network and therefore the “entanglement threshold.” As a corollary, such a soft system being in water can readily respond to vibrations during sonication and exhibit intensive diffusive reptation, circumventing any topological obstacles. It explains why the dense pellet of TCNTs can be created and why it can be re-dispersed in water again. It is worth noting that the acid treatment in Ref. 5 was not strong enough to make the CNTs soft sufficiently to overcome the entanglement threshold. Another example is that even though single-walled CNTs (SWNT), being protonated in superacids, perform a rigid-rod nematic self-arrangement in those superacids into an entangled network of long stiff filaments as a secondary structure,²⁴ the entanglement threshold is overcome only partially. Note that the filaments themselves in Ref. 24 are far from being aligned as dense as TCNTs in our pellet shown in Fig. 3, indicating that the “SWNT spaghetti” (dubbed so from Ref. 24) seems to remain “undercooked” to yield the relevant forces.

To illustrate the dramatic difference between a rigid-rod nematic system and our system behavior which is brought by softening, we measured shear viscosity at shear rate 0.1 s^{-1} (see Fig. 4). In Fig. 4 (square symbols), one may notice the absence of the pronounced hump which is a characteristic for a rigid-rod nematic self-arrangement in Ref. 24 (see open circles in Fig. 4) and a rather low viscosity for volume fractions up to 4 vol %, which confirms that the final alignment in both systems is governed by completely different mechanisms.

The question is how the coherent solid with aligned domains is possible. From the basic physics analogy, the dense solution of TCNTs can be regarded as an athermal liquid crystalline polymer²⁵ and each free individual TCNT as a semiflexible macromolecule for which the inequality holds

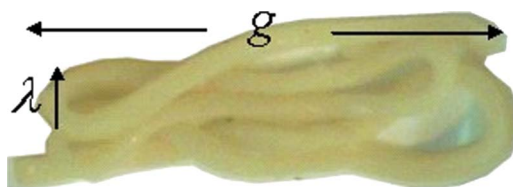


FIG. 5. (Color online) A fragment of self-alignment in real noodles which follow the same mechanism.

$$L \gg P \gg d, \quad (1)$$

where L is the contour length of a TCNT, and P is the persistent length,^{21,24–26} which is the length of an approximately straight portion of a free individual TCNT. Note that for a single-walled CNT the persistent length is more than several μm .²⁴ The persistence length of a pristine multi-walled CNT depends on the number of shells but is always much greater than that of a SWNT.²⁷ From microscopy images of individual TCNTs,¹⁸ one can estimate $d=15 \text{ nm}$, $P=300 \text{ nm}$, and $L=30 \mu\text{m}$, thus Eq. (1) fulfills and individual TCNTs can be considered as semiflexible macromolecules.

To account for the phenomenon of self-alignment, let us introduce an effective temperature $T_{\text{eff}} = \kappa/P$ (in energy units) which is the characteristic of the chaotically distributed elastic energy in the system due to structural disorder. Yet, for the system of TCNT coils being an athermal system (which means that the relevant physical quantity is the free energy F divided by T_{eff}), all conformation changes are entropy driven and the temperature disappears from corresponding equations for the normalized orientation distribution function.²⁵ Introduce the dimensionless parameter $c = \rho_P(\pi/4)P^2d$ (in the case of the Onsager theory for rods, c would be proportional to the second virial coefficient defining the interaction of rods), where ρ_P is the number density of persistent segments.²⁵ The parameter c determines two lengths of physical relevance in describing a strongly confined semiflexible chain. The first length, $\lambda = P/\alpha$ ($\alpha \approx c^{2/3}$), is the so-called deflection length.²⁵ It appears only due to a TCNT confinement induced by neighboring TCNTs and it measures the “wavelength” of the wriggles and coils of a TCNT squeezed between others; in fact λ is close to the bend size in the illustrating Fig. 5. The counterdistance λ depends on c in power $-2/3$ because the mean-square average deflection $\langle x^2 + y^2 \rangle$ away from the z direction along the counter of a TCNT is proportional to the third power of the counter distance, $\langle x^2 + y^2 \rangle \sim \lambda^3/P$ (see Ref. 25 for details). The second length, $g \sim P \exp(\alpha)/\alpha$, is the global persistent length,²⁵ which determines the orientation domain size (Fig. 5). The length g is very important for the semiflexible system in question (worm-like softened TCNTs) and it measures the stretching in the system undergoing the orientation transition. This stretching is the direct consequence of elastic energy cost for bending and folding a semiflexible TCNT. Indeed, in order to reduce the repulsion due to excluded-volume interactions between TCNTs being squeezed by the surrounding TCNTs, long TCNTs should become parallel, but becoming parallel by simple bending or folding is energetically costly for semiflexible TCNTs. Therefore, the bends or folds should be sufficiently far from each other on the distance g defined

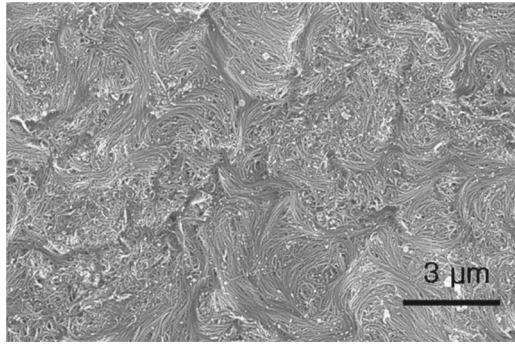


FIG. 6. Domain walls at intermediate magnification. TCNTs are continuous through the domains and domain walls. The structure of domains is unique and can be easily distinguished from a rigid-rod packing.

above (see Fig. 5 for analogy coming from self-alignment of cooked noodles). To substantiate this physical reasoning it is worthwhile treating the bends as a one-dimensional gas of L/g “defects” of concentration λ/g that gives the free energy functional of the statistical mechanical problem:

$$F/T_{eff} \approx (L/g) \ln(\lambda/g/e) + (L/g)(P/\lambda), \quad (2)$$

where the first term on the right-hand side is recognized as an entropy term; e is the Euler number, and the other term is the bend elastic energy $(\kappa/\lambda)/T_{eff} = P/\lambda$ multiplied by the number (L/g) of defects.²⁵ Minimization of the free energy in Eq. (2) with respect to g leads to $g \sim \lambda \exp(P/\lambda) = P \exp(\alpha)/\alpha' \sim P \exp(c^{2/3})/c^{2/3}$.

It is important that if the parameter c is large enough for the orientation transition to occur on the above-described Semenov-Khokhlov mechanism,^{25,26} then $\lambda \gg P$ and $P \gg g$. In addition, the ordering can be obtained not only for excluded-volume interactions, but also for electrostatic and van der Waals ones.²⁵

Now the self-arrangement pattern seen in Figs. 3 and 6 is explained as follows. First, TCNTs can bend at the deflection length $\lambda = P/\alpha$ shorter than initial persistent length P for an isolated TCNT (with the characteristic energy of κ/λ per one bend) in a worm-like manner. This solves the entanglement problem because now crossing TCNTs can make hairpin

bends against each other. The “fingerprints” of the bending are little loopholes scattered all over the scanning electron microscopy (SEM) image in Fig. 6.

Second, water surface tension can put soft worm-like TCNTs close^{5,12} to make the parameter c have its critical value $c \approx 6$ (Ref. 25) for the orientation transition. A rough estimation for water pressure gives

$$\Pi_{water} \sim \gamma S/V \sim \gamma/d \sim 6 \text{ MPa}, \quad (3)$$

where $\gamma \sim 60 \text{ erg/cm}^2$ is the water surface tension at 100 °C and $S/V \sim 100 \text{ m}^2 \text{ cm}^3$ is the characteristic surface to volume ratio in the dense system water/TCNTs. The critical osmotic pressure can be estimated as²⁵ $\Pi_{TCNT} \sim 26.25 T_{eff}/(\pi P^2 d) = 26.25 \kappa/(\pi P^3 d/4) = 1.64 E(d/P)^3 \sim 2 \times 10^{-4} E$. This equation has an easy interpretation if one obtains the pressure as the elastic energy $\sim \kappa/\lambda$ of a curl of size $\lambda = P/c^{2/3}$ per volume $\sim \lambda^2 d$ occupied by the curl and takes into account $\kappa = E\pi(d/2)^4/4$ to get

$$\Pi_{TCNT} \sim (\kappa/\lambda)/(\lambda^2 d) \sim E(d/P)^3. \quad (4)$$

On equating pressures Π_{water} and Π_{TCNT} [Eqs. (3) and (4), one obtains

$$\gamma/d \sim E(d/P)^3, \quad (5)$$

which gives for the Young modulus the estimate about 50 GPa, which is a reasonable reduction comparatively to the values of order of 1 TPa, reported for pristine CNTs.²⁸ Here it is instructive to make an analogy of the TCNT system with another filamentous system—cooked noodles—assuming the $P_{noodles}/d_{noodles} \sim P_{TCNT}/d_{TCNT}$ ratio to be the same for TCNTs and noodles (as far as we claim that the geometrical pictures of self-aligned structures for noodles and TCNTs are indistinguishable and water pressure aligns both materials). Indeed, from Eq. (5) one can find that the ratio of Young’s modulus for TCNT and noodles is inversely equal to the ratio of their diameters,

$$E_{noodles}/E_{TCNT} \sim d_{TCNT}/d_{noodles}. \quad (6)$$

For $E_{TCNT} = 50 \text{ GPa}$, $d_{TCNT} = 15 \text{ nm}$, and $d_{noodle} = 5 \text{ mm}$, one obtains $E_{noodles} \sim 150 \text{ kPa}$, which means that if one stretches a 10 cm cooked noodle for 1 cm then the force will be around 0.3 N, which is around 30 g of the load weight. This

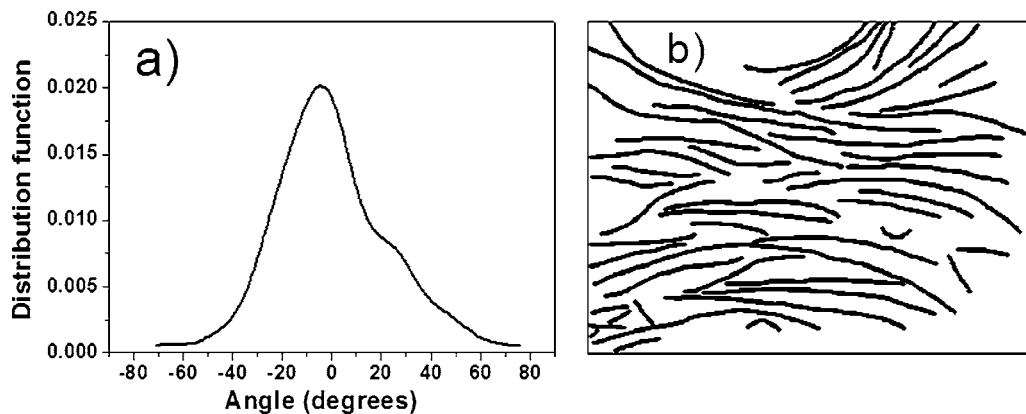


FIG. 7. Orientational order in TCNT solid. (a) The two-dimensional orientation distribution in this domain calculated from its skeleton image (b) of only visible parts of the TCNTs in Fig. 3(b). The angle is counted from the horizontal direction.

estimate is reasonable for a kitchen experiment.

Third, the ordering generates the global persistent length g along which the TCNTs are highly oriented. As far as in the ordered state $\alpha = c^{2/3} \gg 1$, then g can be tens of P . In Figs. 3(a) and 6, the length $g \approx 3 \mu\text{m}$ is seen as the characteristic size of aligned domains. Each domain contains nearly parallel parts of long TCNTs [Fig. 3(b)] and ends up with the pronounced bending in domain walls seen in Fig. 6. Thus, each TCNT participates in several domains. We obtained a value $S_2 \approx 0.7$ for the two-dimensional order parameter $S_2 = \langle 2 \cos(\alpha)^2 - 1 \rangle^5$ by utilizing the skeleton image in Fig. 7(b) and calculating the director orientation distribution [Fig. 7(a)] of visible parts of TCNTs in Fig. 3(b). Even though a three-dimensional order parameter $S_3 = \langle [3 \cos(\alpha)^2 - 1]/2 \rangle$ might be some 10%–20% less, the value is still higher than the theoretical $S_3 = 0.49$ for the system at the onset of the orientational transition.²⁹

Note that for short CNTs ($L < P$), the Onsager theory for rigid rods should be considered.^{25,29} Indeed, a common nematic structure is seen in SEM images for self-arranged ribbons.^{9,19} For nematic crystallinity of short multi-walled CNTs no continuous domain walls but the breaks between domains (where $3 \mu\text{m}$ CNTs end) are seen in Fig. S1(B) of Ref. 16, i.e., each CNT fits exactly one domain. On the contrary, the domain structure of the rosette nanotubes¹⁷ allows one to claim that the mechanism of their self-arrangement is likely the same as for our TCNTs.

After the heat treatment, the connecting functional groups lose oxygen and the direct carbon-carbon links between HCNTs may establish. This makes the HCNT based bulk material an elastomer that cannot be dispersed in water.

Finally, there is an additional non-trivial argument in favor of the suggested mechanism of TCNT self-alignment. Indeed, according to the mechanism, the two relevant lengths λ and g are exponentially different. That means that in a wide range between the two length-scales there is no characteristic scale; the situation known from the geometry of turbulence flow as a so-called intermediate asymptotics.³⁰ Also the local alignment of TCNTs is like the neighboring flow lines. As a result, one can hardly distinguish Fig. 6 from a drawing that visualizes a turbulent flow. It is the intermediate asymptotics that makes the complicated geometry of any semiflexible structures look similar, be it TCNTs or cooked noodles.

IV. CONCLUSION

In conclusion, we have demonstrated that an intensive chemical treatment of multi-walled CNTs with concentrated acid leads to a considerable softening of the TCNTs due to oxidation. We have shown that in this state the TCNTs behave similar to semiflexible polymer macromolecules and can reversibly self-assemble from dense water solution into a solid with a well-defined domain structure of aligned TCNTs. One exciting effect of the softened TCNTs being like long polymer molecules may be their possible collapse into a globular state in an appropriate solution (a coil-to-globule transition similar to the one for DNA macromolecules).^{29,31} If TCNTs are kept at sufficiently high density in the solution

and if after addition of a surfactant they start collapsing, then a highly interwoven structure similar to chain mail (ring armor) may result. Citing Ref. 32, “Two challenges facing the carbon nanotube field are the dispersion of nanotubes in solution and their assembly into useful structures,” we believe that the present work may provide a solution for both.

ACKNOWLEDGMENT

This work was funded by the Creative Research Initiatives Program supported by the Ministry of Science and Technology, Korea.

- ¹M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, *Carbon Nanotubes: Synthesis, Properties, and Applications* (Springer, Berlin, 2001).
- ²C. Park, Z. Qunaies, K. Watson, R. Crooks, J. Smith, S. Lowther, J. Connell, E. Siochi, J. Harrison, and T. Clair, *Chem. Phys. Lett.* **364**, 303 (2002).
- ³C. Niu, E. K. Sichel, R. Hoch, D. Moy, and H. Tennent, *Appl. Phys. Lett.* **70**, 1480 (1997).
- ⁴K. Esumi, M. Ishigami, A. Nakajima, K. Sawada, and H. Honda, *Carbon* **34**, 279 (1996).
- ⁵M. S. P. Shaffer, X. Fan, and A. H. Windle, *Carbon* **36**, 1603 (1998).
- ⁶P. M. Ajayan, O. Stephen, C. Collier, and D. Trauth, *Science* **265**, 1212 (1994).
- ⁷Z. W. Pan, S. S. Xie, B. H. Chang, C. Y. Wang, L. Lu, W. Liu, W. Y. Zhou, W. Z. Li, and L. X. Qian, *Nature* **394**, 631 (1998).
- ⁸B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, and P. Poulin, *Science* **290**, 1331 (2000).
- ⁹Y. Li, C. Xu, B. Wei, X. Zhang, M. Zheng, D. Wu, and P. M. Ajayan, *Chem. Mater.* **14**, 483 (2002).
- ¹⁰H. Pan, L. Liu, Z. Guo, L. Dai, F. Zhang, D. Zhu, R. Czerw, and D. L. Carroll, *Nano Lett.* **3**, 29 (2003).
- ¹¹M. Sano, A. Kamino, J. Okamura, and S. Shinkai, *Science* **293**, 1299 (2001).
- ¹²V. V. Tsukruk, H. Ko, and S. Peleshanko, *Phys. Rev. Lett.* **92**, 065502 (2004).
- ¹³M. Olek, J. Ostrander, S. Jurga, H. Möhwald, N. Kotov, K. Kempa, and M. Giersig, *Nano Lett.* **4**, 1889 (2004).
- ¹⁴N. Chakrapani, B. Wei, A. Carrilo, P. M. Ajayan, and R. S. Kane, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 4009 (2004).
- ¹⁵M. F. Islam, A. M. Alsayed, Z. Dogic, J. Zang, T. C. Lubensky, and A. G. Yodh, *Phys. Rev. Lett.* **92**, 088303 (2004).
- ¹⁶W. Song, I. A. Kinloch, and A. H. Windle, *Science* **302**, 1363 (2003).
- ¹⁷H. Fenniri, B. Deng, A. E. Ribbe, K. Hallenga, J. Jacob, and P. Thyagarajan, *Proc. Natl. Acad. Sci. U.S.A.* **99**, suppl 2, 6491 (2002).
- ¹⁸H. Xie, H. Lee, W. Youn, and M. Choi, *J. Appl. Phys.* **94**, 4967 (2003).
- ¹⁹Y. Li, J. Wei, X. Zhang, C. Xu, D. Wu, L. Lu, and B. Wei, *Chem. Phys. Lett.* **365**, 95 (2002).
- ²⁰G. Maurin, I. Stepanek, P. Bernier, J.-F. Colomer, J. B. Nagy, and F. Henn, *Carbon* **39**, 1273 (2001).
- ²¹L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Oxford, 1986).
- ²²M. Monthieux, B. W. Smith, B. Bouteaux, A. Claye, J. E. Fischer, and D. E. Luzzi, *Carbon* **39**, 1251 (2000).
- ²³K. H. An, K. K. Jeon, J. Moon, S. J. Eum, C. W. Yang, G. Park, C. Y. Park, and Y. H. Lee, *Synth. Met.* **140**, 1 (2004).
- ²⁴V. A. Davis, L. M. Ericson, A. N. G. Parra-Vasquez, H. Fan, Y. Wang, V. Prieto, J. A. Longoria, S. Ramesh, R. K. Saini, C. Kittrell, W. E. Billups, W. W. Adams, R. H. Hauge, R. E. Smalley, and M. Pasquali, *Macromolecules* **37**, 154 (2004).
- ²⁵G. J. Vroege and T. Odijk, *Macromolecules* **21**, 2848 (1988); T. Odijk, *ibid.* **16**, 1340 (1983).
- ²⁶A. R. Khokhlov and A. N. Semenov, *J. Phys. A* **15**, 1361 (1982).
- ²⁷A. E. Cohen and L. Mahadevan, *Proc. Natl. Acad. Sci. U.S.A.* **100**, 12141 (2003).
- ²⁸M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, *Nature* **381**, 678 (1996).

²⁹A. Yu. Grosberg and A.R. Khokhlov, *Statistical Physics of Macromolecules* (AIP Press, New York, 1994).

³⁰G. I. Barenblatt, *Scaling, Self-Similarity, and Intermediate Asymptotics* (Cambridge University Press, Cambridge, UK, 1996).

³¹P. W. Zhu and D. H. Napper, Phys. Rev. E **61**, 2859 (2000).

³²G. R. Dieckmann, A. B. Dalton, P. A. Johnson, J. Razal, J. Chen, G. M. Giordano, E. Munoz, I. H. Musselman, R. H. Baughman, and R. K. Draper, J. Am. Chem. Soc. **125**, 1770 (2003).