

SELF-ASSEMBLING OF MULTI-WALLED CARBON NANOTUBES INTO A REVERSIBLY WATER DISPERSIBLE PELLET

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Introduction

Carbon nanotubes (CNTs) have attracted increasing interest since their discovery because of the novel 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. Two challenges facing the carbon nanotube field are said to be the dispersion of nanotubes in solution and their assembly into useful structures [2]. Lightly etched in H₂SO₄/H₂O₂ single-walled CNTs were shown to make rings [3]. Being oxidized and thus hydrophilic, the CNTs can soften enough to be bent by water surface tension into various “needle eyes” and “nooses” [4]. Nitric acid was used for preparation of multi-walled CNT self-organized ribbons [5].

The distinctive feature of previous works on disentanglement and alignment is that mostly shortened CNTs (either by ball-milling or chemical cutting) were used. In our work we used a severe nitric acid treatment of long pristine multi-walled CNTs (PCNTs) which not only made CNTs hydrophilic and self-repelling in water solution, but also softened them to that extent that treated CNTs (TCNTs) attained the properties of semiflexible polymers. This change resulted in a self-arrangement of TCNTs into a dense domain structure with a strong alignment upon drying the solution.

Experimental

The preparation process involves a concentrated acid treatment of CNTs to add hydrophilic functional groups on CNT surfaces as described in our recent paper [6]. TCNTs of 2.5 grams were added into 50 ml deionized distilled water, and then subjected to intensive sonication to form homogeneous and stable suspensions of individual TCNTs. TEM images of TCNTs from the suspension showed that the aggregates and entanglements of PCNTs were disentangled [6]. On heating in order to remove water out of the concentrated TCNT suspension in a 100 ml beaker, a hard

cylindrical black pellet formed by self-organization (Fig.1). For recovering CNTs to their initial non-oxidized state without a change in the architecture, a part of the pellet was additionally heated at 1200 °C under vacuum for 1 h to produce a heated TCNT (HCNT) pellet.



Figure 1. Self-organized reversibly water dispersible pellet.

In sharp contrast to PCNTs, TCNTs in the pellet were self-organized into compact domain structures [Fig. 2(a)]. The nanotubes in each domain are in a good alignment [Fig.2(b)]. The density of the pellet was about 0.8 g/cm³, which corresponds to packing

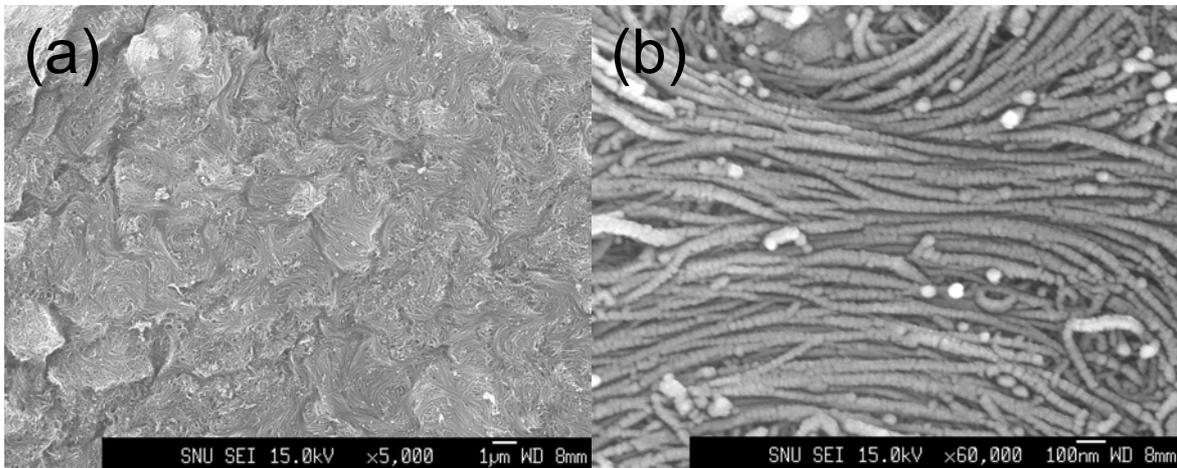


Figure 2. SEM images of the as produced TCNT pellet. (a) Surface morphology of the TCNT pellet showing compact domain structure. (b) A higher magnification image showing the alignment in one domain selected from Fig. 2(a). Gold particles, used for the SEM image resolution enhancement of the low conductivity oxidized TCNTs, thicken individual TCNTs.

fraction about 50% for both TCNTs and HCNTs. The TCNT pellet could imbibe water up to 150% of its weight and expand simultaneously. After the following 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 completely dispersed to form aqueous suspension. 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.

Results and Discussion

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 polymers after severe acid treatment. Indeed, the TCNTs should yield water surface tension compression to come close to each other. It can be possible only for sufficiently soft TCNTs. Also 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 [7] was not strong enough to make the CNTs soft sufficiently to overcome the entanglement threshold.

From the basic physics analogy, the dense solution of TCNTs can be regarded as an athermal liquid crystalline polymer [8] and each TCNT as a semiflexible macromolecule for which the inequality holds

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

where d is the diameter, L is the contour length of a TCNT, and P is the persistent length on which the TCNT is still “straight”. From microscopy images of individual TCNTs one can estimate $d \approx 15$ nm; $P \approx 300$ nm; $L \approx 30 \mu\text{m}$, thus Eq. (1) fulfils.

The self-arrangement pattern seen in Fig. 2 is explained as follows. First, TCNTs with small elastic constant κ can bend at the deflection length λ shorter than initial persistent length P with the characteristic energy of κ/λ per one bend in a worm-like manner. This solves the entanglement problem. The “fossils” of the bending are little loopholes scattered all over the SEM image in Fig. 2(a). Second, water surface tension can put soft worm-like tubes close [7] to have the critical concentration for the orientation transition [8]. A rough estimation for water pressure gives $\Pi_{\text{water}} \sim \gamma S/V \sim 6$ MPa, where $\gamma \sim 60$ erg/cm² is the water surface tension at 100 °C and $S/V \sim 100$ m²/cm³ is the characteristic surface to volume ratio in the system water/TCNTs. Let us introduce an effective “temperature” (in energy units) $T_{\text{eff}} = \kappa/P$ which is the characteristic of the chaotically distributed elastic energy in the system. For the system of TCNT coils being an athermal system, all conformation changes are entropy driven and the temperature disappears from corresponding equations for the normalized orientation distribution function [8]. Still the net elasticity is determined by T_{eff} , indicating the easiness of a rearrangement of the system by external forces (water surface tension in our case). The critical osmotic pressure can be estimated as [8]

$$\Pi_{\text{tubes}} \sim 26.25 T_{\text{eff}} / (\pi P^2 d / 4) = 26.25 \kappa / (\pi P^3 d / 4) = 1.64 E (d/P)^3 \sim 2 \times 10^{-4} E. \quad (2)$$

Equating both pressures gives for the Young modulus E the estimate about 50 GPa, which is a reasonable reduction comparatively to the values of order of 1 TPa, reported for pristine nanotubes [9]. Third, the ordering generates the global persistent length g along which the TCNTs are highly oriented. In the ordered state g can be tens of P . In Fig. 2(a) the length g is seen as the characteristic size of aligned domains. Each domain contains nearly parallel CNTs [Fig. 2(b)] and ends up with the pronounced bending in domain-walls [Fig. 2(a)].

Conclusions

Summarizing, the existence of a bulk self-arranged and well-aligned material produced in the form of a hard reversibly water dispersible pellet indicates that severe nitric acid treatment of pristine multi-walled carbon nanotubes turns CNTs into semiflexible polymer-like units that can be engineered in various structures (e.g. composites).

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