

# Utilizing polymers for shaping the interfacial behavior of carbon nanotubes

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A major obstacle for utilization of carbon nanotubes is their tendency to bundle and pack into ropes that further entangle into networks, rendering the tubes insoluble in aqueous and organic liquids, and thus almost un-processable. As was shown recently, physically adsorbed block-copolymers may be used for exfoliating and dispersing carbon nanotubes in aqueous and organic media. In this approach entropic repulsion among polymeric layers attached to CNT induce steric repulsion among the polymer-decorated tubes. The tube–polymer interactions are relatively weak, do not depend on the detailed chemistry of the interface and their range is tuned by the molecular weight and density of the polymeric layers, rather than by the chemical composition of the monomers. Combining theoretical modeling and experimental studies we demonstrate that this approach may be used for engineering the interfacial behavior of carbon nanotubes in a variety of systems.

## 1. Introduction

The recent discovery of carbon nanotubes (CNT)<sup>1,2</sup> has initiated an ever growing interest in exploring and exploiting their unique properties. Emerging applications for single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT) in the fields of nanoelectronics and nanomaterials include usage of SWNTs as electron field emission sources,<sup>3,4</sup> chemical sensors<sup>5</sup> and nanoelectronic devices.<sup>6,7</sup> CNT-based nanocomposites form a new class of lightweight super strong functional materials with potential for air and space technologies,<sup>8</sup> energy storage<sup>9</sup> and biomedical applications.<sup>10</sup>

SWNTs are crystalline tubuline graphitic structures, characterized by a diameter in the range of 0.8–2 nanometres and a typical length of microns resulting in an aspect ratio (length/diameter) significantly larger than 1000. SWNTs are characterized by superb mechanical, electrical and optical

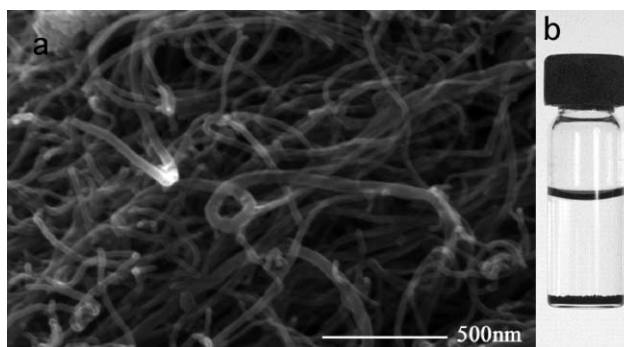
properties that result from the combination of their chemical composition, electronic structure and nanometric dimensions.<sup>11</sup>

While of great potential, a major obstacle for CNT utilization is their tendency to aggregate. SWNTs pack into bundles or “ropes” that typically contain 100–500 SWNTs arranged in a close packed triangular lattice held by dispersion forces.<sup>2</sup> The over micron-long ropes and MWNTs further entangle into networks, rendering the tubes insoluble in aqueous and organic liquids, and thus almost un-processable (Fig. 1).

Development of efficient pathways for de-agglomeration and formation of

stable dispersions of individual tubes in liquid media and polymeric matrices has been identified as one of the major challenges in the field of SWNT based material science and engineering.<sup>13</sup> The world effort dedicated to improving the processability of CNTs has lead to the development of a variety of strategies for exfoliating bundled SWNTs and dispersing the individual tubes. These include covalent modification,<sup>14–16</sup> complexation *via*  $\pi$ – $\pi$  interactions<sup>17</sup> and adsorption of charged surfactants.<sup>18–22</sup>

These approaches rely on (severe to mild) modification of the extended graphene  $\pi$ -system (the origin of the strong dispersion attraction) leading to



**Fig. 1** (a) A scanning electron microscopy<sup>11</sup> micrograph of as-prepared MWNT powder.<sup>12</sup> Typical external diameter of the tubes is 10–20 nm. (b) An image of a bottle containing coagulated MWNT powder in water following sonication and a day long incubation. Similar behavior is observed for SWNT powders.

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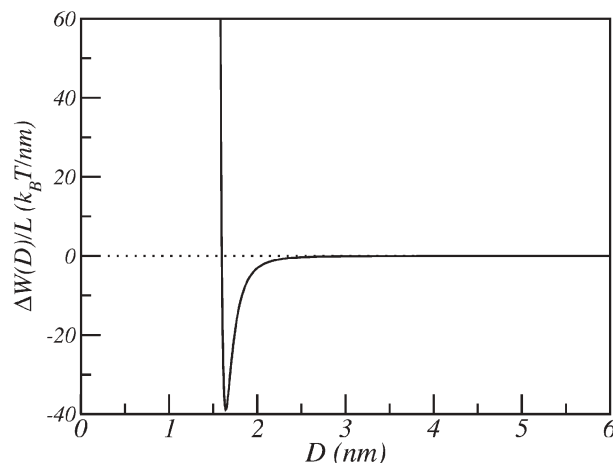
modification of the electronic structure and consequently the physical properties of the tubes.<sup>23–25</sup> An alternative more tender approach is offered by synthetic and natural polymers.<sup>26–29</sup>

## 2. Polymers and CNT—tuning the interaction potential

What is the essence of polymer–CNT interactions, and what makes polymers attractive agents for CNT based material technology? The answer is found in the inherent features of the inter-tube potential.

In Fig. 2 we present the inter-tube potential for two parallel SWNTs as a function of their distance, as derived by Girifalco *et al.*<sup>30</sup> a large attractive interaction at short inter-tube distance (less than 2 nm) is observed, with a minimum of about  $40 \text{ kT nm}^{-1}$ . The short-range attraction decreases to below  $kT$  within 2.5 nm. For typical 1 micron long tubes at contact with each other, the potential shown in Fig. 2 predicts a contact energy of 40 000 times the thermal energy, the origin of SWNT bundling. A short-range potential is typical for hollow structures with two (SWNTs) or three (fullerenes) nanometric dimensions, and differs from the long range attraction observed in (mesoscopic) colloidal systems, whose interaction range is a few times the size of the particles, typically in the 100s nm to micron scale.

The inherent fast decay of the attraction between SWNTs may be exploited for manipulating their interfacial behavior. Instead of aiming to attenuate the strong short-range attraction, it is possible to utilize a relatively weak, but long-range repulsion for creating a barrier that would prevent the tubes from approaching the attractive region of the potential. A good example is the osmotic (steric) repulsion among end-attached or adsorbed polymer layers in a good solvent. Actually, this approach has long been used for preparation of colloidal dispersions, and is known as “steric stabilization”.<sup>31</sup> Among the most efficient agents for steric stabilization are block-copolymers comprising covalently linked incompatible moieties (designated A–B–A or A–B), or an end-activated polymer (A–x). When dissolved in a selective solvent that acts as a “good solvent” for one of the blocks (*i.e.*, A),

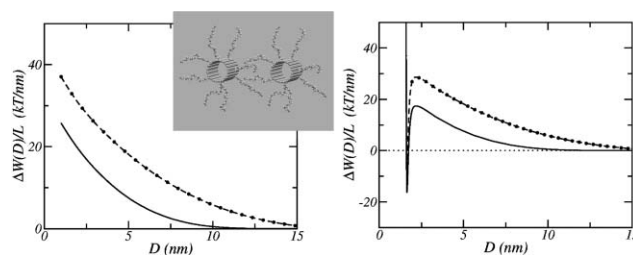


**Fig. 2** Inter-tube potential for two parallel SWNTs in vacuum as calculated by Girifalco *et al.*<sup>30</sup> The distance  $D$  is measured from the center of the nanotubes. In all the calculations presented here the diameter of the nanotube is assumed to be 1.1 nm, equivalent to an (8,8) SWNT.<sup>30</sup>

dissolving it readily and increasing its spatial dimensions, while simultaneously acting as a “poor solvent” for the other block (B), the polymer may adsorb onto a colloid or a nanoparticle, and form a surface layer of dangling (A) moieties. The dangling swollen chains repel other polymer-decorated objects, as demonstrated in Fig. 3, and result in the formation of a long-lived dispersion. An interesting observation is that there exists a regime of polymer chain length where the polymers are too short to prevent the aggregation of colloidal particles or metallic nanoparticles, while their length suffices for dispersing CNTs.<sup>32</sup> Polymers of that chain length may be utilized for purification and separation of CNTs from undesirable by-products, as discussed below.

The utilization of block-copolymers for shaping the interfacial behavior of CNTs has far-reaching consequences for

the engineering of CNT-based materials and devices, as it is generic, relies on non-specific interactions, is applicable to different solvents, matrices and processing schemes, and should not affect the physical and electronic properties of the individual tube. The basic assumption in this work is that the polymers adsorb to the surface of the nanotube by a combination of weak van der Waals interactions and solvophobic effects. These two types of interactions are not chemical in nature and are not expected to modify the intrinsic properties of the nanotubes. While this is our working hypothesis, we do not have direct experimental evidence that the properties of the nanotubes are unchanged. It will be interesting to directly probe the electronic structure of polymer-decorated nanotubes by spectroscopic methods. Below we describe a few aspects explored by us.



**Fig. 3** Left: the repulsive interactions between two parallel CNTs with end-tethered polymers with chain length  $n = 50$  (line) and  $n = 100$  (dotted line). Right: the total interaction between two parallel CNTs with end-tethered polymers. The total interaction is obtained by adding the attractions shown in Fig. 2 with the repulsions shown in the left panel. The cartoon shows the source of the repulsive interactions due to the crowding of the polymer chain in the inter-tube region. The calculations are for a line density of polymers of  $3.3 \text{ nm}^{-1}$ .<sup>25,32</sup>

### 3. Dispersion of individual SWNTs in organic and aqueous media

Recently we have shown that stable long-lived dispersions of exfoliated SWNTs can be formed in aqueous and organic media using block-copolymers as dispersing agents.<sup>32</sup> The process is simple: a powder of as-prepared SWNTs is sonicated in an aqueous or organic solution of a block-copolymer (for example Pluronic, PEO-PDMS-PEO, poly(styrene-*bt*-butyl acrylate) forming a black ink-like dispersion. X-Ray scattering, cryo-TEM<sup>32,33</sup> and neutron scattering<sup>34</sup> suggest that the most abundant species in the dispersions are individual tubes and small bundles (<4 SWNTs).<sup>34</sup> The concept is demonstrated in Fig. 4: while gentle sonication leads to exfoliation of SWNT ropes, selective adsorption of the block-copolymers presents a steric barrier

for re-bundling. A great advantage of this stabilization method is that the dispersion may be dried and re-dispersed without agglomeration of the tubes.<sup>32,33</sup>

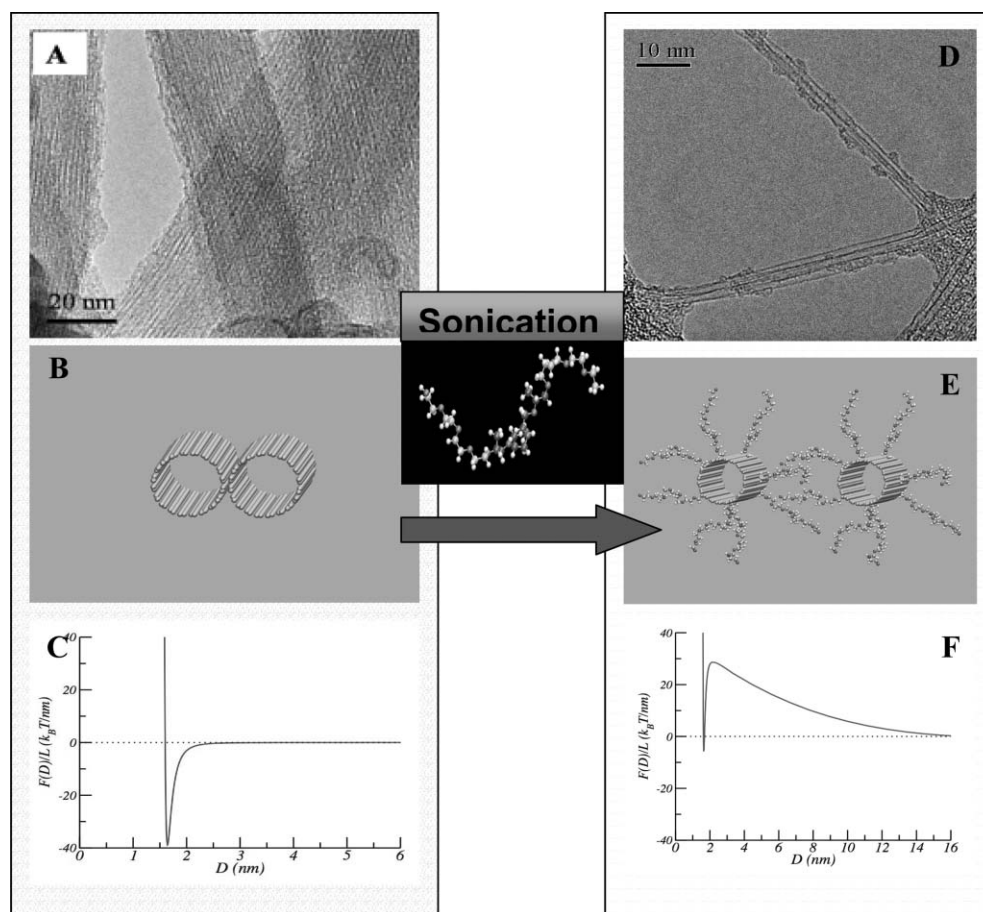
### 4. Utilizing dimensional selectivity for non-destructive purification of CNT from colloidal mixtures

Colloidal carbonaceous particles, graphite and metal nanoparticles are common contaminations in powders of SWNTs, while non-exfoliated bundles are often found in SWNT dispersions. The observation that polymer-particle interactions are a sensitive function of both the dimensions and density of the dispersed particles and polymer chain-length, is the key for a novel purification approach, recently demonstrated by us:<sup>32</sup> using block-copolymers of intermediate chain length, such that the

non-adsorbing moiety is long enough to disperse individual SWNTs but not colloidal carbonaceous species, dispersions of a crude CNT-colloidal mixture were prepared. We found that individual tubes and small bundles are preferentially dispersed while metal nanoparticles, large bundles, and carbonaceous colloids coagulate and precipitate.

### 5. CNT-polymer nanocomposites

CNT-polymeric nanocomposites may be prepared by filling a polymeric matrix with CNTs. Due to their high aspect ratio, a connected (percolating) CNT-network is expected to form at a low volume fraction.<sup>11</sup> A marked increase in the mechanical strength and electrical conductivity are observed above the percolation threshold, as the connected network simultaneously provides a mechanical backbone and a pathway



**Fig. 4** A dry powder of as-prepared SWNTs is composed of molecular crystals known as bundles or ropes (A) that form due to strong cohesion between the tubes (B), resulting from the total interaction energy (C) that exhibits a strong minimum at small separation  $D$ . Sonication of the SWNT powder in block-copolymer solutions (where the solvent is selective) may lead to anchoring of the polymers to the CNT surface (D, E) and modification the inter-tube potential due to steric repulsion (F).

for electrical conductivity. Predictions suggest that percolation of SWNTs should commence at concentrations below 0.001 wt%. Yet, due to difficulties in dispersing de-agglomerated tubes in the polymeric matrix and poor adhesion and wetting at the CNT–polymer interface, the measured values are higher and strongly depend on the matrix and the processing method.

Here as well, block-copolymers offer an efficient versatile solution: as is well known in the plastics industry, block-copolymers are excellent promoters of adhesion and wetting. By choosing a block-copolymer that is chemically compatible with the target matrix, and co-dispersing the CNTs with the target matrix polymer, it is possible to prepare CNT–polymer nanocomposites. The quality of the composites is judged by the measured values of the electrical percolation threshold. Indeed, bulk volume–conductivity measurements of composites prepared by co-dispersion exhibit percolation thresholds in the range of 0.04 to 0.09 wt% for SWNTs (similar to those reported for strongly interacting polymer–CNT composites<sup>35</sup>) and 0.5 to 0.8 wt% for MWNTs.<sup>36</sup>

The approach presented here may be utilized also for preparation of CNT–polymeric composites *via* melt blending,<sup>37</sup> and electron spinning of CNT–polymer fibers.<sup>38</sup> The block-copolymers promote dispersion of the tubes within the matrix and improve adhesion and wetting at the CNT–polymer interface while preserving the

unique properties of the unmodified tubes.

## 6. Nanotubes attracted to surfaces

Several applications of CNTs require the placement of the tubes on surfaces. Can we utilize polymers that are used for dispersion of the tubes for controlling the binding of the CNTs to a surface? Recent theoretical calculations<sup>39</sup> show that functionalizing the free end of the polymer with a moiety that is attracted to the surface enables the control of the optimal surface–CNT distance as well as the binding interaction. An example is shown in Fig. 5 for two different polymer molecular weights. The specific calculations shown are for CNT–graphite and the figure shows the presence of two minima separated by a large barrier. The barrier is the result of the steric polymer–surface interactions, the primary minimum is due to the bare CNT–graphite interaction while the secondary minimum is due to the functional group–surface attraction. The short chain length shown may not present a large enough barrier to stabilize the surface–tube interaction at  $D = 4.5$  nm, however, the longer chain length presents an impenetrable steric barrier and a relatively strong minimum at  $D = 9$  nm. Both the strength and the range of interactions can be manipulated by the proper choice of polymer molecular weight and surface coverage.<sup>39</sup> Note that the same polymer that is used

to control the surface–CNT distance disperses the individual tubes in solution as discussed above.

## 7. Summary and conclusions

Bundling, aggregation, and agglomeration have been identified as the major obstacles for realization of the technological potential of CNTs. Whether the final goal is a nanotransistor<sup>40</sup> a CNT-FET array<sup>41</sup> or a low-percolation composite material<sup>35,42,43</sup> the ability to exfoliate the bundles into individual tubes and disperse the exfoliated tubes in a medium are necessary prerequisites.

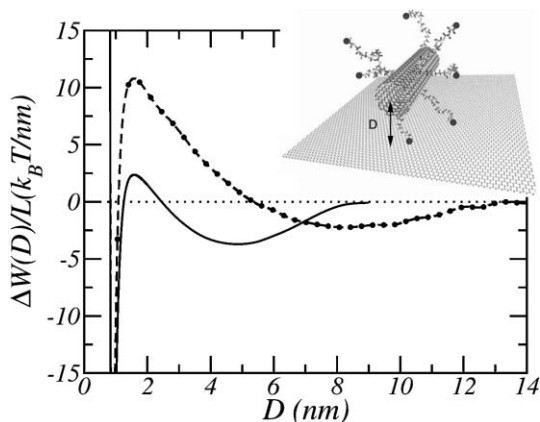
Over the last few years polymers have been shown to serve as efficient tools for engineering the interfacial behavior of CNTs.<sup>44</sup> Two very different approaches have been described. The first relies on specific chemical interactions between CNTs and the functional groups comprising the polymer (monomers). An alternative approach, emphasized in this paper, is based on the utilization of non-specific steric interactions. In this approach, entropic repulsion among polymeric layers attached (adsorbed, grafted) to CNTs drive exfoliation and dispersion of the CNTs. The interactions are relatively weak, do not depend on the detailed chemistry of the CNT–polymer interface and their range is tuned by the molecular weight and density of the polymeric layers, rather than by the chemical composition of the monomers.

While currently used for dispersion of CNTs in liquids and polymeric matrices, this approach may be utilized for more advanced applications where alignment of CNTs, controlled self-assembly into pre-designed 3-D structures, and assignment onto patterned surfaces are required. We believe that these goals may be achieved by application of external fields (electrical, magnetic<sup>45</sup> or mechanical (shear alignment)) to the polymer-decorated CNTs.

These are only a few examples out of the wealth of opportunities offered by CNT–polymer interactions. A broader overview of the field was recently summarized in a review paper (ref. 44).

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**Fig. 5** The total interaction per unit length between a CNT and a graphite surface.  $D$  measures the distance from the center of the tube to the surface as shown in the cartoon. The full line is for  $n = 50$  and the dashed line with filled circles is for  $n = 100$ . The strength of the functional group–surface attraction is  $5 k_B T$ , while the polymer line density is  $4 \text{ nm}^{-1}$ .<sup>39</sup>

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