

The role of surfactants in dispersion of carbon nanotubes

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Abstract

The discovery of carbon nanotubes offers exciting opportunities for the development of novel high property materials. Disaggregation and uniform dispersion are critical challenges that must be met to successfully produce such high property materials, since carbon nanotubes tend to self-associate into micro-scale aggregates. This results in products with inferior mechanical and electric performance. Recognizing this problem, extensive research has been reported in the literature on development of dispersion technologies based on both mechanical and chemical approaches. Here, we review recent progress and advances that have been made on dispersion of carbon nanotubes in aqueous and organic media by non-covalent adsorption of surfactants and polymers. Carbon nanotube structure, properties and mainly self-assembly are discussed in detail. © 2006 Elsevier B.V. All rights reserved.

Keywords: Carbon nanotubes; Dispersion; Stabilization; Surfactants; Polymers

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1. Introduction

For many industrial applications a uniform and stable dispersion of particulate matter plays an important role. This

requirement is especially critical when submicron or nanometer-sized particles are involved. In such ranges the surface chemistry controls the dispersion state of the particles within a final product. It is extremely important to learn how to manipulate the surface properties in order to achieve a product with the desired properties.

A surfactant's property of accumulation at surfaces or interfaces has been widely utilized to promote stable dispersions of solids in different media [1–5]. Those amphiphilic

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molecules, i.e., compounds having both polar and apolar groups, adsorb at the interface between immiscible bulk phases, such as oil and water, air and water or particles and solution, act to reduce the surface tension. The distinct structural feature of a surfactant originates from its ‘duality’: the *hydrophilic* region of the molecule or the polar head group; and the *hydrophobic* region or the tail group that usually consists of one or few hydrocarbon chains. Surfactants are classified according to the charge of their head groups, thus cationic, anionic, nonionic or zwitterionic are known.

Two important features which characterize surfactants, namely adsorption at interface and self-accumulation into supramolecular structures, are advantageously used in processing stable colloidal dispersions. The adsorption of surfactants onto inorganic and organic surfaces usually depends on the chemical characteristics of particles, surfactant molecules and solvent. Thus, the driving force for the adsorption of ionic surfactants on charged surfaces is the Coulombic attractions, which are formed, for example, between the surfactant’s positively-charged head group and the negatively-charged solid surface. The mechanism by which nonionic surfactants adsorb onto a hydrophobic surface is based on a strong hydrophobic attraction between the solid surface and the surfactant’s hydrophobic tail. Once the adsorption of surfactant molecules on particle surfaces is established, self-organization of the surfactant into micelles (aggregative structures of surfactants) is expected to occur above a critical micelle concentration (CMC).

Carbon nanotubes (CNT) have a unique set of properties that position them for a wide scope of possible applications in suspensions and polymer based solutions, melts and composites [6–9]. Their outstanding characteristics include high mechanical properties, namely tensile strength and elastic modulus, and still remarkable flexibility, excellent thermal and electric conductivities, low percolation thresholds (loading weight at which a sharp drop in resistivity occurs) and high aspect ratios (length to diameter ratio, L/D), while the latter provides the nanotubes with additional advantage over spherical fillers to obtain high property composites [10].

Main challenges for integration of this unique nano-material include: (1) uniform dispersion; (2) preferential alignment in liquid and melt phases; and (3) mass-production of high-purity material at low costs. This review article focuses mainly on the first challenge; that of developing homogeneous dispersions of carbon nanotubes, particularly with the aid of surface active agents (surfactants and block copolymers). Various sources of stabilization of classical colloidal suspensions, such as surface charge effect, surfactant used and adsorption mechanism, will be examined to find out whether they are still valid for CNT dispersion systems.

2. Carbon nanotubes

Carbon nanotubes have been attracting great interest due to their wide scope of possible applications, such as composite reinforcement material [11–13], hydrogen containers [14], field emission sources [15], super-capacitors [16], molecular sensors

[17] and scanning probe tips [18]. Offering attractive mechanical/electric/thermal properties, carbon nanotubes could constitute a model system for evaluation of the potential to achieve a significant improvement in bulk properties by adding nano-scale modulators at low weight percents. In the following section, the structure, main characteristics and entanglement of CNTs are discussed in detail.

2.1. Structure and properties of carbon nanotubes

The discovery of the C_{60} molecule in 1985 by a group of chemists from Rice University (Texas, US) has evoked a tremendous interest among the world scientific community and led to the development of a completely novel branch of chemistry called *Fullerene-Chemistry* [19]. Fullerenes are geometric cage-like structures of carbon atoms that are composed of hexagonal and pentagonal faces. Carbon nanotubes are long, slender fullerenes, in which the walls of the tubes are hexagonal carbon (graphite-like structure), and the end caps contain pentagonal rings (Fig. 1a). CNTs were observed for the first time by Sumio Iijima in 1991 [20].

Theoretically, it is possible to construct carbon tubules by rolling up a hexagonal graphene sheet, as shown in Fig. 2 [23]. In graphite, sp^2 hybridization occurs, where each atom is connected evenly to three carbons (120°) in the xy plane, and a weak π bond is present in the z axis. The sp^2 set forms the hexagonal (honeycomb) lattice typical of a sheet of graphite. The p_z orbital is responsible for van der Waals interactions. The free electrons in the p_z orbital move within this cloud and are no longer local to a single carbon atom [24]. This phenomenon lies behind the reason why graphite (and CNT, accordingly) can conduct electricity, as opposed to diamond, which behaves as insulator because all electrons are localized in the bonds within the sp^3 framework [25]. Besides being responsible for high conductivity, the delocalized π -electrons of carbon nanotubes could be utilized to promote adsorption of various moieties on the CNT surface via π – π stacking interactions.

The exact properties of CNT are extremely sensitive to their degree of graphitization, diameter (or chirality), and whether they are in single wall or multi wall form (Fig. 1a and b, respectively). Single wall carbon nanotubes (SWNT), which are seamless cylinders, each made of a single graphene sheet, were first reported in 1993 [26]. Multi wall carbon nanotubes (MWNT), consisting of two or more seamless graphene cylinders concentrically arranged, were discovered two years previously [20]. The production method is often aimed at processing a particular type of carbon nanotubes, thus MWNTs are most commonly produced via non-catalytic means, whereas

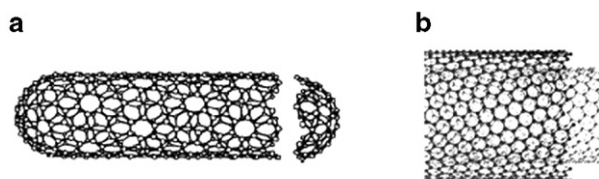


Fig. 1. Computer-generated images of carbon nanotubes [21,22].

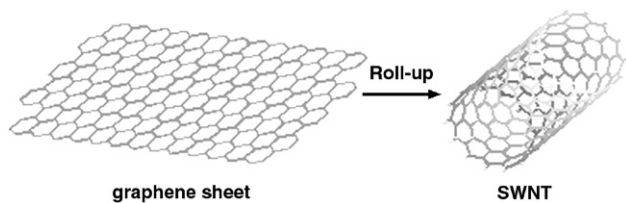


Fig. 2. It is possible to create a single wall carbon nanotube by rolling-up a graphene sheet [23].

SWNTs are usually dominant products under catalytic growth conditions. Furthermore, the production method dictates the quality of the generated tubes (as do their properties) viz., distribution of diameters and lengths, degree of entanglement, and amount of impurities (encapsulated catalyst particles, amorphous carbon, polyhedral graphite particles etc.) [27]. Among various processing techniques, such as arc-discharge, laser vaporization, or electrolysis, according to Refs. [28–30] it appears that the chemical vapor deposition (CVD) method has the highest potential for growing large quantities of pure and crystalline carbon nanotubes.

Among various attractive characteristics, it was mainly the electric properties of carbon nanotubes that stimulated large-scale industrial production of CNT-based materials. However, the electronic response of individual nanotubes is reported to be sensitive to various parameters, such as the synthesis method, defects, chirality, diameter and degree of crystallinity [31]. Generally, the thermal and electric conductivities (TC and EC, respectively) of single nanotubes are thought to be higher than graphite. For example, the TC of graphite along its planar direction is 1000 W/m K, while the TC of SWNT and MWNT is 2400 and 1980 W/m K, respectively [32,33]. However, the reported values for bundles of CNT resemble those of in-plane and cross-plane graphite.

It is known that solids with high aspect ratios can produce three-dimensional networks when incorporated into polymer materials. When added as well-dispersed fillers, they provide a conductive path through the composite. Therefore, carbon nanotubes ($L/D > 1000$) were shown to increase both thermal [34,35] and electric [36–38] conductivities of polymers at low percolation thresholds (up to a few weight percents). Nevertheless, the strong dependence of percolation limits on the CNT state of dispersion has to be emphasized. Thus, to improve SWNT dispersion in high density polyethylene (HDPE), the tubes were dispersed with the aid of sodium dodecyl sulfate (SDS) surfactant [39]. The percolation threshold for this system was reported at about 4 wt.% CNT loading, as demonstrated in Fig. 3. Even lower percolation limits were obtained with polystyrene and epoxy filled CNT composites, thus 0.5 vol.% and 0.04 wt.% loadings, respectively, were reported [40,41].

Because the carbon–carbon bond observed in graphite is one of the strongest in nature, carbon nanotubes are excellent candidates for the stiffest and strongest material ever synthesized. Despite large variations in the reported values, carbon nanotubes were shown to exhibit mechanical performance higher than that of classic advanced fibers, like carbon and Kevlar. As with electric properties, the mechanical strength of

the tubes depends on the crystallinity of the material, number of defects (often controlled by the synthesis method), diameter, etc. Mechanical properties of SWNT usually exceed those of MWNT, thus measurements of Young's modulus give results in the range of 10^3 GPa and 500 GPa, respectively [42–45]. Smaller size and massive arrangement in ropes make the measurement of the mechanical properties of SWNT more complex and less precise [46].

Reinforcement effect of carbon nanotubes was demonstrated for various polymeric systems [47–49]. Dynamic-mechanical analysis (DMA) of MWNT-poly(methyl-ethyl methacrylate) (PMEMA) nanocomposites showed that the storage modulus E' was improved by 230% with the embedment of only 1 wt.% of tubes. However, adding the same amount of CNT, which was initially dispersed by Triton X-100 surfactant (polyethylene oxide (9) nonyl phenyl ether), the improvement in E' dropped by almost 50% [50]. A similar tendency was found when glass transition temperatures, T_g , of the neat polymer and surfactant-contained polymer were compared. This surfactant-induced plasticization effect was also reported for epoxy [51] and polyethylene glycol matrices [52].

Fig. 4 shows stress–strain curve of pure polycarbonate (PC) and those of 2 wt.% and 5 wt.% MWNT-PC composites [53]. As compared to pure PC modulus a 70% increase was observed due to incorporation of 5 wt.% of as-received carbon nanotubes. Even a higher increase was reported for the epoxide-modified nanotubes.

Clearly, the intrinsic properties of polymeric materials can be significantly improved by the embedment of CNT. Sufficient wetting and uniform dispersion is required for the effective utilization of the tube properties.

2.2. Aggregation and poor solubility of carbon nanotubes

Nano-scale dimensions of CNT turn dispersion into a challenge, since as the surface area of a particle increases, so does the attractive forces between the aggregates. High aspect ratios, combined with high flexibilities [54], increase the possibility of

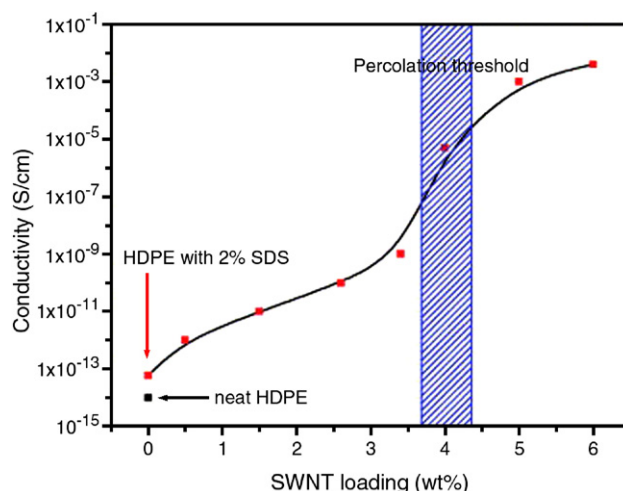


Fig. 3. The conductivity of HDPE filled with SDS-coated SWNT [39].

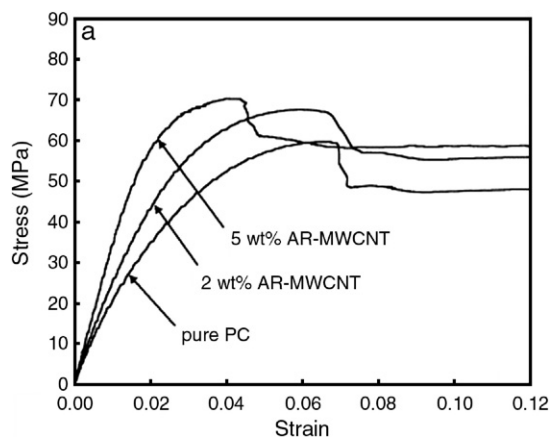


Fig. 4. Stress–strain curves of as received (AR) MWNT composites and pure PC [53].

nanotube entanglement and close packing [55]. The low dispersability stems from the tendency of pristine nanotubes to assemble into bundles or ropes (Fig. 5), which contain hundreds of close-packed CNT tightly bound by van der Waals attraction energy of 500 eV/ μm of tube–tube contact [56]. The range of the attractive van der Waals inter-particle potential was recently determined by the number of microscopic vs mesoscopic dimensions [57].

Following the first report on a CNT-polymer composite, much effort was made to produce functional high property materials by imbedding the nanofiller into various polymeric matrices [58–64]. Highly entangled carbon nanotubes, which are difficult to disperse in polymer solution and melt, result in composites with performance far below the theoretical predictions [65]. Carbon nanotubes assembled in ropes were shown to act as crack-initiators and decreased composite elastic properties. Furthermore, a prerequisite for the successful realization of CNT properties in a composite structure is the effective utilization of their high aspect ratio, for which their disaggregation and preferential alignment are essential. Therefore, very different results have been reported on the mechanical behavior of CNT-based composites, showing that the parameters required to optimize the behavior of these nanocomposites depend on many factors, among them the quality of CNT dispersion, the

final aspect ratio (whether the nanotubes were shortened as a result of disaggregative treatment) and the strength of the CNT-matrix interfacial properties. Inhomogeneous mixtures are far more common phenomenon in SWNT reinforced composites rather than MWNT.

The solubility of carbon nanotubes may be necessary for their chemical and physical examination, since it allows easy characterization and facilitates their manipulation. Intensive research was addressed to overcoming the poor solubility of CNT in either water or organic solvents.

Solubility of SWNT at various solvents, such as, dimethylformamide (DMF), chloroform, acetone, toluene, benzene, etc., was studied in terms of Hansen solubility parameters ($\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$) [66]. It was found that the tubes were suspended very well in solvents with dispersive component (δ_d^2) between certain boundaries (17–18 $\text{MPa}^{1/2}$); they were precipitated in solvents with high polar (δ_p^2) and hydrogen-bonding (δ_h^2) components. However, the dispersion state had no specific dependency on the total solubility parameter (δ_t^2).

Highly polar solvents such as DMF, methylpyrrolidine and hexamethylphosphoramide (HMPA) were shown to properly wet SWNT [67]. Wetting measurements of individual carbon nanotubes in various organic liquids were performed using atomic force microscopy [68,69]. The wetting properties of carbon nanotubes could be significantly improved via oxidation by strong acids, like H_2SO_4 or HNO_3 , or mixture of acids [70]. The procedure results in the formation of carboxylic moieties, preferentially on the end caps of the CNT, since the regions where pentagons are located suffer more strain (higher chemical reactivity) compared with that of purely hexagonal lattice. Under these conditions, the end caps of the nanotubes are opened and acidic functionalities, which could be suitable for further derivatization (esterification or amidization [71–73]), are formed at these defect sites and at the side walls. Thus, long-chain alkylamide-functionalized nanotubes were obtained according to Fig. 6, where surface-bound COOH groups are converted into thionyl chloride groups and subsequently reacted with amine [74]. Octadecyl-amide functionalized MWNT were reported to exhibit good solubility in carbon disulfide (CS_2) and toluene [72], and improved dispersion in polypropylene (PP) matrix [52]. Significant enhancement of mechanical properties

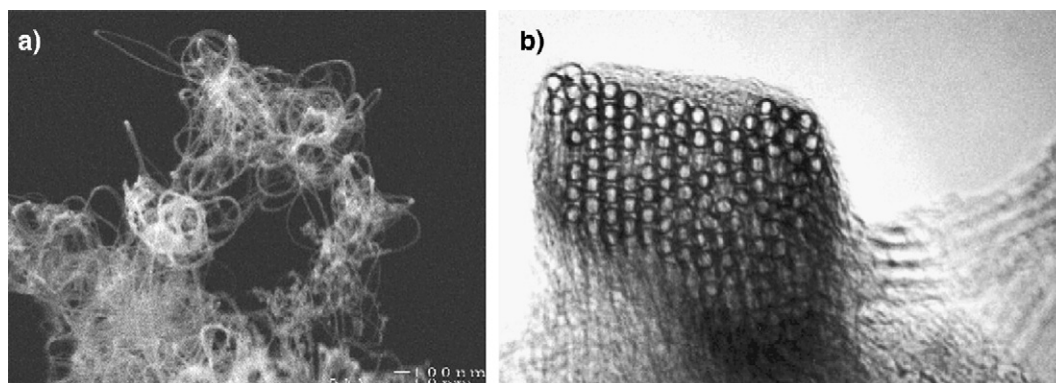


Fig. 5. (a) SEM image of a SWNT bundles; (b) TEM image of the cross section of a SWNT bundle. Images were obtained from Smalley's group webpage: www.ruf.rice.edu/~smalley/image_gallery.htm.

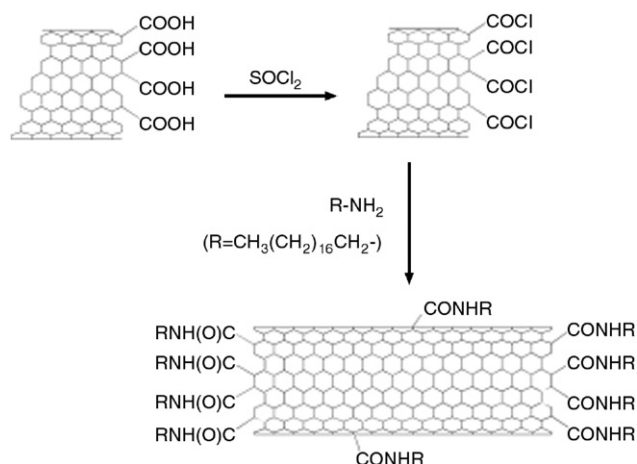


Fig. 6. Schematic presentation of amidization process of oxidized carbon nanotubes [74].

was obtained via reinforcement of poly(vinyl alcohol) by functionalized SWNT with multiple surface hydroxyl groups [75].

Emphasizing the difficulty to obtain soluble and dispersed carbon nanotubes, the most effective methods of dispersing the tubes are summarized below.

2.3. Current approaches for dispersing carbon nanotubes

Much effort has been invested in developing approaches for reproducible dispersions of individual carbon nanotubes. As stated earlier, in order to develop high property CNT-based materials, fully utilizing unique properties of the tubes, the thermodynamic drive toward aggregation must be overcome. Therefore, a dispersion method, as an integral step of the production chain, has to be selected in accordance with the processing conditions of the CNT-based material.

There are two distinct approaches for dispersing carbon nanotubes: the mechanical method and methods that are designed to alter the surface energy of the solids, either physically (non-covalent treatment) or chemically (covalent treatment). Mechanical dispersion methods, such as ultrasonication and high shear mixing, separate nanotubes from each other, but can also fragment the nanotubes, decreasing their aspect ratio [76]. Chemical methods use surface functionalization of CNT to improve their chemical compatibility with the target medium (solvent or polymer solution/melt), that is to enhance wetting or adhesion characteristics and reduce their tendency to agglomerate. However, aggressive chemical functionalization, such as the use of neat acids at high temperatures, might introduce structural defects resulting in inferior properties for the tubes [77]. Non-covalent treatment is particularly attractive because of the possibility of adsorbing various groups on CNT surface without disturbing the π system of the graphene sheets. In the last few years, the non-covalent surface treatment by surfactants or polymers has been widely used in the preparation of both aqueous and organic solutions to obtain high weight fraction of individually dispersed nanotubes. A detailed discussion on the surfactant-and polymer-stabilized dispersions of carbon nanotubes is presented in Section 4.

Although the electronic properties of nanotubes are compromised via functionalization, their utility for rheological modification of material blend remains profound. There are several approaches to introducing covalent side wall functionalization of the tubes. These include the organometallic approach to produce MWNT with chlorinated polypropylene [78], fluorination with molecular fluorine and further substitution by alkyl groups, and addition of nitrenes, carbenes or radicals [74].

3. Characterization of CNT dispersion

Besides the obvious difficulty in obtaining stable and homogeneous dispersions of nanotubes, another complication is finding a valid method to evaluate their state of dispersion. Agglomerates of carbon nanotubes could be visualized directly or, alternatively, mechanical or electric response of CNT-based materials could indirectly indicate the state of filler dispersion [77]. Thus, if the dispersion is poor, the mechanical properties will probably decrease relatively to pure polymer.

Visualization of CNT-based samples by optical microscopy enables to access mainly micrometer-sized agglomerates, while atomic force microscopy (AFM) is used to monitor suspended CNT at nano-scale level [79]. However, by AFM one can probe only a few nanotubes at a time, which might not be representative of the whole sample. Imaging of CNT-based polymeric composites by scanning or transmittance electron microscopy (SEM and TEM, respectively) often requires pre-treatment by means of gold or carbon sputtering or microtome slicing of the sample, which might cause a defect in the original pattern of the composite. Solutions of carbon nanotubes are best viewed with cryo-TEM, which is ideally suited for imaging of wet samples [80–82].

Characterization of MWNT suspensions by particle size analyzer based on dynamic light scattering technique was reported to be effective in indicating the agglomerate size reduction with surfactant adsorption [52]. However, in that work the measurement assumed spherical particles, resulting in an average value for the length of the CNT particles. As a result, the reported dimensions of nanotubes exhibit average sizes in the micrometer range. It is noted though that the dynamic light scattering technique in principle can be applied to rod-type and disk-type particles [83,84].

The discovery of nanotube fluorescence [85] has led to a precise method of detecting individual nanotube dispersion [86]. A nanotube in an aligned bundle does not emit because of energy transfer to neighboring tubes, particularly to the metallic ones. Thus, the dispersion process can be monitored by examining transient fluorescent emission as a function of various parameters, like the type of surfactant used [80], sonication time and surfactant concentration [86] and functionalization [87]. The spectral structures A, B and C in Fig. 7 are interpreted as a superposition of distinct electronic transitions from a variety of isolated nanotubes. In contrast, broadened and red-shifted adsorption spectra are typical of aggregated in bundles nanotubes (D).

On various occasions small angle neutron scattering (SANS) [88,89], Raman spectroscopy [86,90], size exclusion chromatography (SEC) [91] were applied to evaluate CNT dispersions. UV–vis scanning of the tube suspensions enabled to plot CNT

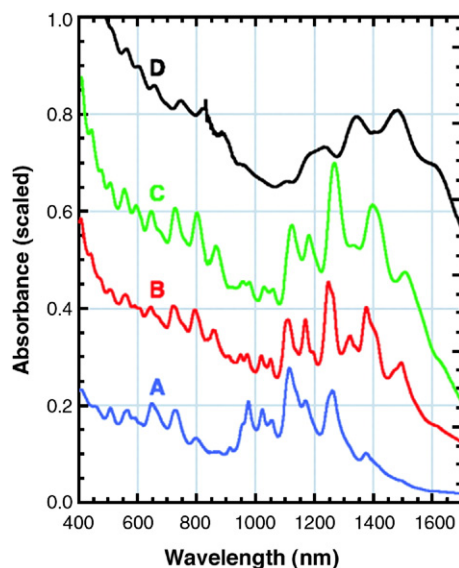


Fig. 7. SWNT adsorption spectra in aqueous suspension of SDS surfactant. Traces A, B and C are from individual nanotubes at different diameters, coated by SDS micelles prior/after poly(vinylpyrrolidone) wrapping. The top trace D is the spectrum of aggregated nanotubes in SDS micelles [85].

concentration with increasing sediment time and to conclude on surfactant stabilization efficiency [92].

4. Specific applications of surfactants for dispersing carbon nanotubes

In a typical dispersion procedure, after the surfactant has been adsorbed on the nanotube surface, ultrasonication for minutes or hours (with ultrasonication tip or bath, respectively) may help a surfactant to debundle nanotubes by steric or electrostatic repulsions. Recent reports [87,93] show that according to this procedure the outermost nanotubes in a bundle are treated more than the innermost tubes and that the nanotubes remain predominantly bundled after surfactant has been added. Therefore, mechanical exfoliation of the bundles prior to surface treatment must occur in order to obtain individual carbon nanotubes.

A mechanism of nanotube isolation from a bundle (Fig. 8i), with the combined assistance of ultrasonication and surfactant adsorption, was proposed [86]. The role of ultrasonic treatment is likely to provide high local shear, particularly to the nanotube bundle end (ii). Once spaces or gaps at the bundle ends are formed, they are propagated by surfactant adsorption (iii), ultimately separating the individual nanotubes from the bundle (iv).

Generally, ionic surfactants are preferable for CNT/water-soluble solutions. Alternatively, nonionic surfactants are proposed when organic solvents have to be used. Further discussion on surfactant-assisted dispersions of carbon nanotubes will be conducted according to the mediums' nature, thus we focus on aqueous and organic solutions.

4.1. Water-soluble dispersions of carbon nanotubes

Carbon nanotubes can be dispersed in water when coated by adsorbed surfactants, preferentially with those that have

relatively high HLB (Hydrophile-Liphophile Balance). This non-covalent method is straightforward and classically employed to disperse both organic and inorganic particles in aqueous solutions. The nature of surfactant, its concentration, and type of interaction are known to play a crucial role in the phase behavior of classical colloids [94] as well as carbon nanotubes [51,89,93,95].

Knowing the surface charge of carbon nanotubes in different media is absolutely essential for understanding the interaction (adsorption) mechanism with ionic surfactants, and to predict colloidal stability of CNT solutions. While zeta-potential analysis of MWNT showed that the tubes are negatively charged in water [92], some groups demonstrated insufficient debundling power of the anionic surfactant SDS due to charge-repulsions [52], while others reported on uniform colloidal dispersion of SDS-coated CNT [92].

The effect of head-group charge was investigated for various CNT-based systems [52,96], revealing no clear conclusion on the superiority of either cationic or anionic surfactants in dispersing the tubes. It seems that the adsorption mechanism of ionic surfactants, which is promoted by electrostatic interactions with CNT surface, is heavily controlled by the purification process and wall-functionalization of the tube, which in turn determine its surface charge.

Self-assembly structures (hemicylinders) of adsorbed non-ionic surfactants on graphite surfaces were shown to form strong alignment with the graphite symmetry axis [97]. In analogy to the model of epitaxial adsorption on graphite, the adsorption mechanism on nanotube walls (graphene) was suggested to produce specific self-organization of surfactant molecules (Fig. 9). While previous works suggested the formation of SDS cylindrical micelles around SWNT [85] (Fig. 9a), helices or double helices [98], as well as hemimicellar adsorption of a surfactant [85] (Fig. 9b), a recent article [89] suggests that structureless random adsorption with no preferential arrangement of the head and tail groups is responsible for the stabilization of the dispersions (Fig. 9c).

Among the ionic surfactants, SDS [85,89,92,95,99–103] and dodecyl-benzene sodium sulfonate (NaDBBS) [79,104–106] were commonly used to decrease CNT aggregative tendency in water. The benzene ring along the surfactant was proposed to be one of the main reasons for high dispersive efficiency of

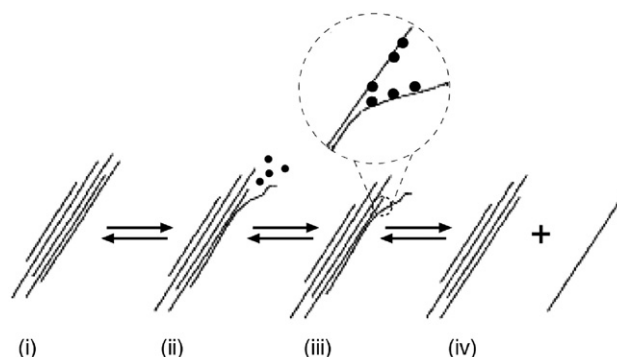


Fig. 8. Mechanism of nanotube isolation from bundle obtained by ultrasonication and surfactant stabilization [86].

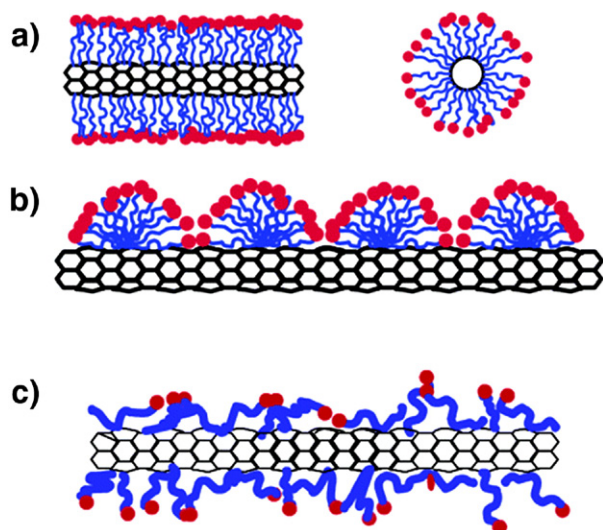


Fig. 9. Schematic representations of the mechanism by which surfactants help to disperse SWNT. (a) SWNT encapsulated in a cylindrical surfactant micelle (both cross section and side-view); (b) hemimicellar adsorption of surfactant molecules on a SWNT; (c) random adsorption of surfactant molecules on a SWNT [89].

NaDDBS [79] and even better efficiency of Dowfax surfactant (anionic alkyldiphenyl-oxide disulfonate), the latter having twice the charge of NaDDBS and a di-benzene group [105]. π -stacking interactions of the benzene rings onto the CNT surface are believed to increase the adsorption ratio of surfactants [79] as well as of other highly aromatic molecules [107] and rigid conjugated polymers [108]. Moreover, it was shown that not only aromatic groups but also naphthenic (saturated rings) groups provide good surfactant-tube affinity. Thus, Aerosol OS surfactant (sodium diisopropylnaphthalene sulfonate) showed higher fractions of individual tubes compared to the results obtained with NaDDBS and Dowfax surfactants, as was confirmed by UV–vis spectroscopy analysis [105].

The advantage of a dispersant containing a carbon double bond, and with similar head group and tail length, was confirmed by particle size analysis of Tween-60 and Tween-80 (polyethylene oxide (20) sorbitan monostearate and monooleate, respectively) nonionic surfactants [52]. The higher surface activity was attributed to the Tween-80 tail group having a carbon unsaturated bond, this being the only difference in the chemical structure of Tween-60 and Tween-80 surfactants. Fig. 10 demonstrates SEM image of highly dispersed MWNT in polyethylene glycol (PEG) matrix, which were obtained with the assistance of Tween-80.

The utilization of surfactant-coated CNT has become almost a standard procedure for various applications. Thus, chemical functionalization of SDS-coated nanotubes by aryldiazonium salts was reported [87,103]. Surfactants, such as cetyltrimethylammonium bromide (CTAB) [109] and O π -10 (polyethylene oxide (10) nonylphenyl ether) [110], were successfully used during in-situ polymerization of CNT-polymer composites. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) microspheres were dropped into aqueous solution of MWNT and CTAB (or NaDDBS) to produce carbon nanotube-adsorbed

polymeric microspheres [111]. Recondensation of SDS-dispersed SWNT in polymer solution stream enabled the creation of rigid fibers and ribbons of preferentially oriented nanotubes [99,101]. Motivated by biological application prospects of carbon nanotubes, Triton X-100 wetted SWNT were further treated with PEG to prevent adsorption of streptavidin proteins on the side walls of the tubes [112]. The addition of a weakly bound semiflexible polymer to the NaDDBS/SWNT system helped to increase the dispersion and generated highly oriented nanotubes in the polymer solution when sufficient shear stresses were provided [104].

According to the so-called “unzipping” mechanism [86], a surfactant has to get into the small spaces between the bundle and the isolated tube, and to prevent them from re-aggregating. Then, surfactants with too bulky hydrophobic groups will be hindered to penetrate into the inter-tube region, and show reduced debundling efficiency. However, bulky hydrophilic groups were reported to have an advantage in the case of nanotubes suspended with nonionic surfactants probably due to the enhanced steric stabilization provided by longer polymeric groups [80].

4.2. Dispersions of carbon nanotubes in organic solvents

Compared to water-soluble systems, thus far only limited research work has been carried out with surfactant-assisted dispersions in organic solvents. As opposed to aqueous solutions, hydrophobic carbon nanotubes are expected to be wetted by organic solvents, and therefore, to less self-assemble in bundles and ropes. However, carbon nanotubes were shown to exhibit a sufficient solubility only in a limited number of solvents, namely, DMF, dimethyl acetamide (DMAc) and dimethyl pyrrolidone (NMP) [113]. Unfortunately, immersion of SWNT in DMF was found to damage the CNT structure [114].

To produce MWNT-epoxy composites, the dispersion of the filler in acetone was increased by adding a nonionic surfactant, polyoxyethylene 8 lauryl [115]. This procedure generated a nanocomposite with improved thermo-mechanical properties. In contrast, the addition of carbon nanotubes without the surfactant only had moderate effects on the polymer glass transition temperature and its elastic modulus. The influence of

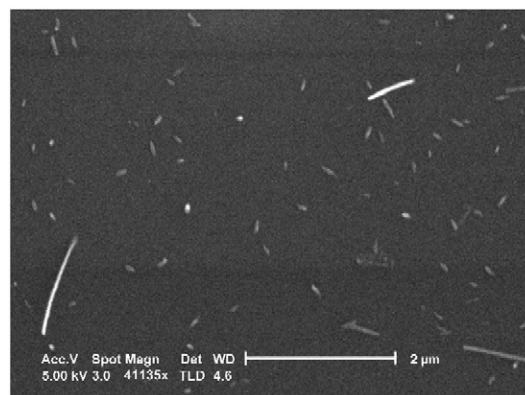


Fig. 10. SEM image of 1 wt.% MWNT-PEG composite with Tween-80.

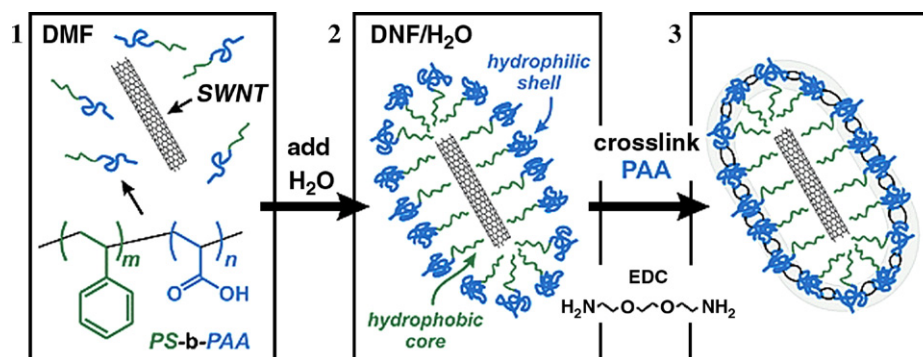


Fig. 11. The general strategy for encapsulating SWNT within shells of amphiphilic block copolymer PS-*b*-PAA [118].

another nonionic surfactant, Tergitol NP-7 (polyethylene oxide (7) nonyl phenyl ether) in the processing of CNT-epoxy composite was also investigated [51]. The thermo-mechanical response of PMEMA was reported to be significantly improved by only 1 wt.% of MWNT dispersed in tetrahydrofuran (THF) with the aid of Triton X-100 surfactant [50].

Pristine MWNT were shown to form large agglomerates in polypropylene-Decalin solution [52]. Although surface functionalization of carbon nanotubes somewhat improved their dispersion, additional surfactant assistance was required to obtain individual nanotubes. Within the Span (sorbitan) group of surfactants the state of dispersion was enhanced as the degree of tail unsaturation increased, reaching a maximum of three C=C bonds per tail in the case of Span-85 (sorbitan trioleate). This finding supports the assumption that attractive interactions are formed between CNT graphene sheets and unsaturated bonds of surfactant molecules.

4.3. Stabilization of carbon nanotube dispersions by polymers

Physical association of polymers with carbon nanotube surfaces was shown to enhance the dispersion of CNT in both water [116,117] and organic solvents [118], as well as to enable separation of nanotubes from carbonaceous and metal impurities [57,119]. Two mechanisms were suggested: “wrapping” [117] which is believed to rely on specific interactions between a given polymer and the tubes. For example, the reversible association of SWNT with linear polymers, polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS), in water was identified as being thermodynamically driven by the elimination of a hydrophobic interface between the tubes and the aqueous medium [117]. A very different, kinetic mechanism suggests that long-ranged entropic repulsion among polymer-decorated tubes acts as a barrier that prevents the tubes from approaching [57,93]. Recent small angle neutron scattering studies demonstrated a non-wrapping conformation of polymers in CNT dispersions [120].

Non-covalent modification of SWNT by encasing the tubes within micelles of cross-linked copolymer polystyrene-*block*-polyacrylic acid (PS-*b*-PAA) was demonstrated (Fig. 11) [118]. CNT were first ultrasonicated in DMF solution of the copolymer (Fig. 11, step 1) and micellization of the amphiphile was induced by adding water to the nanotube suspension (step 2).

Finally, the PAA blocks of the micellar shells were permanently cross-linked by adding a diamine linker (step 3). This encapsulation was shown to enhance the dispersion of SWNT in a variety of polar and nonpolar solvents.

The Pluronic surfactants are triblock copolymers based on ethylene oxide and propylene oxide. They are commonly used in biomedical applications due to their low toxicity and non-irritating behavior. Aiming to investigate CNT interactions with human epidermal tissues, dispersions of MWNT with the Pluronic surfactant F-127 were obtained [121]. The surfactant added at low percents had a positive effect on the tube debundling; however, with the addition of 5% (w/v) F-127 larger agglomerates were present that often resembled the non-surfactant control samples. A similar result was reported for MWNT-PEG composites [52]. The motive behind using Pluronic block copolymers was to create high steric stabilization, by attaching the central polyoxypropylene block, which is insoluble in water, to the surface of the tubes, while the water-soluble polyoxyethylene chains extend into the PEG aqueous solution. In practice, the incorporation of Pluronic surfactants showed no improvement in CNT dispersion. This was attributed to a bridging mechanism — long polymeric molecules of the surfactant adsorbed onto the surfaces of adjacent nanotubes, bridging them together and creating a loose network. However, dispersions of individual CNT stabilized by Pluronics were also reported [80,122].

A study of the stabilization effect produced by different diblock and triblock copolymers led to the conclusion that selective interaction of the different blocks with solvent is essential in order to obtain stable colloidal dispersions of SWNT [93].

5. Conclusions

The potential of carbon nanotube integration in a wide scope of applications was realized long ago. For successful utilization of their properties disaggregation and uniform dispersion of CNT in various media are essential. Different approaches were suggested to decrease the nanotube agglomeration, namely ultrasonication, high shear mixing, and methods, which are aimed to alter the surface chemistry of the tubes either covalently (functionalization) or non-covalently (adsorption). This review focuses on non-covalent surface modification via

adsorption of surfactants and polymers. A key conclusion is that the behavior of surfactants in dispersing the carbon nanotubes is similar to that of dispersing solid particles, i.e. classical colloidal chemistry.

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References

- [1] Lee BI, Rives JP. *Colloids Surf* 1991;56:25.
- [2] Seelenmeyer S, Ballauff B. *Langmuir* 2000;16:4094.
- [3] Clarke JG, Wicks SR, Farr SJ. *Int J Pharm* 1993;93:221.
- [4] Green JH, Parfitt GD. *Colloids Surf* 1988;29:391.
- [5] Singh BP, Menchavez R, Takai C, Fuji M, Takahashi M. *J Colloid Interface Sci* 2005;291:181.
- [6] Assouline E, Lustiger A, Barber AH, Cooper CA, Klein E, Wachtel E, et al. *J Polym Sci B Polym Phys* 2003;41:520.
- [7] Pötschke P, Fomes TD, Paul DR. *Polymer* 2002;43:3247.
- [8] Haggemueller R, Gommans HH, Rinzler AG, Fischer JE, Winey KI. *Chem Phys Lett* 2000;330:219.
- [9] Wang H, Hobbie EK. *Langmuir* 2003;19:3091.
- [10] Thostenson ET, Li C, Chou T-W. *Compos Sci Technol* 2005;65:491.
- [11] Tai NH, Yeh MK, Liu JH. *Carbon* 2004;42:2774.
- [12] Ogasawara T, Ishida Y, Ishikawa T, Yokota R. *Compos A Appl Sci Manuf* 2004;35:67.
- [13] Gojny FH, Wichmann MHG, Köpke U, Fiedler B, Schulte K. *Compos Sci Technol* 2004;64:2363.
- [14] Liu C, Fan YY, Liu M, Cong HT, Cheng HM, Dresselhaus MS. *Science* 1999;286:1127.
- [15] Sugie H, Tanemura M, Filip V, Iwata K, Takahashi K, Okuyama F. *Appl Phys Lett* 2001;78:2578.
- [16] Frackowiak E, Beguin F. *Carbon* 2002;40:1775.
- [17] Kong J, Franklin NR, Zhou C, Chapline MG, Peng S, Cho K, et al. *Science* 2000;287:622.
- [18] Dai HJ, Hafner JH, Rinzler AG, Colbert DT, Smalley RE. *Nature* 1996;384:147.
- [19] Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. *Nature* 1985;318:162.
- [20] Iijima S. *Nature* 1991;354:56.
- [21] Dresselhaus MS, Dresselhaus G, Saito R. *Carbon* 1995;33:883.
- [22] Iijima S. *Physica B* 2002;323:1.
- [23] Odom TW, Huang J-L, Kim P, Lieber CM. *J Phys Chem B* 2000;104:2794.
- [24] Terrones M. *Annu Rev Mater Res* 2003;33:419.
- [25] Knupher M. *Surf Sci Rep* 2001;42:1.
- [26] Iijima S, Ichikashi T. *Nature* 1993;363:603.
- [27] Baughman RH, Zakhidov AA, De Heer WA. *Science* 2002;297:787.
- [28] Ge M, Sattler K. *Appl Phys Lett* 1994;67:710.
- [29] Li WZ, Xie SS, Qian LX, Chang BH, Zou BS, Zhou WY, et al. *Science* 1996;274:1701.
- [30] Che G, Lakshmi BB, Martin CR, Fisher ER, Ruoff RS. *Chem Mater* 1998;10:260.
- [31] Roche S. *Ann Chim Sci Mater* 2000;25:529.
- [32] Che J, Cagin T, Goddard WA. *Nanotechnology* 2000;11:65.
- [33] Berber S, Kwon Y-K, Tomanek D. *Phys Rev Lett* 2000;84:4613.
- [34] Ounaies Z, Park C, Wise KE, Siochi EJ, Harrison JS. *Comput Sci Tech* 2003;63:1637.
- [35] Biercuk MJ, Llaguno MC, Radosavljevic M, Hyun JK, Johnson AT, Fisher JE. *Appl Phys Lett* 2002;80:2767.
- [36] Andrews R, Jacques D, Rao AM, Rantell T, Derbyshire F, Chen Y, et al. *Appl Phys Lett* 1999;75:1329.
- [37] Grunlan JC, Mehrabi AR, Bannon MV, Bahr JL. *Adv Mater* 2004;16:150.
- [38] Kim B, Lee J, Yu I. *J Appl Phys* 2003;94:6724.
- [39] Zhang Q, Rastogi S, Chen D, Lippits D, Lemstra PJ. *Carbon* 2006;44:778.
- [40] Safadi B, Andrews R, Grulke EA. *J Appl Polym Sci* 2002;84:2660.
- [41] Sandler J, Shaffer MSP, Prasse T, Bauhofer W, Schulte K, Windle AH. *Polymer* 1999;40:5967.
- [42] Krishnan A, Dujardin E, Ebbesen TW, Yianilos PN, Treacy MMJ. *Phys Rev B* 1998;58:14013.
- [43] Popov VN, van Doren VE, Balkanski M. *Phys Rev B* 2000;61:3078.
- [44] Yu M-F, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS. *Science* 2000;287:637.
- [45] Xie S, Li W, Pan Z, Chang B, Sun L. *J Phys Chem Solids* 2000;61:1153.
- [46] Belin T, Epron F. *Mater Sci Eng B* 2005;119:105.
- [47] Thostenson ET, Ren Z, Chou T-W. *Comput Sci Tech* 2001;61:1899.
- [48] Schadler LS, Giannaris SC, Ajayan PM. *Appl Phys Lett* 2001;89:8141.
- [49] Qian D, Dickey EC, Andrews R, Rantell T. *Appl Phys Lett* 2000;76:2868.
- [50] Velasco-Santos C, Martinez-Hernandez AL, Fisher F, Ruoff R, Castano VM. *J Phys D Appl Phys* 2003;36:1423.
- [51] Cui S, Canet R, Derre A, Couzi M, Delhaes P. *Carbon* 2003;41:797.
- [52] Vaisman L, Marom G, Wagner HD. *Adv Funct Mater* 2006;16:357.
- [53] Eitan A, Fisher FT, Andrews R, Brinson LC, Schadler LS. *Comput Sci Tech* 2006;66:1159.
- [54] Lourie O, Cox DE, Wagner HD. *Phys Rev Lett* 1998;81:1638.
- [55] Thess A, Lee R, Nikolaev P, Dai H, Petit P, Robert J, et al. *Science* 1996;273:483.
- [56] Girifalco LA, Hodak M, Lee RS. *Phys Rev B* 2000;62:13104.
- [57] Shvartzman-Cohen R, Nativ-Roth E, Baskaran E, Levi-Kalishman Y, Szeifer I, Yerushalmi-Rozen R. *J Am Chem Soc* 2004;126:14850.
- [58] Xie XL, Aloys K, Zhou XP, Zeng FD. *J Therm Anal Calorim* 2003;74:317.
- [59] Ajayan PM, Schadler LS, Giannaris C, Rubio A. *Adv Mater* 2000;12:750.
- [60] Haggemueller R, Gommans HH, Rinzler AG, Fischer JE, Winey KI. *Chem Phys Lett* 2000;330:219.
- [61] Coleman JN, Curran S, Dalton AB, Davey AP, Mc Carthy B, Blau W, et al. *Synth Met* 1999;102:1174.
- [62] Ko F, Gogotsi Y, Ali A, Naguib N, Ye H, Yang G, et al. *Adv Mater* 2003;15:1161.
- [63] Wu T-M, Lin Y-W. *Polymer* 2006;47:3576.
- [64] Pötschke P, Brünig H, Janke A, Fischer D, Jehnichen D. *Polymer* 2005;46:10355.
- [65] Xie X-L, Mai Y-W, Zhou X-P. *Mater Sci Eng R-Rep* 2005;49:89.
- [66] Ham HT, Choi YS, Chung JJ. *J Colloid Interface Sci* 2005;286:216.
- [67] Ausman K, Piner L, Lourie O, Ruoff RS, Korobov M. *J Phys Chem B* 2000;104:8911.
- [68] Barber AH, Cohen SR, Wagner HD. *Phys Rev Lett* 2004;92:186103.
- [69] Barber AH, Cohen SR, Wagner HD. *Phys Rev B* 2005;71:115443.
- [70] Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, et al. *Science* 1998;280:1253.
- [71] Sun Y-P, Huang W, Lin Y, Fu K, Kitaygorodskiy A, Riddle LA, et al. *Chem Mater* 2001;13:2864.
- [72] Qin Y, Liu L, Shi J, Wu W, Zhang J, Guo Z-X, et al. *Chem Mater* 2003;15:3256.
- [73] Chen J, Hamon MA, Hu H, Chen Y, Rao AM, Eklund PC, et al. *Science* 1998;282:95.
- [74] Tasis D, Tagmatarchis N, Georgakilas V, Prato M. *Chem Eur J* 2003;9:4001.
- [75] Liu L, Barber AH, Nuriel S, Wagner HD. *Adv Funct Mater* 2005;15:975.
- [76] Lu KL, Lago RM, Chen YK, Green MLH, Harris PJF, Tsang SC. *Carbon* 1996;34:814.
- [77] Hilding J, Grulke EA, Zhang ZG, Lockwood F. *J Dispers Sci Technol* 2003;24:1.
- [78] Blake R, Gun'ko YK, Coleman J, Cadek M, Fonseca A, Nagy JB, et al. *J Am Chem Soc* 2004;126:10226.
- [79] Islam MF, Rojas E, Bergey DM, Johnson AT, Yodh AG. *Nano Lett* 2003;3:269.

- [80] Moore VC, Strano MS, Haroz EH, Hauge RH, Smalley RE. *Nano Lett* 2003;3:1379.
- [81] Kedem S, Schmidt J, Paz Y, Cohen Y. *Langmuir* 2005;21:5600.
- [82] Dror Y, Pyckhout-Hintzen W, Cohen Y. *Macromolecules* 2005;38:7828.
- [83] Ivakhnenko V, Eremin Y. *J Quant Spectrosc Radiat Transfer* 2006;100:165.
- [84] Pecora R. *Pure Appl Chem* 1984;56:1391.
- [85] O'Connell MJ, Bachilo SM, Huffman CB, Moore VC, Strano MS, Haroz EH, et al. *Science* 2002;297:593.
- [86] Strano MS, Moore VC, Miller MK, Allen MJ, Haroz EH, Kittrell C, et al. *J Nanosci Nanotech* 2003;3:81.
- [87] Dyke CA, Tour JM. *Nano Lett* 2003;9:1215.
- [88] Wang H, Zhou W, Ho DL, Winey KI, Fisher JE, Glinka CJ, et al. *Nano Lett* 2004;9:1789.
- [89] Yurekli K, Mitchell CA, Krishnamootri R. *J Am Chem Soc* 2004;126:9902.
- [90] Shen K, Curran S, Xu H, Rogelj S, Jiang Y, Dewald J, et al. *J Phys Chem B* 2005;109:4455.
- [91] Duesberg GS, Burghard M, Muster J, Philipp G, Roth S. *Chem Commun* 1998;3:435.
- [92] Jiang L, Gao L, Sun J. *J Colloid Interface Sci* 2003;260:89.
- [93] Shvartzman-Cohen R, Levi-Kalisman Y, Nativ-Roth E, Yerushalmi-Rozen R. *Langmuir* 2004;20:6085.
- [94] Rosen MJ. *Surfactants and interfacial phenomena*. Hoboken, NJ: John Wiley and Sons; 2004.
- [95] Hertel T, Hagen A, Talalaev V, Arnold K, Hennrich F, Kappes M, et al. *Nano Lett* 2005;5:511.
- [96] Chatterjee T, Yurekli K, Hadjiev VG, Krishnamootri R. *Adv Funct Mater* 2005;15:1832.
- [97] Patrick HN, Warr GG. *Colloid Surf A Physicochem Eng Asp* 2000;162:149.
- [98] Richard C, Balavoine F, Schultz P, Ebbesen TW, Mioslowski C. *Science* 2003;300:775.
- [99] Poulin P, Vigolo B, Launois P. *Carbon* 2002;40:1741.
- [100] Steimetz J, Glerup M, Paillet M, Bernier P, Holzinger M. *Carbon* 2005;43:2397.
- [101] Fugami K, Sano M. *New Diam Front Carbon Technol* 2005;15:53.
- [102] Vigolo B, Penicaud A, Coulon C, Sauder C, Pailler R, Journet C, et al. *Science* 2000;290:1331.
- [103] Dyke CA, Tour JM. *Chem Eur J* 2004;10:812.
- [104] Camponeschi E, Florkowski B, Vance R, Garrett G, Garmestani H, Tannenbaum R. *Langmuir* 2006;22:1858.
- [105] Tan Y, Resasco DE. *J Phys Chem B* 2005;109:14454.
- [106] Matarredona O, Rhoads H, Li Z, Harwell JH, Balzano L, Resasco D. *J Phys Chem B* 2003;107:133357.
- [107] Chen RJ, Zhang Y, Wang D, Dai H. *J Am Chem Soc* 2001;123:3838.
- [108] Chen J, Liu H, Weimer WA, Halls MD, Waldeck DH, Walker GC. *J Am Chem Soc* 2002;124:9034.
- [109] Barraza HJ, Pompeo F, O'Rear EA, Resasco DE. *Nano Lett* 2002;2:797.
- [110] Zhang X, Zhang J, Wang R, Zhu T, Liu Z. *Chem Phys Chem* 2004;5:998.
- [111] Jin H-J, Choi HJ, Yoon SH, Myung SJ, Shim SE. *Chem Mater* 2005;17:4034.
- [112] Shim M, Wong Shi Kam N, Chen RJ, Li Y, Dai H. *Nano Lett* 2002;2:285.
- [113] Kim B, Lee Y-H, Ryu J-H, Suh K-D. *Colloid Surf A Physicochem Eng Asp* 2006;273:161.
- [114] Monthieux M, Smith BW, Burtiaux B, Claye A, Fisher JE, Luzzi DE. *Carbon* 2001;39:1251.
- [115] Gong X, Liu J, Baskaran S, Voise RD, Young JS. *Chem Mater* 2000;12:1049.
- [116] Bandyopadhyaya R, Nativ-Roth E, Reggev O, Yerushalmi-Rozen R. *Nano Lett* 2002;2:25.
- [117] O'Connell MJ, Boul P, Ericson LM, Huffman C, Wang Y, Haroz E, et al. *Chem Phys Lett* 2001;342:265.
- [118] Kang Y, Taton TA. *J Am Chem Soc* 2003;125:5650.
- [119] Yudasaka M, Zhang M, Jabs C, Iijima S. *Appl Phys A* 2000;71:449.
- [120] Dror Y, Pyckhout-Hintzen W, Cohen Y. *Macromolecules* 2005;38:7828.
- [121] Monteiro-Riviere NA, Inman AO, Wang YY, Nemanich RJ. *Nanomedicine* 2005;1:293.
- [122] Szleifer I, Yerushalmi-Rozen R. *Polymer* 2005;46:7803.