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Double-walled carbon nanotube dispersion *via* surfactant substitution

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A new approach for the stabilisation of double-walled carbon nanotubes in aqueous media was developed. A low molecular weight surfactant was used in the first stage for the debundling of the nanotubes followed by substitution with a higher molecular weight surfactant or non-ionic surfactants. Dispersions were characterized by optical density measurements, SEM and DLS. The presence of remaining low molecular weight surfactant was investigated by FT-IR. Double walled carbon nanotube dispersions showed good dispersion stability and non-detectable amounts of the initial surfactant, which was completely removed. Such a method could be useful for preparation of stable aqueous dispersions of carbon nanotubes with low concentration of surfactants, which is especially important for toxicity studies.

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, because the surface chemistry controls the dispersion state of such 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.

The ability of surfactants to accumulate on surfaces or interfaces has been widely used to promote stable dispersions of solids in different media.[1,2] Those amphiphilic molecules, *i.e.*, compounds having both polar and non-polar groups, adsorb at the interface between immiscible bulk phases, such as oil and water, air and water or particles and solution, and act to reduce the surface tension.

Carbon nanotubes (CNT) have a unique set of properties making them good candidates for a wide range of possible applications in suspensions and polymer-based solutions, melts and composites.[3] Their outstanding characteristics include attractive mechanical properties, namely tensile strength and elastic modulus, and still remarkable flexibility, excellent thermal and electrical conductivities, low percolation thresholds (loading weight at which a sharp drop in resistivity occurs) and high aspect ratios (length to diameter ratio). Thus, they allow the preparation of composites with new or improved properties.[4]

The main challenge for integration of this unique nanomaterial is the preparation of uniform dispersions of CNT in the continuous phase. A major obstacle to this separation effort is the aggregation of nanotubes. The highly polarizable nanotubes readily form bundles (or ropes) with a van der Waals binding energy of *ca.* 500eV per micrometer of tube-tube contact.[5] This makes all attempts to separate them by size or type or to use them as individual macromolecular species difficult. Moreover, the electronic structure of an individual single-walled CNT (SWNT) can be disturbed because of bundling. Debundling these ropes to yield individual nanotubes is consequently non-trivial.

CNT can be dispersed in water when coated with adsorbed surfactants, preferentially with those having relatively high HLB (hydrophilic-lipophilic balance). This non-covalent method is straightforward and classically employed to disperse both organic and inorganic particles in aqueous solutions. The nature of the surfactant, its concentration, and type of interaction are known to play crucial roles in the phase behavior of classical colloids[6] as well as CNT.[7]

Knowledge of 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 suspensions. While zeta-potential analysis of multi-walled CNT (MWNT) has shown that the tubes are negatively charged in water,[8] some groups demonstrated insufficient debundling power of the anionic surfactant sodium dodecyl sulfate (SDS) due to charge repulsion.[9] Among the ionic surfactants, SDS[10] and dodecyl-benzene sodium sulfonate (NaDDBS)[11] were commonly used to decrease the CNT aggregative tendency in water. The benzene ring of the latter (π-stacking) was suggested to be one of the main reasons for the high dispersive efficiency of NaDDBS.[12]

Physical association of polymers with the surface of CNT was shown to enhance their dispersion in both water and organic solvents, and is another way for non-covalent CNT stabilization.[13] Two mechanisms were suggested: "wrapping",[14] which is believed to rely on specific interactions between a given polymer and the tubes; however, recent small-angle neutron scattering studies evidenced a non-wrapping conformation of polymers in CNT dispersions.[15]

Another kind of compounds which can be used for dispersion of CNT in water for specific biomedical application are carbohydrate derivatives, such as natural polysaccharides (gum arabic)

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or synthetic sugar surfactants (*e.g.* sucrose fatty acid esters or alkylpolyglucosides, APG). Gum arabic (GA), a natural gum, is a substance extracted from two sub-Saharan species of the acacia tree. It is used primarily as a thickener and texture modifier, especially in the food industry. Gum arabic consists of a mixture of a polysaccharide (M.Wt. $\sim 0.25 \times 10^6$; major component) and a hydroxyproline-rich glycoprotein (M.Wt. $\sim 2.5 \times 10^6$; minor component).[16] Sucrose fatty acid esters are synthetic surfactants made from sucrose and various fatty acid esters. They are used as food additives and in various pharmaceutical formulations. As an example, Surfhope 1216 is a sucrose ester of lauric acid (C12 fatty chain).[17] Application of such carbohydrate macromolecules or surfactants, with a good toxicological profile, for carbon nanotube stabilization should bring both steric repulsion and better stabilisation of the dispersion in water. In the case of a diblock polymer surfactant, simple mixing of the polymer and CNT does not lead to similar interactions as with low molecular weight (LMW) surfactants.[18] This can be attributed to the fact that polymer chains are not able to penetrate within the aggregates of CNT. Steric hindrance prevents any reaction between the polymer chains and chemical functionalities at the surface of the nanotubes, or creates an insufficient amount of interactions between macromolecular chains and the outer wall.[19]

Our purpose here was to assess the effects of combination of different types of surfactants (SDS, Tween 20, Surfhope 1216, Montanov 82, cholates) and a polymer surfactant (gum arabic, high molecular weight (HMW) surfactant) for the aqueous dispersion of double-walled CNT (DWNT).

In this work, the surfactant SDS is first used for exfoliation and surface coating of the carbon nanotubes. It can penetrate easily inside the aggregates of carbon nanotubes and is useful for improving the dispersibility. It is widely used for the preparation of stable aqueous CNT dispersions.[20] However, this surfactant does not protect individual nanotubes from agglomeration during film drying.[21] In order to achieve better stabilization, wrapping of CNT with more or less amphiphilic polymers chains has been used. The hydrophobic part of the polymer is strongly anchored to the hydrophobic nanotube surface with a polymer layer of sufficient thickness, while the hydrophilic parts, when fully ionized, impart sufficient ionic charge to the CNT surfaces. For this reason, various polymeric dispersants such as PmPV,[22] starch,[23] and peptides[24] have been used to improve the dispersion stability of CNT by surface wrapping. Moreover, the direct application of polymers does not lead to exfoliation of nanotube bundles due to their hydrodynamic diameters which are of the same order as CNT ones.

In our strategy, different kinds of surfactants and one polymer surfactant have been tested for the dispersion of CNT. CNT bundles were first homogeneously exfoliated and dispersed in water with SDS. Then, this surfactant was replaced at the CNT surface by different saccharidic compounds, either a polymer (gum arabic) or a mixture of non-ionic sugar surfactants (Surfhope 1216, Montanov 82). This enables us to assess the efficiency of both classes of compounds in the substitution method. A comparison of the dispersion and stabilisation efficiency of CNT by different surfactants alone (SDS, Tween20, sodium cholate, sodium deoxycholate, Surfhope 1216, Montanov 82, gum arabic), before testing the substitution method, has also been performed. Pioneering work[25] in this field was the use of SDS for dispersion of SWNT followed by polymer wrapping with polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS) in order to obtain reversibly solubilized SWNT in water. Similar technology was applied by Didenko *et al.*[26] for the preparation of nanotube suspensions with specific, fluorescent properties. The authors dispersed the SWNT in SDS aqueous solution and obtained the fluorescent labelled polyvinyl pyrrolidone (f-PVP) polymer wrapping the SWNT surface. Also, such a route was used for preparation of carbon nanotube-based thermal pastes for improving the thermal conductivity, where the authors firstly prepared SWNT dispersion in acetone using polyoxyethylene lauryl ether, $C_{12}H_{25}(OCH_2CH_2)_nOH$, n = 4 (Brij 30), followed by transfer of the SWNT into ethyl cellulose and polyethylene glycol (PEG) methyl ester solution in PEG.[27]

In our study we used optical density measurements of the supernatant of centrifuged CNT dispersions for an estimation of the CNT concentration in the supernatant (with calibration curve obtained with CNT dispersions of known CNT amount, stabilised with various surfactants[28]). Optical density measurements have been widely used to quantify the amount of CNT present in a suspension.[29,30]

The presence of the SDS in the dispersion or on the CNT surface after substitution was evaluated by *in situ* IR monitoring[31] of both the carbon nanotubes and the surfactants remaining in supernatant after centrifugation (and drying).[32] The use of a non-toxic surfactant may be very important in the field of the medical applications of CNT, as well as for the investigation of their toxicity.

2. Experimental

2.1. Carbon nanotubes

Double-walled carbon nanotubes (DWNT) were synthesized by a catalytic chemical vapour deposition (CCVD) method[33] under hydrogen atmosphere with 18 mol.% of CH_4 at 1000 °C, using Mo in addition to Co in a MgO-based catalyst. The catalyst was then easily removed by a mild acidic treatment (HCl). The DWNT were washed with deionised water until neutrality, filtered and dried overnight at 80 °C in air. Analyses of TEM images of individual CNT have shown that most of them (*ca.* 80%) were DWNT with an outer diameter ranging between 1 and 3 nm. They are individual or gathered in small diameter bundles (10–30 nm) which can be up to *ca.* 100 μm in length.[33]

2.2. Surfactants

Sodium dodecyl sulfate, Tween 20, sodium cholate hydrate, sodium deoxycholate and gum arabic (GA) were purchased from Aldrich and were used as received. Specific surfactants used in the food and pharmaceutical industry, Surfhope 1216 and Montanov 82, were kindly provided by Mitsubishi Kagaku Foods Corp. and Seppic, respectively.

2.3. Calibration curve preparation

For preparation of the calibration curves for measurement of the CNT concentration in dispersions, respective surfactant solutions of 25 mg in 500 ml were prepared. Required amounts of DWNT for each concentration of 100 mg/L, 50 mg/L, 25 mg/L,

12.5 mg/L, 6.2 mg/L, 3.6 mg/L and 1.8 mg/L were added to the surfactant solution and dispersed by a homogenizer (Yellow line DI 25 basic from IKA®-WERKE GMBH&Co.KG with dispersion tool S25N-18G) at 15000 rpm for 5 min followed by sonication in an ultrasonic bath (USC 600T, VWR International with effective power of 120 W) for 1 hour. CNT dispersions were immediately transferred into the measuring cell and the absorbance of the dispersion was measured at 850 nm. At this wavelength collected data displayed a linear dependence of absorbance [A] *vs.* DWNT concentration.

2.4. Sedimentation rate evaluation

Study of the sedimentation rate was based on the measurement of the optical density of the CNT dispersions *vs.* time. For such experiments 10 mg of CNT were dispersed in the surfactant solution (respective amount in order to evaluate the effect of the surfactant concentration) by a homogeniser at 15000 rpm for 2 minutes followed by sonication in an ultrasonic bath for 1 hour, and samples of dispersions were taken in order to measure their optical density. The concentration of CNT in dispersion was calculated according to the calibration curve.

2.5. Stability of the DWNT dispersions after centrifugation

For evaluation of the DWNT dispersions stability after centrifugation, dispersions were prepared by the same procedure as for the sedimentation rate study. Centrifugation was carried out at 3000 rpm for 30 min. After centrifugation, the optical density of the samples was measured.

2.6. Substitution of SDS by gum arabic or non-ionic surfactants

In our experiments the required amount of DWNT was dispersed in 25 ml of the SDS solution (2.5 mg of surfactant) by a homogenizer at 15000 rpm for 2 min followed by sonication in an ultrasonic bath for 1 hour. Then, the sample was filtered on a cellulose nitrate membrane (CNM) and redispersed in 25 ml of the second surfactant solution (1mg) using a sonication bath for 1 hour. In our opinion, this is enough time to activate the process of substitution of the first surfactant onto the CNT walls by the second one. The sample was kept under magnetic stirring overnight to reach the adsorption/desorption equilibrium and was repeatedly (3 times) filtered/washed on CNM for removal of the first surfactant from the dispersion. Then the sample was redispersed in 25 ml of the second surfactant solution (0.5 mg) to reach the concentration of surfactant above the critical micellar concentration (CMC) in solution and to avoid its desorption from the CNT surface. Gum arabic is a natural plant extract and it is a mixture of different macromolecules thus different data of CMC for such materials were published.[34,35] Moreover, Garti *et al.*[36] reported that no CMC was detected for such a kind of gum. The CMC of Surfhope 1216 is reported to be about 0.05%wt. in aqueous solution.[37] The substituted CNT dispersion was centrifuged at 3000 rpm for 30 min and the absorbance of the CNT dispersion was measured. In our work, the concentration of the initial surfactant was selected at 100 mg/L, as a minimum amount to obtain a stable suspension of DWNT at 100 mg/L in water, meanwhile the second surfactant concentration was limited to a maximal non-toxic concentration for cytotoxicity study (40 mg/L).[38]

2.7. Dispersion characterisation

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed on a JEM 1011 Microscope (JEOL Japan, operated at 100 kV) and a SEM-FEG JEOL JSM 6700F (operated at 1 kV) respectively. Samples were drop-deposited on Si/SiO_2 substrates and dried quickly with an IR lamp (drying in a few seconds).

In situ FT-IR spectroscopy study of the CNT dispersion was carried out on a Nicolet 510P FT-IR Spectrometer. Optical density study of the CNT dispersions was made on a Perkin Elmer Lambda2 UV-VIS spectrophotometer using quartz cells. Absorbance at 850 nm was selected because it does not usually have strong features associated with particular types of nanotubes, therefore results are not dependent on the presence of these nanotube types in a particular sample. Aggregates size measurement was performed using a Malvern Zetasizer 3000 equipped with a 633nm He–Ne laser. The Dynamic light scattering method was used to get the Brownian motion coefficient to calculate the particle size distribution.

3. Results and discussion

The carbon nanotube graphene-like structure (sp^2 hybridization) results in a material that possesses a unique combination of mechanical, electrical, thermal, and optical properties. Unfortunately, the limited number of side groups (Table 1), confirmed by X-ray photoelectron spectroscopy data[39] and Boehme titration,[40] that can interact with the surrounding solvent sufficiently

Table 1 Characterisation of the DWNT after extraction with HCl

Type of DWNT	Carbon content by elementary analysis (at.%)	Specific surface area (BET, m^2/g)	[COOH] (groups/nm^2)
Pristine DWNT	98	985	4.7

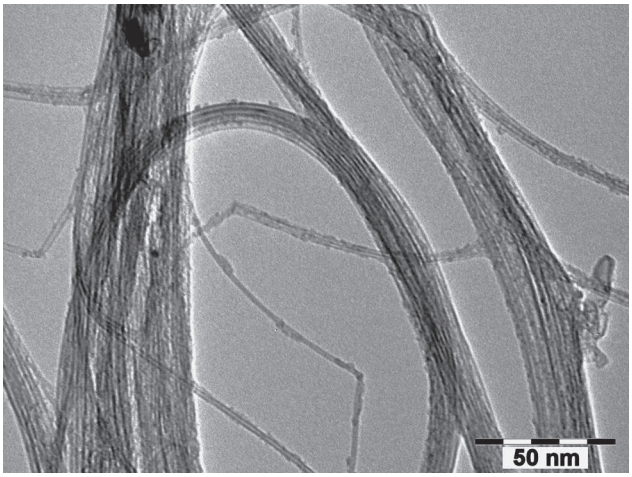

Fig. 1 Typical image of the DWNT bundles after catalyst dissolution.

to overcome the large intertube attraction energy responsible for their bundling results in a material with poor dispersibility. Fig. 1 shows a typical TEM image of the starting DWNT material used in this work. The DWNT are either individual or gathered into small-diameter bundles (usually 10–30 nm, less than 50 nm).

Fig. 2 shows the absorbance values of the DWNT dispersions of known concentration (after sonication in ultrasonic bath for 1 hour) which were used as calibration curves for CNT concentration determination. These results also show that a highest dispersibility is obtained for DWNT dispersed and stabilized with Surfhope 1216 and Montanov 82 surfactants which can penetrate inside the carbon nanotube ropes and exfoliate them, but at the same time build sufficient steric stabilization layers onto the nanotubes surface (although Montanov 82, which is a mixture of hexadecanol and an alkylpolyglucoside with a short (C10) fatty chain, is not supposed to be so efficient for stabilisation), leading to the higher absorbance value at the same concentration of DWNT. The lowest value in the studied range of surfactants was obtained with gum arabic (GA) and can be explained by the fact that significantly large molecules of GA (MW $\sim 2.5 \times 10^6$) having comparable hydrodynamic diameter with CNT cannot penetrate inside the ropes of nanotubes; even when we prepared stable dispersions of DWNT, GA did not stabilize individual DWNT, but rather ropes. Such a phenomenon leads to the lowest absorbance value due to the larger size of the stabilized particles. Average absorbance values obtained in the case of SDS or Tween 20 can be explained because they are the more hydrophilic, with the lowest fatty chain/polar head volume ratio of the series. Thus, probably they provide a too small contact area with nanotube walls and it is necessary to increase their concentration in the dispersion for the complete coating and hydrophilisation of the CNT walls in order to stabilize the dispersions.

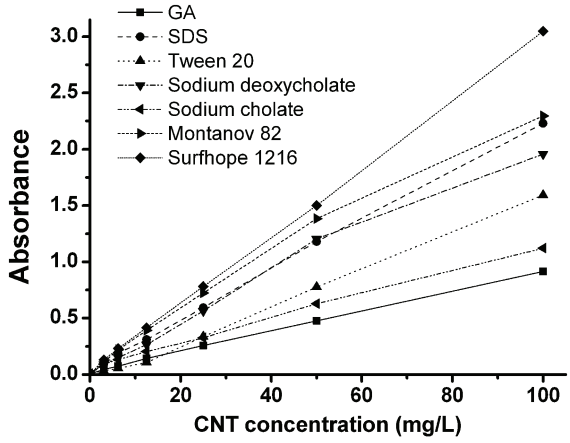

Fig. 2 Absorbance of the DWNT dispersions stabilized with different surfactants.

For the dynamic study of the DWNT dispersion stability, we studied the sedimentation rate of the DWNT from water dispersions stabilized with different surfactants (Fig. 3).

Study of the sedimentation rate of the CNT dispersions at the highest concentration (100 mg/L) has evidenced some differences (Fig. 3). The dispersion of DWNT stabilized with sodium cholate lost most of the DWNT within the first 20 h followed by slow sedimentation and, finally, reached the lowest concentration of DWNT in dispersion after 450 hours (22 mg/L). In contrast, sedimentation of the dispersion of DWNT stabilized with SDS was very slow at the beginning with a final concentration of nanotubes of *ca.* 39 mg/L. The same result was obtained for the suspension of nanotubes stabilized with Tween 20, but in the first hours the dispersion lost *ca.* 30% of the CNT, which were, probably, in the form of large aggregates. Dispersions stabilised with Surfhope also experienced a quite fast destabilisation as compared to the others. DWNT dispersions stabilized with GA have shown average behaviour that can be explained by the formation of well stabilized CNT, but present in the form of aggregates. Even if this rationalization cannot explain fully the order of the series observed, the differences in the sedimentation rates should depend on the charge of the surfactant (some are ionic—SDS, deoxycholate—while some others are non ionic—Tween, Montanov, Surhope), and should depend on the aggregated/single CNT ratio. At the end of the sedimentation experiments (450 h) we typically obtained stable suspensions in a range of concentrations between 20 and 35 mg/L.

Another kind of study of the sedimentation of the DWNT dispersions *vs.* time is the effect of surfactant concentration on

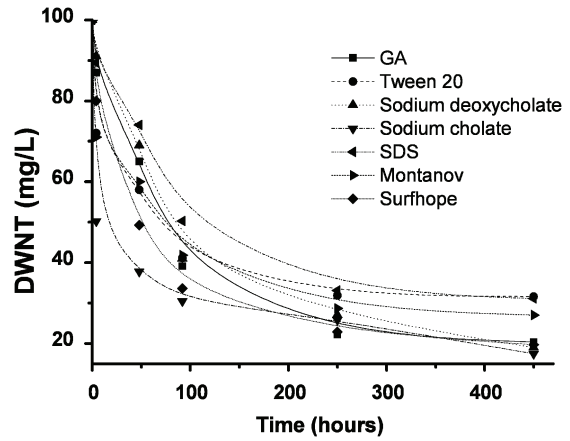

Fig. 3 Sedimentation rate of the DWNT dispersions stabilized with different surfactants. Initial concentration of the DWNT: 100 mg/L; concentration of the surfactants: 50 mg/L.

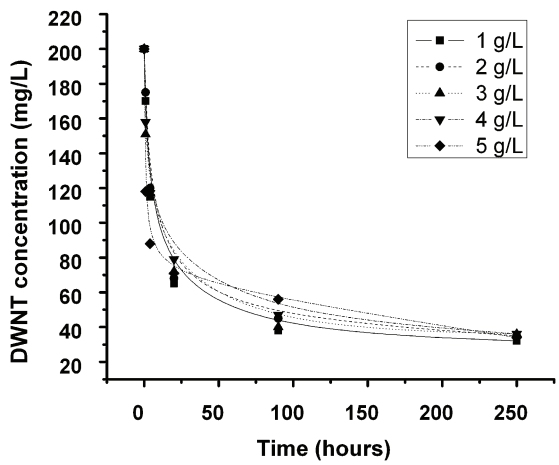

Fig. 4 DWNT sedimentation rate depending on gum arabic concentration (initial concentration of the DWNT in dispersion: 200 mg/L).

the stability of the suspensions in water (Fig. 4). For this study, DWNT at an initial concentration of 200 mg/L were stabilized with GA at different concentrations, from 0.1 to 0.5 g/L. The results revealed nearly insignificant effect of the surfactant concentration on the final amount of DWNT in dispersion after 270 hours. Using the surfactant at very low concentration, 1 mg/L for example, we observed by visual inspection a large amount of large aggregates of DWNT in the mm range, which were not dispersed during sonication and initially present at the bottom of the flask.

Centrifugation of the DWNT suspensions at 3000 rpm for 30 minutes led to a decrease in the concentration of DWNT kept in suspension. In the case of GA, the final concentration was *ca.* 10–12 mg/L, almost whatever the GA concentration.

We then investigated the combination of two surfactants, by using first SDS which can easily penetrate inside the aggregates and exfoliate the CNT in aqueous media, and then carbohydrate polymer surfactant (GA) or mixtures of carbohydrate based surfactants (Surfhope and Montanov), more bulky and with a higher fatty chain/polar head volume ratio compared to SDS. Then, they can have a steric effect on the stabilisation, due to their size and the conformations they can adopt on the carbon nanotube surface.

Comparison of the mechanisms of the different surfactants effects and proposed combination, or in other terms, substitution of a LMW surfactant with a HMW one, is summarised in Fig. 5. Experiments on surfactants substitution were performed with two surfactants commonly used for CNT dispersions: SDS and GA. In our experiments we first prepared dispersions of carbon nanotubes with respective concentrations of 100; 78; 50; 33; 23; and 16 mg/L, stabilized with SDS with concentration of 100 mg/L (this concentration of SDS is toxic, so it is not possible to use such nanotube dispersions directly for any toxicity study). Dispersions prepared by sonication for 1 hour were filtered and washed 3 times in order to remove the free surfactant which was not adsorbed onto the CNT surface, and then redispersed by sonication in GA solution (40mg/L). The dispersions were filtered again and washed with water in order to remove SDS, which was substituted from the nanotube walls. Finally, CNT were dispersed again in aqueous solution of GA (20 mg/L) using sonication for 1 hour. The resulting stable dispersions of carbon nanotubes were centrifuged at 3000 rpm for 30 minutes and

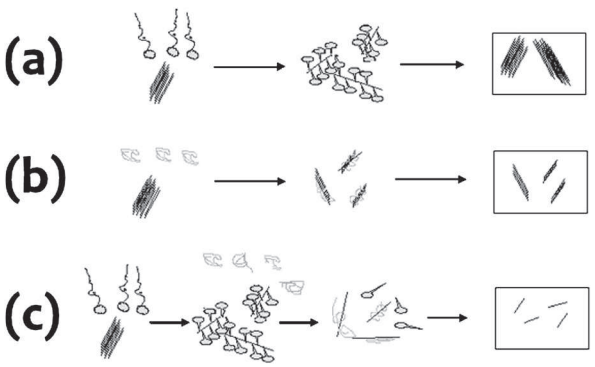

Fig. 5 Schematic illustration of the mechanisms of stabilization with different surfactants: (a) LMW surfactant; (b) HMW surfactant; (c) substitution of LMW surfactant by HMW surfactant.

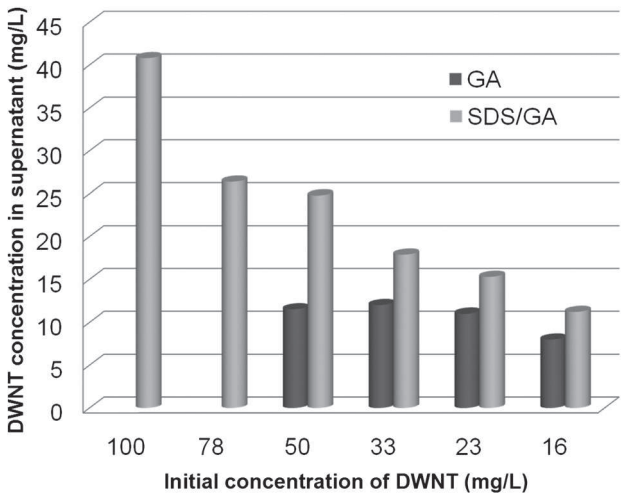

Fig. 6 Concentration of the CNT dispersed in supernatant, with and without substitution of the SDS with GA, after centrifugation (3000 rpm; 30 min); on the right: initial concentration of the CNT. ([SDS] = 100 mg/L; [GA] = 40mg/L).

absorbance of the supernatant was measured. Using the calibration curve for the GA stabilized carbon nanotubes, the concentration of DWNT in the supernatant was estimated. Experimental results are presented in Fig. 6. On the one hand, as one can see from Fig. 6, in the supernatant of the GA stabilized samples, obtained directly without substitution, we observed insignificant differences whatever the initial CNT concentration. On the other hand, samples of dispersions obtained after substitution showed direct dependence of the remaining CNT in the supernatant on the initial DWNT concentration. With increasing the initial DWNT amount we increased the concentration of DWNT in the dispersion after centrifugation. One explanation could be that we observed in GA stabilized samples a small amount of stabilized individual tubes/small aggregates which depends not on the surfactant or CNT concentration, but forms spontaneously *via*, probably, mechanical agitation. In the case of substitution, this happens because during the preparation of the CNT dispersion with SDS we have formed a greater amount of individual tubes which are kept in dispersion after substitution with GA. Secondly, we also observed an increase in the carbon nanotube concentration in the supernatant by 1.5–2.0 times as compared to the carbon nanotubes stabilized with GA only, in one step.

The presence or absence of SDS in our system after substitution is important data for our study to validate the efficiency of the process. *In situ* IR monitoring of the dispersions of DWNT was performed before and after substitution, as well as IR characterisation of the DWNT stabilized with GA. Results are presented in Fig. 7. Comparison of IR spectra of the supernatant of the DWNT dispersions revealed only one difference. On the spectrum of the DWNT dispersion stabilized with SDS a signal is observed between 950 and 1150 cm^{-1}, which is related to the sulfate group of the SDS. Such a signal was not evidenced in the other two spectra, which can be interpreted as confirmation of the SDS substitution during the experiment, and complete removal of SDS from the dispersion. Or, if we still have some SDS molecules present in the system, it could be undetectable

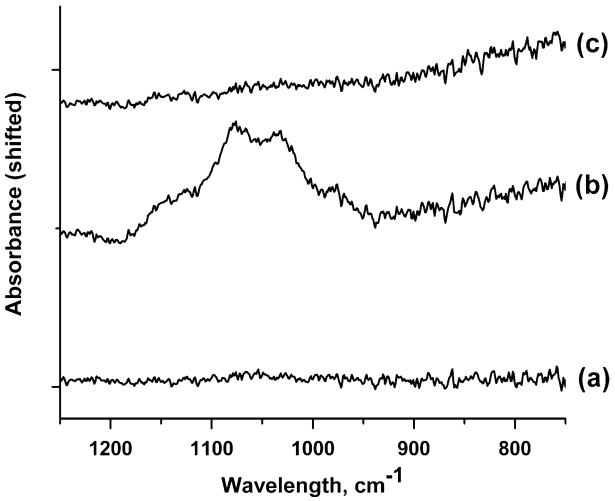

Fig. 7 *In situ* IR monitoring of the DWNT dispersions: (a) GA; (b) SDS; (c) substituted DWNT dispersions.

traces of surfactant, which are not toxic (SDS is toxic at concentrations higher than 15 mg/L).[41]

The study of other surfactants (Tween 20, sodium cholate, sodium deoxycholate, Surfhope 1216, Montanov 82) for

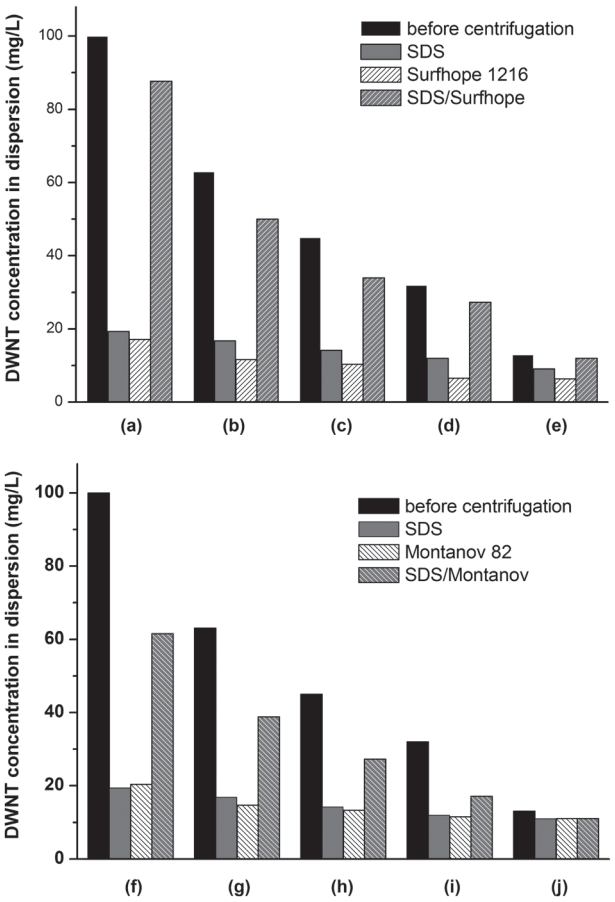

Fig. 8 DWNT concentration in the centrifuged samples, with and without SDS substitution, with different starting concentrations of DWNT: 100 mg/L for (a) and (f); 62.5 mg/L for (b) and (g); 45 mg/L for (c) and (h); 32.5 mg/L for (d) and (h); and 15 mg/L for (e) and (j) samples.

Table 2 Aggregate size determination by DLS

DWNT/ surfactant	Aggregate size (nm) by		
	intensity[a]	volume[a]	number
DWNT/SDS	290.0 (0.64); 1246.1 (0.36)	23.6 (0.50); 1084.8 (0.50)	23.6
DWNT/GA	179.6 (0.14); 39034 (0.86)	189.3 (0.58); 38864 (0.42)	171.1
DWNT after surfactant substitution	20.3 (0.08); 213.3 (0.20); 524.1 (0.72)	18.8 (0.98); 537 (0.02)	14.1

[a] The values in parentheses correspond to the fraction of each species.

replacement of SDS in these substitution experiments was carried out. Most promising results were obtained with the system where SDS was substituted with Surfhope 1216 (Fig. 8). Note that in the case of the substitution of SDS by Surfhope 1216 we have kept around 75 wt.% of CNT in dispersion, even after centrifugation for ½ hour at 3000 rpm. DWNT dispersions were analysed by dynamic light scattering (DLS) in order to evaluate the size of nanotube/surfactant aggregates formed in the presence of different types of surfactants as well as after substitution of SDS with GA (Table 2). For such measurements, supernatants of the centrifuged DWNT dispersions stabilized by SDS, GA and after substitution were used. We must note that results obtained for CNT, which are not spherical and are nanomaterials with high aspect ratio (2500–5000), are only qualitative because the analysis of the DLS data is performed with models valid only for spherical particles, which is the only shape that can be described by one unique number. We measured some properties of our particles and assumed that this referred to a sphere, hence deriving our unique number (the diameter of this sphere) to describe our particles. This ensures that we do not have to describe our 3-D particles with three or more numbers which although more accurate is inconvenient for data processing. We can see that this can lead to some interesting effects depending on the shape of the object and this is illustrated by the example of equivalent spheres of cylinders. However, if our cylinder changes shape or size then the volume/weight ratio will change and we will at least be able to say that it got larger/smaller *etc.* with our equivalent sphere model. Thus, the value of the aggregates size of the DWNT sample, stabilized by GA (Table 2), is evidence of the hypothesis of the stabilization mechanism when GA adsorbs and builds the stabilization barrier on the nanotube aggregates. The average size of aggregates by number is approximately one order of magnitude higher compared to the SDS stabilized and substituted carbon nanotubes. The lower value of the average size for the substituted CNT may be explained by the fact that we used ultrasonication twice, during SDS exfoliation, and again for redispersion in GA solution. Such a phenomenon was observed by Bandyopadhyaya *et al.*,[42] when a CNT suspension in GA was dried in air at room temperature, and redispersed in pure water showed better stability and lower aggregates size, as measured by cryo-TEM. Peak analyses by volume and by intensity have shown that a majority of small aggregates are present in the dispersions.

Deposits, cast from the DWNT dispersions supernatant stabilized with SDS (Fig. 9(a)), after substitution with Surfhope 1216 at 40 mg/L (Fig. 9(b)) and finally after dispersion in

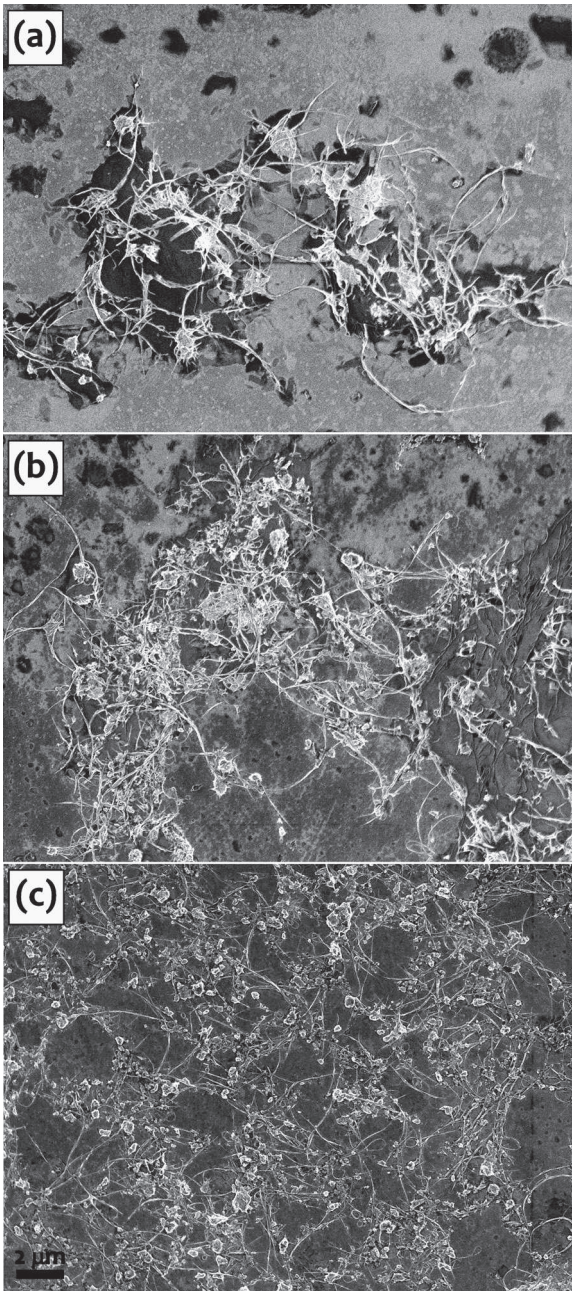

Fig. 9 SEM micrographs of the DWNT prepared (a) in the presence of SDS; (b) after substitution of the SDS with Surfhope 1216 (40 mg/L); (c) after substitution in Surfhope 1216 at 20 mg/L and centrifugation.

Surfhope 1216 at 20 mg/L (Fig. 9(c)), were studied by scanning electron microscopy. The DWNT conformation in the cast DWNT sample after stabilization with SDS has a typical topology, described in the literature.[43] During drying of the dispersion drop, phase separation takes place and coatings of SDS molecules are observed (Fig. 9(a)). In the case of DWNT stabilized after substitution with Surfhope 1216 at 40 mg/L (Fig. 9(b)), the bundles of DWNT look thinner and the proportion of individual nanotubes seems higher. The latter appear darker and with low contrast due to charge effects at the operating acceleration voltage. Surfactant coating is still visible. In the case of samples cast from CNT dispersion after substitution of SDS with Surfhope at 20 mg/L (final step, Fig. 9(c)), the dispersion state is clearly improved.

The preparation of DWNT dispersions in water *via* surfactant substitution may be used for applications in composite materials to replace, for example, the use of block copolymers which usually have good affinity with the matrix. Other areas of application are substitution with biocompatible or bio polymers with which good dispersions of CNT could be obtained using for example PEG derivatives for bioconjugation.

Conclusions

We have shown that through substitution of a low molecular weight anionic surfactant (SDS), which can more easily exfoliate bundles of carbon nanotubes, by non-ionic ones with a sugar polar head (such as Surfhope 1216), CNT can be well dispersed in water. Moreover, the dispersions showed better stability after centrifugation compared to regular dispersions with each surfactant alone. Low molecular weight surfactant molecules were successfully removed during the substitution process and were not found in dispersions using FT-IR. The dynamic light scattering method was used for the evaluation of the average aggregate size in the dispersions and suggested the presence of individual tubes or very small aggregates. We envision that the surfactant substitution method will be very important in all fields of CNT applications, including biology and medicine as well as toxicological studies where both the stability and the absence of additional toxic species are extremely important.

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