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Colloidal and rheological characterization of SWCNT in biological media

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ABSTRACT

We report on the colloidal and rheological characterization of suspensions of commercial single-walled carbon nanotubes (SWCNT) and oxidized single walled carbon nanotubes (SWCNT-oxi24h), in water and fetal bovine serum (FBS). The effects of two surfactants, dodecyl-benzene sodium sulfonate (SBDS) and sodium dodecyl sulfate (SDS) at different concentrations (0.5–2.0%) on the zeta potential and the rheology of the suspensions is also investigated. SWCNT suspensions were characterized by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The colloidal stability was determined by measurements of zeta potential in the physiological pH range 6.0 < pH < 8.0. Rheological measurements were implemented at concentrations of 1 and 1.5 mg/ml, and temperatures of 25°C, 30°C, and 37°C. The results obtained show that SWCNT suspensions in FBS, with and without addition of surfactants, depict a high tendency to aggregate with the bovine serum albumin (BSA), a process we could further characterize using Molecular Dynamics (MD) simulation. SWCNT suspensions were characterized by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The colloidal stability was determined by measurements of zeta potential in the physiological pH range 6.0 < pH < 8.0. Rheological measurements were implemented at concentrations of 1 and 1.5 mg/ml, and temperatures of 25°C, 30°C, and 37°C. The results obtained show that SWCNT suspensions in FBS, with and without addition of surfactants, depict a high tendency to aggregate with the bovine serum albumin (BSA), a process we could further characterize using Molecular Dynamics (MD) simulation. SWCNT suspensions in aqueous media show a negative zeta potential between −60 and −80 mV, whereas in FBS the stability is lower, with values of 20 mV. We observed no significant changes in the zeta potential with the different surfactants. The viscosity values obtained are smaller in water than in FBS, demonstrating the higher stability in water.

KEYWORDS

SWCNT; viscosity; zeta potential; surfactant; molecular dynamics simulation

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I. Introduction

Carbon nanotubes (CNTs) discovered by Iijima [1], are hollow seamless nanocylinders curled by graphite joints. According to the number of graphene layers, CNTs are conventionally classified as Single-Walled- (SWCNT) or Multi-Walled- (MWCNTs) Carbon Nanotubes. Since their discovery, numerous studies have developed very creative CNTs applications, including multifaceted sensors, and those in nanotechnology, material science, electronics, optics, gas storage and biomedicine [2–7].

Notably, the biomedical applications of CNTs have increased spectacularly in the preceding decades [4,8–10]. CNTs have been shown to become potentially useful systems for biomedical applications in cellular imaging [2–4] and promising drug carriers for targeted drug delivery systems in cancer therapies [8,9,11–13]. In particular, we have previously shown that SWCNT suspensions are excellent candidates as contrast agents (CAs) for magnetic resonance imaging (MRI), as they orient parallel to the external magnetic field and induce faster translational diffusion of water molecules moving along their longitudinal axis [14,15]. However, further progress in all these applications remains hindered by difficulties to obtain homogeneous and stable suspensions of SWCNT in water or biological media, mostly derived from their hydrophobic nature, as they tend to bundle via strong cohesive Van der Waals interactions, eventually becoming insoluble in aqueous environments [16,17].

Two main strategies have been devised to disperse CNTs in aqueous media: covalent functionalization by attaching functional groups on the CNT surface and noncovalent functionalization by physical adsorption of amphiphilic molecules (dispersants) [18–21]. However, chemical modifications of SWCNT may perturb their intrinsic properties: electronic and chemical structures (e.g., conductivity and strength). In contrast, noncovalent adsorption of surfactants [22–25] or polymers [16,25–28] respects the nanotubular structure and may result in homogenous, stable, CNTs suspensions [29]. More specifically, surfactants such as sodium dodecyl sulfate (SDS), and proteins as Bovine Serum Albumin (BSA) have been proposed, providing excellent nanotube stabilization and separation capabilities [29]. Stable suspensions of CNTs can therefore be safely used to develop therapeutic and diagnostic applications [2,30].

In recent years, many reports have emerged about the interactions of CNTs with proteins at the molecular level [31,32], a crucial aspect for their use in biomedical applications. The adsorption–desorption process of bovine serum albumin (BSA) on CNTs has been investigated by reflectometry [31] and spectroscopic methods have been used to investigate the interaction SWCNT with human serum albumin [32]. However, the molecular basis of the interactions between CNTs with surfactants and proteins, and how they determine the stability of the suspensions and their biomedical applications, remain insufficiently understood.

In this work, we provide an extensive colloidal and rheological characterization of SWCNT suspensions in aqueous media as water and FBS, in the presence of surfactants or not. The study has been done with two surfactants: dodecyl-benzene sodium sulfonate (SBDS) and sodium dodecyl sulfate (SDS). Molecular Dynamics (MD) simulations were used to interpret the interactions between SWCNT and surfactants or proteins and how they can determine the colloidal and rheological properties.
II. Materials and methods

2.1. Materials and preparation of SWCNT suspensions in aqueous and FBS media

We used Commercial Single Walled Carbon Nanotubes (SWCNT, Sigma–Aldrich, diameter: 2–10 nm; length: 1–5 µm and density 1.3–2.3 g/cm³) synthesized by chemical vapor deposition (CVD). The samples contained 40–60% nanotubes contaminated with residual 17 wt% Ni and 4 wt% Y. SWCNT were oxidized in HNO₃ under reflux for 24 h (SWCNT-oxi24h) following the methodology described by Cerpa et al. [15]. TXRF analysis of the oxidized CNTs showed residual paramagnetic metals of 3.2% Ni and 0.64% Y after 24-h oxidation [15].

FBS (GIBCO) was purchased from Thermo Fisher Scientific and SBDS and SDS surfactants from Sigma-Aldrich. Different solutions of these surfactants were prepared with concentrations between 0 and 2 wt%.

For the rheological study, stable and homogeneous suspensions of SWCNT were prepared at different concentrations of solids (1 and 1.5 mg/mL) in water and FBS media. All dispersion experiments were carried out with double distilled water. The samples were dispersed during 15 min with an ultrasonic bath 140 W, 25 kHz (Hielscher, Germany).

2.2. Structural characterization of SWCNT suspensions

In a previous paper from our laboratory [15], the purity and size distribution of SWCNT and SWCNT-oxi24h powder were evaluated by X-ray Fluorescence spectrometry, Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), Raman and Infrared spectroscopy.

In this work, the structural characterization of SWCNT suspensions was performed using TEM with Energy Dispersive X-ray analysis (EDAX) and AFM.

Transmission Electron Microscopy (JEOL JEM 2100-EX) was used to determine the particles size of SWCNT in the suspension. Briefly, a few drops of SWCNT suspensions with 0.005 mg/mL of solids concentration were placed on a copper grid and evaporated prior to observation by microscopy.

AFM images of SWCNT suspensions were obtained with a commercial AFM (Nanotech Electronica, Cervantes Full Mode AFM System), in the tapping mode and monocrystalline silicon cantilevers (Nano sensors Point Probe Plus, Germany) with a constant force 2.8 N/m and resonance frequency 75 kHz in air. The SWCNT were dispersed in water and FBS by ultrasonic agitation (ultrasound bath, 15 min) at a concentration of about 5.10⁻⁴ mg/mL. Two microliters of dispersion were deposited onto a cleaved muscovite mica substrate and let air-dry for subsequent AFM inspection.

2.3. Colloidal characterization of SWCNT suspensions

SWCNT suspensions were characterized by measuring the zeta potential as a function of pH using the microelectrophoresis technique assisted with laser Doppler velocimetry (Zetasizer NanoZS, Malvern, United Kingdom). The zeta potential of suspensions was determined at 25.0 ± 0.1°C, for pH values between 4 and 9, broader than the physiological pH range (6-8).

SWCNT were dispersed in either 1 ml of deionized water or FBS at a solids concentration of 0.1 g/L using 10⁻² M KCl as electrolyte. HCl and KOH (0.1 M) were used for pH
adjustments. In addition, zeta potential measurements were also performed for suspensions dispersed with two surfactants: SBDS and SDS at different concentrations (0–2% wt). The zeta potentials were estimated in all cases using the simple Smoluchowski equation [33]. Depending on the magnitude of the zeta potential, the spherical Smoluchowski approximation may overestimate the actual zeta potential by up to 20%. Three replicate measurements were made for each sample.

2.4. Rheological measurements of SWCNT suspensions

Rheological measurements were carried out with a rotational rheometer (Thermo, Haake Rheo-Stress 6000, Germany) using a double-cone and plate system (60 mm in diameter, 2° cone angle), provided with a solvent trap to reduce evaporation. A three-stage measuring program was used, with a linear increase of shear rate from 0 to 1000 s⁻¹ in 300 s, a plateau at 1000 s⁻¹ for 120 s and a further decrease to zero shear rate in 300 s. Measurements were made for different concentrations of SWCNT suspensions (1 and 1.5 mg/mL), temperatures of 25, 30, 37°C ± 0.1°C, using either water or FBS as dispersing medium.

2.5. Molecular dynamics simulation (MD) of the adsorption of BSA on a CNT surface

MD simulations were done with the Forcite module of the Materials Studio 7.0 software [10] in the NVT ensemble (number of particles N, volume V and temperature T, constants) and maximum simulation times of 1000 ps using a time step of 1fs. The temperature was controlled by a Nose-Dynamics Hoover thermostat [34] and kept constant at 310 K. The model contained one of the chains of the BSA protein and a SWCNT with and without carboxylic groups. As stated above, we consider that the BSA protein is predominant in the behavior of FBS. This assumption allows us to keep the number of atoms to a minimum and reduce computational time speeding up the calculation. More complex models including water molecules and longer simulation times are needed for an in-depth analysis of the system from a molecular simulation perspective, The BSA chain could move freely throughout the simulation time while the SWCNT position was fixed at the center of the model. Two independent simulations were run on each system for 1 ns with samples collected for analysis every 5 ps. Only the BSA chain could move freely throughout the simulation time. The CVFF force field [35] was used to model the interactions between both the CNT and the BSA. To build the models, a (6, 6) armchair CNT with and without carboxylic groups and the chain A of the BSA protein were put inside a periodic cell of 150x150x150 Å³. Initially, the centers of mass of both molecules were placed at approximately 70 Å apart from each other (due to the large size of the BSA chain, the distance between the CNT surface and the nearest atoms of the BSA chain is about 15 Å). This long distance was chosen to minimize the interactions between the molecules (Figure 1).
III. Results and discussion

3.1. Structural characterization of SWCNT suspensions

SWCNT dispersed in water and FBS were observed by TEM and some representative pictures of the degree of dispersion/agglomeration are shown in Figure 2. SWCNT tend to form bundles or entangled ropes owing to their high Van der Waals attraction and p–p interactions among their inter-tubes. It can be observed in Figure 2(a). In addition, it can be seen that there exists a high tendency for aggregations of the SWCNT in spherical shapes especially in the suspensions prepared in FBS.

Figure 1. Initial model of chain A of BSA and a (6, 6) SWCNT before starting the MD simulation.

Figure 2. TEM of SWCNT-oxi24h in (a) aqueous and (b) FBS suspensions without surfactants. The images were collected in air for dried suspensions.
Figure 3 shows the 2D and 3D representations of AFM images characteristic of SWCNT dispersed in water, FBS and SWCNT-oxi24h dispersed in FBS. The surface texture of samples is observed. We can see the presence of individual SWCNT when water is used as dispersion medium. In contrast, a large aggregation is detected when FBS is used. A different morphology is shown for SWCNT-oxi24h dispersed in FBS without surfactant. In Figure 3(c), it can be seen that FBS covers CNTs. We delve into this aspect in Section 3.4, where the use of molecular dynamics simulations shows that the presence of a SWCNT disrupts the structure of the protein due to the existence of favorable interactions between the surface of the SWCNT and the protein amino acids in the side chains. In addition, the height profile of SWCNT, FBS, and SWCNT-oxi24h dispersed in FBS without surfactant is shown in Figure 3 (a2, b2, c2). The height obtained is around 12 nm, 130 nm and 150–200 nm for SWCNT dispersed in water, FBS and SWCNT-oxi24h dispersed in FBS without surfactant, respectively. The height increases when SWCNT-oxi24h is dispersed in FBS. The AFM images of Figure 3 (c, c1) allow us to conclude that the FBS covers SWCNT producing aggregation and instability of the system.
3.2. Colloidal characterization of SWCNT suspensions

The colloidal stability of the suspensions was evaluated by measuring their zeta potential at different conditions. Figure 4 shows the zeta potential for suspensions of SWCNT and SWCNT-oxi24h using two dispersing media: water and FBS. Figure 4(a) shows the zeta potential values obtained as a function of pH for SWCNT. It can be seen that for the two dispersion media used, water and FBS, the zeta potential values in the studied pH range are below $-25 \text{ mV}$, a limit established by different authors to obtain an unstable suspension and with tendency to aggregation [36]. On the other hand, the zeta potential values of SWCNT-oxi24h obtained as a function of pH are shown in Figure 4(b). A clear difference can be observed in the zeta potential values when water is the dispersion medium. The zeta potential values are between $-60 \text{ mV}$ and $-80 \text{ mV}$ for the pH range of 4 to 8, while the values obtained for the FBS are less than $-25 \text{ mV}$ and these remain constant in the pH range studied. We think that the difference observed when SWCNT-oxi24h is dispersed in water is due to the presence of negatively charged carboxyl groups, which leads to an increase in the zeta potential absolute values. These results could indicate that the type of SWCNT used in the suspensions does not affect their behavior, while the effect of the BSA protein present in the FBS appears to dominate, considering that BSA is the main component in the FBS. Section 3.2, using molecular dynamics models, explains this effect. A similar behavior was observed by Kam et al. [4].

3.2.1. Effect of surfactants on the colloidal properties of SWCNT suspensions

The effect of surfactants on the CNTs behavior has been investigated by many researchers. Jiang et al. [37] found a ratio of 1:4 for CNT-SDS to obtain stable aqueous suspensions when the CNTs used were previously submitted to acid treatment. UV–vis spectroscopy was used to quantitatively characterize the stability of the dispersions for the first time. The CNT/SDS dispersion exhibits extreme stability, with the supernatant CNT concentration decreasing only 15% compared with a decrease of 50% for the bare CNTs. The interaction between CNTs and SDS through the hydrophobic segment causes a higher negative surface charge and steric repulsion, which improves the stability of the CNT/SDS dispersion. They concluded that the surfactant containing a single, long, straight-chain hydrophobic segment and a terminal hydrophilic segment proves to be a suitable dispersant for the stable
CNT dispersion. Rastogi et al. [38] reported a stable aqueous dispersion of CNTs (non-functionalized multiple wall) with a ratio of 1:520 for CNT-SDS. A comparative analysis on dispersion of multiwalled carbon nanotubes (MWNTs) with four surfactants – Triton X-100, Tween 20, Tween 80, and sodium dodecyl sulfate (SDS) was studied. The experimentally observed trend of dispersing power of surfactants is consistent with their chemical structures. An optimum CNT-to-surfactant ratio was determined for each surfactant. This parameter was shown to affect the nanotube dispersion significantly. Surfactant concentration above or below this ratio was shown to deteriorate the quality of nanotube dispersion. Yu et al. [39] achieved an ideal aqueous dispersion of 1:1.5 in the CNT-SDS system, for nonfunctionalized MWCNTs. The surfactant molecules were adsorbed on the surface of the MWCNTs and prevented re-aggregation of MWCNTs so that a colloidal stability of MWCNT dispersions could be maintained for several months. There is a relatively large discrepancy in the ideal equilibrium concentrations of the suspensions, which can be explained by the influence of the surface and length of the CNTs, as well as the methods and equipment used for dispersion. Furthermore, the presence of surface acid groups, which are commonly introduced during the purification of nanotubes, could increase hydrophilicity and improve dispersion stability [38]. We work with a maximum concentration of surfactant of 2 wt% that corresponds to a ratio of 1:0.05 for CNT-SDS and CNT-SDBS.

The zeta potential vs concentration (wt%) of SBDS and SDS surfactants for SWCNT and SWCNT-oxi24h suspensions in water (pH = 4.6) and FBS (pH = 7.6) media are shown in Figure 5.

![Figure 5](image-url)

Figure 5. Zeta potential vs concentration of surfactants for SWCNT suspended in water (■) and FBS (▲). (a, b) SWCNT and (c, d) SWCNT-oxi24h using SDBS and SDS as surfactants.
Figure 5(a,b) shows that for both dispersion media, there is no significant variation of the zeta potential with the concentration of the surfactants except for 2% water. The values obtained are like those without surfactants.

Nevertheless, we note that the zeta potential values are very different when SWCNT-oxi24h is suspended in water (Figure 5(c,d)). We can conclude that the stability observed could be due to the carboxyl groups on the CNT surfaces. In the case of FBS, the zeta potential remains constant under all conditions.

The zeta potential values of SWCNT are between $-18$ mV and $-35$ mV (Figure 5(a,b)); while for the SWCNT-oxi24h the zeta potential values are between $-55$ mV and $75$ mV (Figure 5(c,d)). The zeta potential of SWCNT and SWCNT-oxi24h suspensions in FBS has a constant value of around $-20.5$ mV and with a pH value = 7.6 for all contents of surfactant used.

In addition, we determine the particle size of the samples with some difficulties due to the agglomeration tendency. We observe a change in relative size according to the colloidal condition. The particle size is 40–700 nm for SWCNT dispersed in water and 500–1600 nm when they are dispersed in FBS. In contrast, the particle size is 40–150 nm and 5–40 nm when SWCNT-oxi24h are dispersed in water and FBS, respectively.

### 3.3. Rheological behavior of single CNTs suspensions

#### 3.3.1. Effect of solids concentration, dispersion medium, and temperature on the viscosity of SWCNT suspension

As it can be expected for very diluted suspensions the viscosity is very low, within the detection limit of the rheometer, and they exhibit a Newtonian behavior, with a constant viscosity with shear rate, as it can be seen in Figure 6. The small curvature of the curve is related to slippage effects and this is reported elsewhere for very low viscosity suspensions [40].

Figure 6(a,b) shows the influence of solids concentration on the viscosity of SWCNT suspensions in water and FBS at a temperature of 25°C. The change of concentration between 1 and 1.5 mg/mL in the suspensions did not cause significant changes in the viscosity values obtained when different suspension media were used. Figure c shows that the viscosity values tend to a slight increase when SWCNT-oxi24h were dispersed in the FBS medium compared to those obtained in water.

Table 1 shows the viscosity values obtained for the SWCNT-oxi24h suspended in water and FBS at 1.5 mg/mL and different temperatures.

It should be noted that the viscosity values at 1.5 mg/mL of SWCNT-oxi24h in water were obtained at pH = 3.4. If the pH value increased to pH = 6.85, the viscosity values in water should decrease even more than the viscosities obtained at pH = 3.4 (2.1–2.3 mPa.s) due to the increase in zeta potential, which indicates that SWCNT become more negative (see Figure 4(b)).

At pH = 6.85, the value of the zeta potential of the suspended SWCNT-oxi24h in water is $-65$ mV while for those suspended in the FBS it is $-20.2$ mV. This indicates that there is an interaction between FBS and the carboxylic groups of the SWCNT-oxi24h so that the value of the zeta potential decreases. This
interaction was confirmed by molecular dynamics simulations (Figure 7). As we showed in Section 3.1, we observed many aggregates by TEM and AFM microscopy (Figures 2 and 3).

The viscosity values of suspensions at 1.5 mg/mL SWCNT in water and FBS were less than 3 mPa.s. The decrease in viscosity values with temperature is smaller in water than in FBS.

Table 1. Viscosity values (mPa.s) of SWCNT-oxi24h suspended in water and FBS.

| Temperature (°C) | Water (pH = 6.2) | SWCNT-oxi24h in water (pH_{susp} = 3.4) | FBS (pH = 7.4) | SWCNT-oxi24h in FBS (pH_{susp} = 6.85) |
|-----------------|------------------|----------------------------------------|---------------|--------------------------------------|
| 25              | 1.8              | 2.3                                    | 2.5           | 2.7                                  |
| 30              | 1.7              | 2.2                                    | 2.3           | 2.6                                  |
| 37              | 1.6              | 2.1                                    | 2.3           | 2.5                                  |

Figure 6. (a) Viscosity vs shear rate of SWCNT-oxi24h suspensions prepared with different solid concentrations in water and (b) FBS at 25°C. (c) Viscosity vs shear rate of SWCNT-oxi24h suspensions in water and FBS at 25°C at 1 mg/ml.
3.4. Molecular modeling simulation of the adsorption of BSA on a CNT surface

The calculations show that during the simulation, both molecules approached each other and some of the amino acid residues of BSA located near the CNT surface. The adsorption of BSA on the surface of the CNTs was already early observed after a few picoseconds of simulation time. The approach between both molecules is clearly seen in Figure 7, which shows the evolution of the distance between the center of mass of the chain and that of the pristine CNT with time. The behavior for the carboxylated CNT is similar and is not shown here for the sake of simplicity. A rapid decrease in the distance between both molecules is seen followed by a stabilization of the position of the BSA around the SWCNT surface. After 1000 ps, the distance between the BSA and the CNT surface remains constant indicating that the BSA adsorbs on the CNT surface and remains bonded to it.

![Figure 7. Time evolution of the distance between the centers of the mass of the protein and the SWCNT.](image)

This behavior is also seen in Figure 8, which shows some selected snapshots of the MD trajectory for the carboxylated CNT.

Figure 9 shows in detail the final conformation of some of the amino acids of the BSA interacting with the CNT surface. It is evident that the interaction between both molecules allows the rearrangement of BSA atoms to fit the surface of the SWCNT and adsorb onto it. The BSA chain changes its initial shape and wraps around the CNT surface.

In Figure 10, the time evolution of the interaction energy between the BSA chain and the CNT surface (interaction energy $= E_{BA+CNT} - E_{BSA} - E_{CNT}$) is shown. Because of the interaction between both molecules, this energy diminishes clearly as the simulation proceeds and is a little more favorable (less positive) for the carboxylated CNT. This means a stronger interaction between the BSA chain and the CNT surface of the functionalized CNT, probably due to more polar Van der Waals interactions and hydrogen bonds between the amino acid residues and the carboxylic groups on the CNT surface.

Although longer simulation times, different initial conformations, the complete structure of the protein and solvated models are necessary to represent what happens in real systems in a more accurate way, these simple simulations show that a favorable non-
**Figure 8.** Representative snapshots of the trajectory: (a) 100 ps, (b) 200 ps, (c) 500 ps, (d) 1000 ps (end of the simulation).

**Figure 9.** Final conformation of BSA-SWCNT after interacting (only the amino acid residues of the BSA chain containing at least one atom being less than 3.5 Å from the SWCNT surface are shown).
covalent interaction exists between a SWCNT and one of the chains of the BSA protein. The evolution of the distance between the BSA and the CNT (Figures 7 and 8) as well as that of the interaction energy over simulation time (Figure 10) support this conclusion.

IV. Conclusions

TEM and AFM images show that SWCNT are aggregated when FBS is used as a dispersion medium. The height change observed by AFM in the SWCNT-oxi24h dispersed in FBS may be due to the favorable non-covalent interaction that is established between the SWCNT and the BSA protein present in FBS. The zeta potential of SWCNT-oxi24h changes with dispersing media. SWCNT-oxi24h suspensions in aqueous media have a negative value between $-60$ and $-80$ mV, whereas in FBS, the values are also negative and remain constant around $-20$ mV. When surfactants are added at different concentrations between 0.5% and 2%, no remarkable changes in the zeta potential are observed. The suspensions showed Newtonian flow behavior and the viscosity values of SWCNT suspensions in water and FBS at 1.5 mg/mL were less than 3 mPa.s. The viscosity decreases with temperature, although the viscosity values obtained in both dispersion media do not present great differences. The viscosity values are slightly smaller in water than in FBS. Molecular dynamics simulations show that the presence of a SWCNT disrupts the protein structure due to the existence of favorable interactions between the SWCNT surface and the protein amino acids on the side chains. There is a clear attractive interaction between both molecules as seen by the time evolution between their centers of mass as well as the decreasing values of the interaction energy.
Disclosure statement

No potential conflict of interest was reported by the authors.

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