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Enriched surface acidity for surfactant-free suspensions of carboxylated carbon nanotubes purified by centrifugation

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ABSTRACT

It is well known that surfactant-suspended carbon nanotube (CNT) samples can be purified by centrifugation to decrease agglomerates and increase individually-dispersed CNTs. However, centrifugation is not always part of protocols to prepare CNT samples used in biomedical applications. Herein, using carboxylated multi-walled CNTs (cMWCNTs) suspended in water without a surfactant, we developed a Boehm titrimetric method for the analysis of centrifuged cMWCNT suspensions and used it to show that the surface acidity of oxidized carbon materials in aqueous cMWCNT suspensions was enriched by ~40% by a single low-speed centrifugation step. This significant difference in surface acidity between uncentrifuged and centrifuged cMWCNT suspensions has not been previously appreciated and is important because the degree of surface acidity is known to affect the interactions of cMWCNTs with biological systems.

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1. Introduction

Carbon nanotubes (CNTs) have unique physiochemical properties that make them useful for the potential diagnosis and treatment of a number of diseases, especially cancer [1–6]. An important consideration for these and other biomedical applications of CNTs is how CNT samples are prepared [7]. In brief, almost all commercial CNT products are supplied as powdered soot that contains some degree of metallic and carbonaceous impurities in addition to CNTs. To prepare samples of pristine, non-functionalized CNTs for biomedical applications, the first step typically involves sonicating a known mass of CNT soot in an aqueous solution of a surfactant (e.g., a biocompatible polymer, protein, or serum) to yield a CNT suspension [8], and a second optional step involves centrifugation of the CNT suspension to remove heavier metal-containing CNTs, bundles, and other agglomerated materials [9]. To prepare oxidized or carboxylated CNT (cCNT) samples for biomedical applications, two methods are commonplace that do not involve the use of surfactants. One method reported by several groups is to sonicate cCNT soot in deionized water before adding the resulting aqueous cCNT suspension to cell culture medium [10–14], while others have reported an additional centrifugation step to purify the aqueous cCNT suspension (herewith called a centrifuged cCNT suspension) before adding this material to cell culture medium or blood [15–18]. Another important consideration for biomedical applications of CNTs is therefore a thorough physiochemical characterization of the exact CNT sample that is presented to living cells or intact organisms [19–28]. At a minimum, this involves some measure of CNT structures, amounts, dimensions, porosities, impurities, and in the case of cCNTs, a measure of surface acidity, defined as the acidic groups covalently attached to cCNT surfaces and potential acidic carbonaceous substances adsorbed to cCNT surfaces (i.e., oxidative debris) [13,29–36].

The acidic surface properties of cCNTs primarily stem from the presence of carboxyl, lactonic, hydroxyl, and phenolic groups, which are generated through reaction of CNTs with acidic liquid oxidants or high-temperature oxygen [37–39]. Acidic groups on cCNT surfaces have been assessed qualitatively using thermogravimetric analysis (TGA) [40–43], semi-quantitatively using Fourier transform-infrared (FT-IR) spectroscopy [24,44–46], and quantitatively using either fluorescence spectroscopy and dye-derivatized cCNTs [47–49], x-ray photoelectron spectroscopy (XPS) [24,43–45,50,51], or acid-base titrimetry [52–55]. While these and other approaches have their advantages and limitations, a survey of

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the literature reveals that they have been used overwhelmingly to assess the surface acidity of un-centrifuged cCNT suspensions, and rarely to assess the surface acidity of cCNT suspensions purified by centrifugation. This is notable because centrifuging an aqueous cCNT suspension without a surfactant should facilitate the removal of hydrophobic, non-oxidized soot components from the supernatant, as opposed to when a surfactant is used where both oxidized and non-oxidized components would be coated by surfactant and suspended in the supernatant. In other words, the process of centrifuging an aqueous suspension of cCNT soot could selectively enrich the centrifuged sample with oxidized carbon material.

Herein, a Boehm titrimetric method for the analysis of surfactant-free suspensions of cCNTs was developed and was used to show that the surface acidities of aqueous suspensions of multi-walled cCNTs (cMWCNTs) and centrifuged cMWCNT suspensions are not equivalent. Specifically, the surface acidities of aqueous cMWCNT suspensions and centrifuged cMWCNT suspensions were 7.46 ± 0.41 and 19.09 ± 0.52 mmol/g, respectively – a result of an increase in suspended oxidized carbon material and a decrease in agglomerated materials in the centrifuged cMWCNT suspensions. This significant difference in surface acidity between un-centrifuged and centrifuged cMWCNT suspensions has not been previously appreciated and is important because the degree of surface acidity is known to affect the biodegradation rates of cCNT samples [56,57], as well as, the *in vitro* and *in vivo* toxicity profiles of cCNT samples [58–61].

2. Experimental

2.1. Materials and solutions

Carboxylated MWCNT (cMWCNT) soot (product SC-M10; lot 1256YJF-070510) was purchased from Nanostructured & Amorphous Materials, Inc. (Houston, TX, USA) and its properties are described in Table 1. Caution, a fine-particulates respirator and other personal protective equipment (PPE) should be worn when handling cCNT soot [62]. Sodium hydroxide and standard buffer solutions of pH 4.00 ± 0.01, 7.00 ± 0.01, and 10.00 ± 0.02 were purchased from Fisher Scientific (Houston, TX, USA). HCl concentrate (0.01 mol), potassium hydrogen phthalate (KHP), and phenolphthalein were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation and standardization of sodium hydroxide

Approximately 200 mg of NaOH was weighed and transferred to a 500.0-mL volumetric flask, dissolved, brought to volume, and stored in a 500-mL polyethylene bottle. All ~0.01 M NaOH solutions were standardized against KHP using phenolphthalein as the indicator. In brief, ~50 mg of KHP was weighed, transferred to a 125-mL Erlenmeyer flask, and dissolved in 25.0 mL of 18.2 MΩ-cm deionized water with five drops of phenolphthalein. Using a 50.00-mL buret, NaOH solutions were titrated to endpoint with KHP. This process was repeated four times to determine the mean concentration and standard deviation (SD) of the standardized NaOH. NaOH solutions were used within seven days of being standardized.

Table 1
Properties of SC-M10 cMWCNT soot reported by the manufacturer.

Synthetic method	CVD
Catalytic metals	Fe, Co, Ni
% Carbon purity	>95
% Metals	<3.7
% Chloride	<1.0
Inner diameter (nm)	5–10
Outer diameter (nm)	10–20
Length (μm)	0.5–2
Oxidizing agents	H_2SO_4 & $KMnO_4$
% COOH	1.9–2.1

2.3. Preparation of cMWCNT suspensions and centrifuged cMWCNT suspensions

The preparation of cMWCNT suspensions and centrifuged cMWCNT suspensions started with the addition of 10.0 mL of 18.2 MΩ-cm deionized water to 10.0 mg of as-received cMWCNT soot that was weighed into a pre-cleaned, 20-mL scintillation vial (Fig. 1). The mixture was sonicated for 60 min using a Branson model 2510 bath sonifier (100 W, 42 kHz) with the bath water being changed every 30 min to maintain the temperature <15 °C; bath sonication was chosen so as to avoid nanotube perturbations induced by intense probe sonication. The purification of aqueous cMWCNT suspensions involved a single low-speed centrifugation step. To accommodate the use of a benchtop centrifuge (Eppendorf, model 5424), 10.0-mL suspensions were divided by transferring 1-mL aliquots into ten 1.5-mL centrifuge tubes, which were each centrifuged for 5 min at 20,000 RCF. The top ~900 μL from each supernatant was collected carefully using a micropipette so as to not disturb the pellet and combined in a pre-cleaned scintillation vial to afford a ~9-mL sample of a centrifuged cMWCNT suspension.

2.4. Raman spectroscopy

Raman spectra were acquired using a Jobin Yvon Horiba HR800 high-resolution LabRam Raman microscope system equipped with a 250-μm entrance slit and an 1100-μm pinhole. The 633-nm laser excitation was provided by a Spectra-Physics model 127 helium-neon laser operating at 20 mW. A 50 × /0.5 *NA* LM-Plan objective was used with a neutral density filter of 1.0. Spectral acquisition was performed with a 1.0-s integration time, a minimum overlap of 50, and a 3-subpixel average; each spectrum was presented as an average of 2 scans. Wavenumber calibration was performed using the 520.5 cm^{-1} line of a crystalline Si wafer. A 15-μL aliquot of either a cMWCNT suspension or centrifuged cMWCNT suspension was deposited on to a crystalline Si wafer and dried at room temperature; spectra were acquired from at least five different regions of dried material across the wafer.

2.5. UV–VIS–NIR spectrophotometry

All UV–VIS–NIR spectrophotometric analyses were performed using a Shimadzu UV-161PC spectrophotometer. All spectra were obtained as a single scan that was background corrected against a deionized water reference using a medium scan speed with 0.5-nm intervals and 1.0-cm quartz cuvettes. Spectra of cMWCNT suspensions and centrifuged cMWCNT suspensions were acquired after dilution with deionized water.

2.6. Dynamic light scattering (DLS)

The particle size distribution of cMWCNT suspensions and centrifuged cMWCNT suspensions diluted 1:10 with deionized water were analyzed by DLS using a 633-nm laser and a backscatter measurement angle of 173° (Zetasizer Nano-ZS 3600, Malvern Instruments, Worcestershire, UK). Ten consecutive 30-s runs were taken per measurement at 25 °C and the instrument was calibrated with polybead standards (Polysciences, Warrington, PA, USA). The particle size, in terms of hydrodynamic diameter, was calculated using a viscosity and refractive index of 0.8872 cP and 1.330,

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