

Optical Fiber Sensor for Detection of Carbon Nanotubes

C. I. L. Justino, A. C. Freitas, T. A. P. Rocha-Santos, A. C. Duarte

Abstract—This work relates the development of an optical fiber (OF) sensor for the detection and quantification of single walled carbon nanotubes in aqueous solutions. The developed OF displays a compact design, it requires less expensive materials and equipment as well as low volume of sample (0.2 mL). This methodology was also validated by the comparison of its analytical performance with that of a standard methodology based on ultraviolet-visible spectroscopy. The developed OF sensor follows the general SDS calibration proposed for OF sensors as a more suitable calibration fitting compared with classical calibrations.

Keywords—Optical fiber sensor, single-walled carbon nanotubes, SDS calibration model, UV-Vis spectroscopy

I. INTRODUCTION

THE actual detection of single-walled carbon nanotubes (SWCNT) in aqueous solutions has been an important subject which attracts the attention of researchers; it due to the high manufacturing rate of nanomaterials as the response to the growing use of SWCNT on different research areas such as for energy and environmental applications, as well as in biology and medicine research, with several scientific interests [1], [2]. The production of CNT has continuously been increased; in 2010, around 2500 t of carbon nanotubes (CNT) were accounted by the ten world major producers of nanomaterials, expecting that the production of CNT will reach to 12800 t in 2016 [3]. Furthermore, the environmental problem is the consequent accidental and quickly release of SWCNT on aquatic ecosystems, groundwater, and soil which allow the contact with the biological species [4].

Due to their insolubility in water (in pristine form), and due to their lipophilicity, CNT can accumulate in the food chain as other biopersistent and lipophilic chemicals; however, such perspective was not proved for CNT [5]. When dispersed in surfactants, and on other organic or aqueous solutions, CNT are functionalized and become hydrophilic, increasing their interaction with organic chemicals. The understanding of the mechanisms of interaction between functionalized SWCNT and the natural environment need to be more studied. The aqueous stability of CNT after adsorption on natural organic matter (NOM) was yet observed by Hyung et al. [6] in a natural source water, where the influence of NOM characteristics (e.g., amount and type of NOM, as well as their aromatic content), and the quality parameters of water (e.g., ionic strength, and pH) on the transport of CNT in natural systems were investigated.

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From such considerations, the improvement of analytical instrumentation to the fast and accurate quantification of nanotubes in aqueous environments is required. Traditional techniques [7] such as optical absorption [8] and Raman [9] spectroscopies are yet used for the optical characterization of CNT. The analytical systems such as optical fiber (OF) sensors or OF-based methodologies have been proposed for environmental, and life sciences applications with low-cost, high sensitivity and versatility, as well as easy operation for various analytes [10]-[15].

From such considerations, the application of OF sensing to monitor SWCNT in solution could constitute an interesting approach for the detection and quantification of CNT in aqueous solutions. The main objective of this work is to apply an Of sensor as a tool to screen SWCNT, in order to monitor the variation of optical power in various SWCNT samples.

II. MATERIALS AND METHODS

A. Dispersion of Single-Walled Carbon Nanotubes

A stock solution of single-walled carbon nanotubes (SWCNT) was obtained through the dispersion of commercially available SWCNT (Sigma-Aldrich) in aqueous solutions of sodium cholate (SC, Sigma-Aldrich) through a non-covalent functionalization; for that, 14 mL of aqueous solution of SC (0.2% w/v) was added to 4 mg of SWCNT. Then, the dispersion was placed in a water bath ultrasonicator (Ultrasonik 57H Ney, 400W, 50/60 Hz) during 60 minutes. The supernatant was collected to centrifuge tubes, which in turn, are placed on a centrifuge (Medifriger BL-S, JP Selecta, Spain) during 5 minutes at a relative centrifugal force of 2000 $\times g$ at 20 °C. The sonication and centrifugation steps were used to unbundle the dispersed SWCNT, and to remove the impurities (e.g., amorphous carbon and graphite), respectively. Approximately 70% of the resulting supernatant was collected to further experiments. The presence of individual SWCNT in the stock solution and their successful separation and dispersion were assessed by optical microscopy (Motic B1-Series). Six different samples of SWCNT in SC (with concentrations of 0.25, 0.20, 0.15, 0.10, 0.05, and 0.01 mg/mL) were prepared through dilutions from the stock solution of SWCNT. Such diluted samples were analyzed by the developed optical fiber (OF) sensor, and by the ultraviolet-visible spectrometry (UV-Vis) as the reference methodology, in order to construct calibration curves with the absorbance values at 500 nm, and the optical power changes, respectively, both against the different SWCNT concentrations. It should be referred that the concentrations of 0 and 0.28 mg/mL were added to the calibration plots, corresponding to the solution without SWCNT (only solvent, SC), and the stock solution of SWCNT, respectively. In addition, five SWCNT solutions were also applied to the two methodologies in order to compare their analytical performance for the quantification of SWCNT.

B. Optical Fiber Methodology for Screening SWCNT

The experimental apparatus used for the OF screening of SWCNT in solution was constituted by an optical source which is a laser diode (1550 nm, Oz Optics, Canada), a monomode OF with core and cladding of 9 and 125 μm , respectively, which is integrated into a directional 50:50 optical coupler, and a photodetector based on an InGaAs photodiode (Oz Optics, Canada) for the measurement of optical power variations. The photodetector was connected to a personal computer through a standard RS-232 serial bus for the acquisition of experimental data with homemade software.

A small section (12 mm) of the two OF cords corresponding to the reference OF and OF probe was uncladded and cleaned with dichloromethane; the reference OF was inserted vertically into a glass tube with an index matching liquid in order to reduce the possible reflections, and the OF probe was inserted into a glass tube with the SWCNT solution, which is successively replaced by another SWCNT solution according to the various concentrations. Each glass tube was filled with 200 μL of sample.

C. Reference Method (Ultraviolet-Visible Spectrometry)

Ultraviolet-visible (UV-Vis) absorption spectra (400-800 nm) were recorded in a spectrophotometer (GBC/Cintra10e) using a quartz optical cell with a path length of 10 mm for the characterization of the interband electronic transitions of the various SWCNT samples. For calibration, the absorbance values at 500 nm were recorded, since it is commonly used to the quantification of different SWCNT dispersions [16].

III. RESULTS AND DISCUSSION

After sonication and centrifugation, homogeneous gray suspensions of SWCNT in SC were obtained. A visual inspection of the images obtained of optical microscopy suggests that SWCNT are dispersed and they are individualized, as shown in Figure 1.

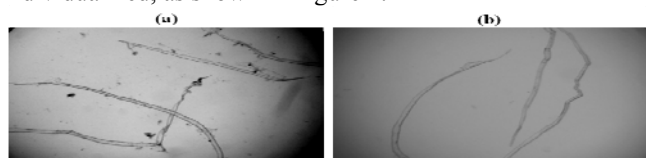


Fig. 1 Optical images (320x) of dispersed SWCNT (a) before, and (b) after the centrifugation step.

Furthermore, the average diameter of dispersed SWCNT was found to be 1.81 nm, as calculated from the frequency of the radial breathing mode of the obtained Raman spectra recorded using a Bruker RFS/100S Raman spectrometer (with a Nd:YAG laser, $\lambda = 1064$ nm, 100 mW).

The characterization of SWCNT by UV-Vis spectroscopy was used for the evaluation of the stability of SWCNT in aqueous solutions of surfactant through their typical interband electronic transitions [8]. The absorbance spectrum, shown in Figure 2, has similar shapes and bands position to typical absorption spectrum of dispersed SWCNT [17]: the electronic transitions between 400-600 nm are assigned to the metallic SWCNT, and the absorbance features between 600-800 nm are assigned to the semiconducting SWCNT.

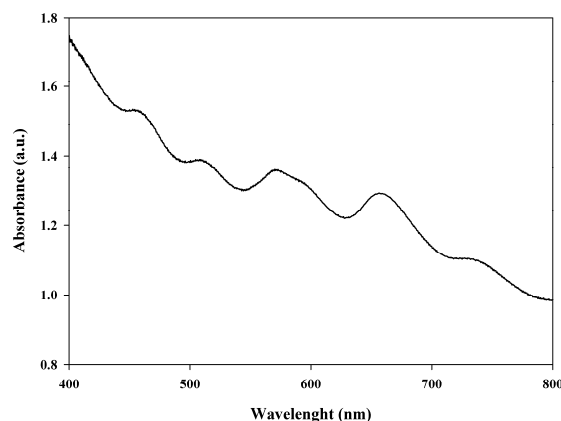


Fig. 2 Absorbance spectrum of dispersed SWCNT in SC between 400 and 800 nm

The stock solution of SWCNT was diluted and six different diluted samples of SWCNT were obtained, as shown in Figure 3, with concentrations of 0.25, 0.20, 0.15, 0.10, 0.05, and 0.01 mg/mL; from Figure 3, the uniformity of such dilutions was also observed.

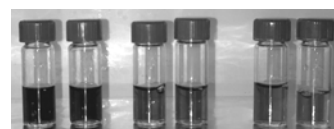


Fig. 3 Diluted samples of SWCNT in SC (with concentrations of 0.25, 0.20, 0.15, 0.10, 0.05, and 0.01 mg/mL, from left to right)

This series of diluted samples was applied to the OF sensor, and a nonlinear relation between the variation of the optical power and the concentration of SWCNT was observed, as shown in Figure 4.

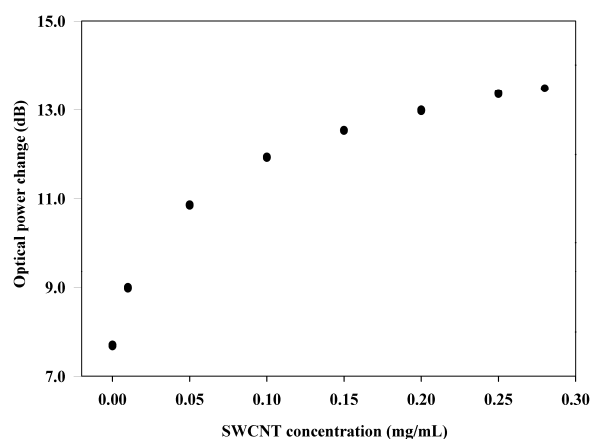


Fig. 4 Analytical response obtained by OF sensor (variation of optical power) for the diluted SWCNT solutions.

The comparison of the obtained calibration plot (Figure 4) with the final part of the cumulative symmetric double sigmoidal (SDS) function [18] reveals an analytical equivalence between them. The SDS calibration model was proposed as a more suitable fitting to the analytical response of OF sensors in comparison to the classical calibration models [18].

After a group of simplifications from the equation corresponding to the final of the SDS model (1), and based on our experimental data (Figure 4), we found the equation (2) which explains our analytical results.

$$\lim_{x \rightarrow +\infty} y = \lim_{x \rightarrow +\infty} \left[a + b \ln \left(\frac{he^{cx} + i}{e^{cx} + j} \right) \right] \quad (1)$$

$$y = k_1 - k_2 \ln(1 + k_3 e^{-x}) \quad (2)$$

The OF methodology was validated by the comparison of its analytical performance with that of an UV-Vis technique as a reference methodology by monitoring the absorbance intensities at 500 nm; a linear model was obtained, as verified in the Figure 5.

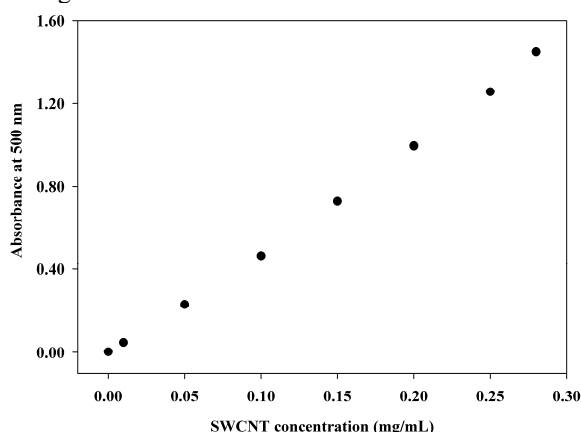


Fig. 5 Analytical response obtained by UV-Vis technique at 500 nm for the various diluted SWCNT solutions

Table I compares the analytical parameters for the calibration models obtained from the analytical response of the two methodologies for the different diluted SWCNT solutions, and corresponding to the experimental data plotted in Figures 4 and 5.

TABLE I
COMPARISON OF THE TWO METHODOLOGIES FOR THE DETECTION OF SWCNT

	OF sensor	UV-Vis method
Calibration equation	$y = 15.94 + 1.77 \ln(1 - 0.99e^{-x})$	$y = -0.018 + 5.12x$
R^2	0.9999	0.998
p value	< 0.0001	< 0.001
LOD ¹ (mg/mL)	4.7×10^{-4}	1.2×10^{-2}

¹Limit of detection (LOD) calculated as three times the residual standard deviation.

From Table I, a high correlation between the respective analytical responses and the concentration of SWCNT was found for both methodologies, which was due to the high values of the determination coefficients (R^2). From Table I, it is also observed that the LOD of the OF sensor was lower than that of the reference methodology (UV-Vis), verifying its better analytical performance.

Five individual samples were also analyzed through OF sensor and UV-Vis spectroscopy in order to compare the analytical performance of both methodologies on the quantification of SWCNT; their respective concentrations were found taken in account the corresponding calibration models identified in Table I.

Figure 6 compares the correlation between the mean concentration of the five individual SWCNT samples with the developed OF sensor and the UV-Vis method.

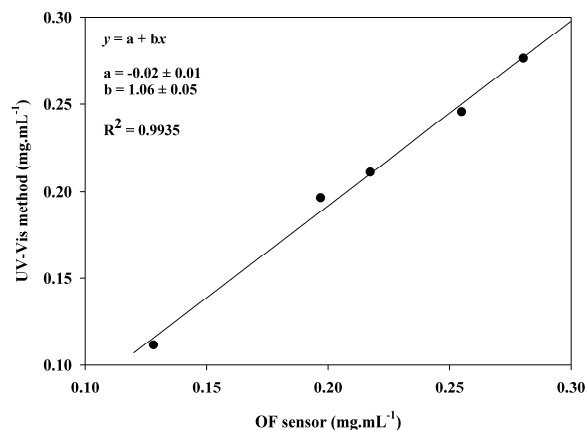


Fig. 6 Comparison of the results obtained with the OF sensor and the UV-Vis method for the five SWCNT samples.

As observed in Figure 6, a linear correlation was found between the two methodologies with a high determination coefficient (R^2) of 0.9935. From an analysis of variance (ANOVA), it was verified that there is not a statistically significant difference ($p = 0.854$) between such two methods for the quantification of SWCNT.

IV. CONCLUSION

The developed OF sensor is considered as an useful tool for the detection and quantification of SWCNT in solutions due to its compact design, less expensive materials and equipment as well as a requirement of low volume of sample (0.2 mL).

In addition, it was verified that the nonlinear calibration model observed for the analytical response with the OF probe follows the general SDS model ($R^2 = 0.9999$), as an adequate alternative to classical calibration models.

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