Talanta 89 (2012) 105–108

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Screening of single-walled carbon nanotubes by optical fiber sensing

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ARTICLE INFO

Article history:
Received 6 October 2011
Received in revised form
23 November 2011
Accepted 27 November 2011
Available online 2 December 2011

Keywords:
Experimental design
Optical fiber sensor
Single-walled carbon nanotubes
SDS calibration model
UV–Vis spectroscopy

ABSTRACT

A methodology based on optical fiber (OF) sensing was developed to screen single walled carbon nanotubes (SWCNT) in aqueous solutions.

This method was validated by the comparison of its analytical performance with that of an ultraviolet–visible (UV–Vis) technique by monitoring the absorbance intensities at 500 nm, and no significant difference ($p = 0.854$) was observed between such two methods.

The results obtained by the OF sensor were encouraging in what concerns a new approach for 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. Additionally, it was concluded that the nonlinear calibration model observed for the analytical response with the OF probe follows the general cumulative symmetric double sigmoidal (SDS) model ($R^2 = 0.9999$), once adapted for the analytical region of interest.

1. Introduction

Carbon nanotubes (CNT) are allotropes of carbon which have arisen great interest in the scientific community due to their various applications in environmental monitoring, bioengineering, biochemistry, and life sciences.

Both the manufacturing rate and the consequent accidental release of CNT to aquatic ecosystems have been increased [1]. According to O'Driscoll et al. [2] the studies of simulated dispersion of CNT in freshwaters, particularly their interaction with natural organic matter, are yet in the beginning but in the near future, results could provide definitive explanations of how the structure of CNT affects the aquatic biota. Furthermore, the relationship between the nature of the functional groups used for surface functionalization of single-walled CNT (SWCNT) and their cytotoxicity has been recently demonstrated by Klapler et al. [3], and Pan et al. [4], thus opening a new research window in the SWCNT field. Then the monitoring of SWCNT in aqueous solutions has become an important issue.

In most applications, SWCNT should firstly be dispersed in organic and aqueous solutions [5,6] in order to assess the optimal conditions for their surface functionalization, either covalently or non-covalently. According to Ham et al. [7] the non-ionic, anionic and cationic surfactants are the most used for the SWCNT dispersion through their non-covalent functionalization. Ultraviolet–visible (UV–Vis) absorbance spectra can provide adequate information about SWCNT purity [8,9] and structure through the evaluation of the singular electronic transitions of SWCNT [10,11]. Besides UV–Vis spectroscopy, the current analytical technique for optical characterization of SWCNT [12,13], the Raman spectroscopy [10,14] and the scanning tunneling spectroscopy [15] are other standard instrumentation of interest.

Currently, optical fiber (OF) sensing is used in environment monitoring and life sciences applications with high sensitivity and versatility [16–24]. A wide range of OF sensors as reflectometers were used to determine the concentrations of different analytes such as hydro-alcohols in solutions [25], or hydrocarbons in water/gasoline mixtures [26]. The use of CNT as sensitive materials in OF sensing has also been studied, for example, to the detection of chemical pollutants [27]. However, the application of OF sensing to monitor SWCNT in solution has never been attempted before, and it could be an interesting approach for detection and quantification of CNT in aqueous solutions.

Therefore, the aim of this paper was to develop a methodology based on OF sensing to screen SWCNT in aqueous solutions, and compare it with a standard methodology based on UV–Vis spectroscopy.

2. Materials and methods

2.1. Dispersion of SWCNT in aqueous solutions

The single-walled carbon nanotubes (SWCNT, #704113, Sigma–Aldrich) used in the experiments were synthesized through

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doi:10.1016/j.talanta.2011.11.074

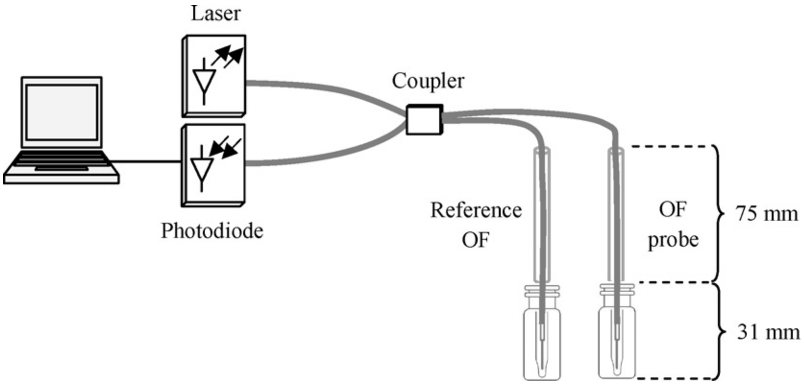

Fig. 1. Experimental set-up for optical fiber (OF) sensing of SWCNT in solution.

cobalt-molybdenum catalysis (CoMoCAT, Southwest Nanotechnologies). For their dispersion, SWCNT have been suspended in distilled water with sodium cholate as an anionic surfactant (SC, $C_{24}H_{39}NaO_5$, Sigma–Aldrich). SWCNT samples were prepared through dispersion of 4 mg of SWCNT in 14 mL of aqueous solution of SC (0.2%, w/v) (Technical Information Bulletin AL-265, Sigma–Aldrich).

The dispersion of SWCNT results from the unbalancing between the van der Waals forces responsible for the aggregation and bundling of synthesized SWCNT, and the mechanical energy provided by the sonication which can lead to the separation and dispersion of SWCNT. All SWCNT samples were maintained in a water bath ultrasonicator (Ultrasonik 57H Ney, 400 W, 50/60 Hz) for periods of 60 and 100 min, in order to compare the influence of sonication time. As the dispersion of SWCNT is affected by dispersant properties and concentration, characteristics of ultrasonic bath such as the ultrasonic frequency, time and temperature of sonication, as well as the geometry and position of vessel in ultrasonic baths [28], all experiments were made in round-bottom flasks, and in each sonication step, only one flask was used at the center of the ultrasonic bath, in order to provide the same sonication characteristics in each sample.

Besides the sonication, the effects of different centrifugation programs were also assessed. The centrifugation of SWCNT samples was performed at a relative centrifugal force (RCF) of 2000 and 10,000 × g during 5 and 10 min at 20 °C (Medifriger BL-S, JP Selecta, Spain) in order to remove graphite, residual catalyst, and amorphous carbon, and approximately 70% fraction of supernatant was collected for subsequent analysis.

2.1.1. Method of design of experiments

The optimization of experimental conditions for the dispersion of SWCNT in SC was evaluated, in order to obtain a statistical data analysis, and understand the relationships between some experimental conditions related to the main steps (sonication and centrifugation) for the preparation of SWCNT solutions. The experimental conditions for the optimal preparation of such samples were found through the application of an experimental design to attain the best SWCNT dispersion monitored by absorbance spectroscopy at 500 nm, which is the wavelength frequently selected to quantify different SWCNT dispersions [29]. The full factorial design determines which factors have significant effects on a response as well as how the effect of one factor varies with the varying level of the other factors. Then, the main effects and interactions of 3 quantitative variables (sonication time – A, centrifugation time – B, and relative centrifugal force, RCF – C) on the dispersion of SWCNT were assessed by UV–Vis spectroscopy at 500 nm, using a 2^3 factorial design with 2 replicates (16 experimental runs).

From the experimental design, the SWCNT sample with more statistically significance on absorbance at 500 nm will dilute to obtain six different SWCNT concentrations in SC. Aliquots of such sample will pipette out, and correctly dilute with fresh SC (0.2%, w/v) to bring up concentrations of 0.25, 0.20, 0.15, 0.10, 0.05, and 0.01 mg/mL. Such dilutions will use to construct a calibration curve with absorbance values at 500 nm against the different SWCNT concentrations.

2.2. Optical fiber methodology for screening of SWCNT in solution

Fig. 1 shows the experimental set-up for optical fiber (OF) screening of SWCNT in solution. It is constituted by a laser diode (1550 nm, Oz Optics, Canada) as optical source, a directional 50:50 optical coupler, and a photodetector with an InGaAs photodiode (Oz Optics, Canada) for measurements of optical power variations. The photodetector was connected to a laptop via standard RS-232 serial bus for data acquisition with homemade software.

A small section (12 mm) of the two OF cords corresponding to the reference OF and OF probe was uncladded, and each of them was inserted vertically into a glass tube which was perfectly adjusted to the vial cap. The uncladded region of each OF cords function as the sensor head and it was immersed in an index matching liquid (ML) in order to reduce the reflection at the corresponding OF section, and in different SWCNT solutions, respectively. Previously, a conical insert was placed into both vials to allow the use of smaller volume (200 μL) of ML and SWCNT solution.

The principle of operation relies on the dependence of the optical power through the fiber (reflected at the OF probe) and the different interfaces (fiber-air and fiber-SWCNT solution); an optical power value was obtained due to the exposure of the sensor head to air, and another analytical signal is associated to its insertion into the SWCNT solution.

The same series of SWCNT dilutions used for absorbance investigations, as described at Section 2.1.1, was also used for OF analysis in order to obtain a calibration curve. On the other hand, five individual SWCNT solutions were also analyzed through OF methodology and UV–Vis spectroscopy (through absorbance intensities at 500 nm) in order to compare the analytical performance of both methodologies.

3. Results and discussion

An experimental design (2^3 factorial design) was used to study the optimal experimental conditions for the preparation of SWCNT samples in order to attain the best SWCNT dispersion monitored by UV–Vis spectroscopy at 500 nm. Three quantitative variables were studied: the sonication time (factor A), the centrifugation time (factor B), and the relative centrifugal force (factor C). Statistics, and

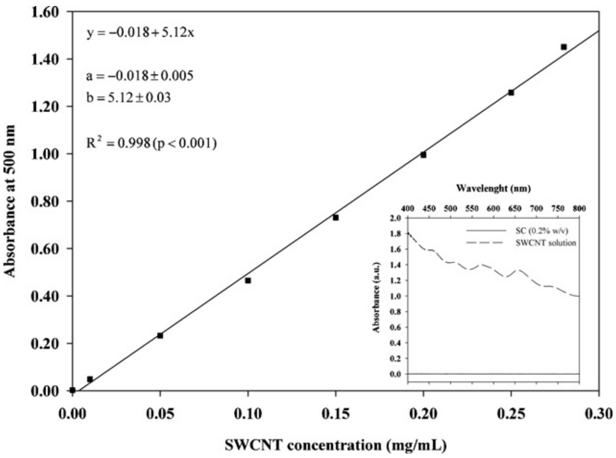

Fig. 2. Calibration plot of absorbance values at 500 nm for different SWCNT concentrations (inset graph: absorbance spectra of SC, and of dispersed SWCNT in SC at 400–800 nm, after 60 min of sonication, and 5 min of centrifugation at 2000 × *g*).

factorial plots (normal probability plot, and Pareto chart) obtained from such experimental design were available in Appendix A (Supplementary data).

From the experimental design procedure based on a full factorial design with two replicates, it was found that the SWCNT solution obtained from 60 min of sonication and centrifuged 5 min at 2000 × *g* was more statistical significance at 500 nm, as verified through the statistics displayed in Table A.2, and through the data interpretation of Fig. A.1I (available in Appendix A, Supplementary data); both values correspond to the low level of each factor.

In order to know the relation between the absorbance intensities at 500 nm and concentration of SWCNT, such sample was diluted to obtain subsamples (according procedures described at Section 2.1.1), and a linear regression was obtained, as shown in Fig. 2; two points were previously added corresponding to the absorbance value for $x = 0$ mg/mL (solution without SWCNT; only with SC), and to the absorbance value for $x = 0.28$ mg/mL (SWCNT solution used to prepare dilutions).

In the inset graph of Fig. 2, it was displayed the absorbance spectrum of SWCNT solution with more statistical significance which was used to prepare dilutions. Such absorbance spectrum (400–800 nm) was recorded in a spectrophotometer (GBC/Cintra10e) in order to provide the typical spectroscopic signature of SWCNT through its interband electronic transitions as a way to verify the presence of SWCNT in such solution. The electronic transitions between 400 and 600 nm are assigned to the metallic SWCNT (M_{11} interband), and the absorbance features between 600 and 800 nm are assigned to the semiconducting SWCNT (S_{22} interband) [12]. In the inset graph of Fig. 2, the absorbance spectrum of SC is also displayed; it is transparent in the entire range allowing easily the observation of characteristics electronic transitions of SWCNT, ensuring that all spectroscopic features observed in the spectrum of dispersed SWCNT in SC are due to the addition of SWCNT.

From Fig. 2 it is also verified a high correlation between the absorbance (y) values recorded at 500 nm, and the concentration of different SWCNT concentrations (x), given by the high determination coefficient ($R^2 = 0.998$), in a determination range from 0 to 0.28 mg/mL. The limit of detection (LOD), calculated as three times the residual standard deviation [30], was 1.2×10^{-2} mg/mL. This calibration curve was then used to provide a comparison between the UV–Vis technique and OF sensing, after the monitoring of SWCNT in five different solutions.

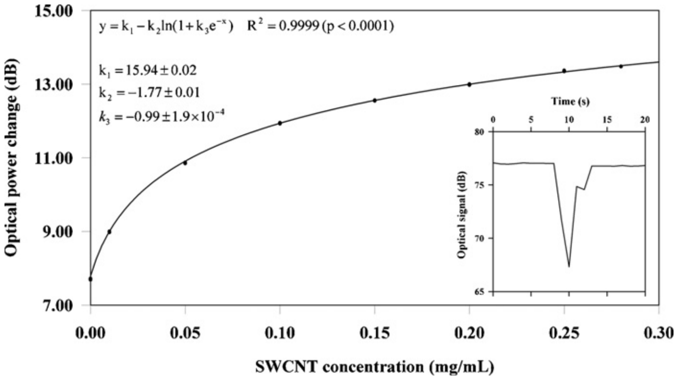

Fig. 3. Calibration plot of the variation of optical power for different SWCNT concentrations (inset graph: optical signal obtained with the dipping of the OF probe in SWCNT solution).

Hence, Fig. 3 shows the relation between the variation of optical power (y) and the concentration of SWCNT (x) which is not linear; different research groups have also recorded such nonlinear behavior of the analytical response of the OF sensors [17,19,21,22,31,32]. The inset graph of Fig. 3 displays the graphical pattern of optical signal obtained with the dipping of the OF probe in SWCNT solution.

From the inset graph of Fig. 3, it can be observed that in the interface OF probe-air, the optical signal remains stable, with small variations which do not affect the analytical signal; the baseline noise was about 1.4% of the analytical signal. When the OF probe is inserted in the solution, a strong optical power change was observed. After the removal of the OF probe from the solution, the optical signal returns to its initial value after 2 s; in this period, the OF probe detects the optical signal of the remaining drop.

On the other hand, it was also verified that the calibration plot (Fig. 3) shows a high degree of similarity with the final part of cumulative symmetric double sigmoidal (SDS) function which has been recently suggested [33] as a more appropriate fitting to the analytical response of OF sensors in comparison to the classical calibration models. For high values of the *X*-axis, that is the region of analytical interest in this particular case, the SDS model can be written as [33]:

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

Therefore, through some simplifications (available in Appendix B, Supplementary data), the following Eq. (2) could be developed for the calibration of the OF sensor:

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

Fig. 3 shows the plot of the calibration model (from Eq. (2)), found from experimental data. The LOD for the developed OF sensor was found to be 4.7×10^{-4} mg/mL (calculated as three times the residual standard deviation), which is better than that for UV–Vis methodology (1.2×10^{-2} mg/mL), suggesting a better analytical performance of the OF methodology.

In order to obtain a comparison of the analytical performance of the developed OF sensor with the UV–Vis spectroscopy, five different SWCNT solutions were analyzed with the determination of respective concentrations. Table 1 shows the results from such five different samples, concerning the determination of their concentrations through the calibration models of OF methodology (in Fig. 3), and UV–Vis spectroscopy (in Fig. 2), respectively.

An analysis of variance (ANOVA) was applied to the results displayed in Table 1, and it showed that there is no a statistically significant difference between the SWCNT concentrations obtained by the two methods ($p = 0.854$). The analytical error determined from the residual standard deviation was about 1.33×10^{-4} mg/mL.

Table 1
Results for five different SWCNT solutions obtained from both OF sensing and UV–Vis technique.

Sample	OF sensing		UV–Vis technique (at 500 nm)	
	Mean[a] (mg/mL)	SD (mg/mL)	Mean[a] (mg/mL)	SD (mg/mL)
1	0.111	0.003	0.1281	0.0001
2	0.21	0.01	0.2173	0.0001
3	0.246	0.004	0.2549	0.0002
4	0.20	0.01	0.1969	0.0000
5	0.28	0.02	0.2803	0.0000

[a] Mean of five measurements; SD – standard deviation.

4. Conclusions

The dispersion of single-walled carbon nanotubes (SWCNT) is fundamental for their application in several research areas. In this work, an experimental design (2^3 factorial design) was applied for the optimization of main experimental parameters, responsible to SWCNT dispersion in surfactant aqueous solutions, and monitored at 500 nm by UV–Vis spectroscopy. It was observed that the centrifugation time was the factor which contributed more significantly to the response, in comparison with the other factors tested (sonication time, and relative centrifugal force). Among the experimental runs corresponding to different SWCNT samples, it was also concluded that the SWCNT sample more statistically significant was taken after 60 min of sonication and 5 min of centrifugation at 2000 × *g*. Such sample was diluted, and a good linear calibration was observed ($R^2 = 0.998$) by plotting the series of SWCNT concentrations against the respective absorbance values at 500 nm. The SWCNT dilutions were screened by an OF sensor, and a nonlinear calibration model was observed on the analytical response (optical power change) of SWCNT dilutions monitoring with the OF probe. After the analysis of five individual SWCNT samples, no significant difference between the two methodologies was observed. It was also concluded that the nonlinear calibration follows the general SDS model ($R^2 = 0.9999$) applied to OF sensors as an adequate alternative to classical calibration models. The developed OF sensor is a compact design, and requires low volumes of samples being an interesting approach for the detection and quantification of SWCNT; furthermore, it can be coupled to a separation methodology to improve its selectivity.

Acknowledgments

This work was funded by FEDER under the Operational Program for Competitiveness Factors – COMPETE and by national funds via FCT (Fundação para a Ciência e a Tecnologia, Portugal) within the framework of research project CARDIOSENSOR (references FCOMP-01-0124-FEDER-010902 and PTDC/SAU-BEB/099042/2008. This work was also funded through scholarships – references SFRH/BD/60429/2009, SFRH/BPD/65410/2009, and SFRH/BPD/73781/2010 under QREN-POPH funds, co-financed by the European Social Fund and Portuguese National Funds from MCTES.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.11.074.

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