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Effect of carbon nanotubes on properties of soft materials based on carbon nanotubes–ionic liquid combinations

M.L. Polo-Luque, B.M. Simonet, M. Valcárcel *

Department of Analytical Chemistry, University of Córdoba, E-14071 Córdoba, Spain

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A B S T R A C T

Soft materials resulting from the combination of carbon nanotubes with ionic liquids have aroused analytical interest; thank to their peculiar characteristics. This paper compares the sorption capacity of eight different soft materials obtained from the combination of 1-hexyl 3-methylimidazolium hexafluorophosphate (ionic liquid) with different types of carbon nanotubes. The main characteristics of carbon nanotubes were established by Raman spectroscopy. The results obtained pointed out the critical role of the carbon nanotube types on the stability as well as the sorption capacity of the soft material. By using the adequate carbon nanotube it is possible to improve the LOD 4 times when they are used as sorbent materials for SPE. Working in the recommended conditions the LOD for the analysis of 5 mL of water sample was 5 μg/L of fluoranthene and the precision 5.9%.

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1. Introduction

In analytical chemistry, the sample preparation step is normally a bottleneck, in fact sample preparation gradually becomes a major part of analysis, capable of taking up to 80% of the total time of a complete separation-based analytical process [1]. Although, in past years, several sample treatment systems have been described, in routine laboratories SPE and SPME are probably the most used because they have high reproducibility or robustness [2]. Analytical evolutions of these strategies have been mainly performed in the field of new sorbents as well as in the field of the miniaturization. In general, recent advances in new sorbents are focused on nanotechnology, sol–gel technology, polymers, molecularly imprinted polymers (MIPs), and immunoaffinity-based coatings including immunosorbents with covalent immobilized antibodies or antigens, which have high affinity to the corresponding antigens, or antibodies, allowing the selective extraction (immunoaffinity extraction) from the sample [3,4]. Although the immunosorbents have high selectivity [5], they are instable in most cases and they are only available at high cost [6]. One alternative is the molecularly imprinted polymers because they have a low cost, are stable, and can be used without loss of activity [7]. However, they are difficult to synthesize. Although with a lower selectivity with regard to antibodies or molecularly imprinted polymers, nanoparticles can be an effective alternative in many applications. To this end, CNTs have attracted much attention as promising materials, which are extensively studied in order to make use of their unique structure and remarkable properties. Their strong adsorption affinity to a wide variety of organic compounds, together with their large adsorption surface makes them excellent material for SPE and SPME [8]. CNTs have been also proposed for the determination of many analytes in different sample matrices [9]. One of the most important shortcomings of carbon nanotubes are their tendency to aggregate, which affects the adsorption [10]. From one part, aggregation reduces the effective active surface of carbon nanotube and from the other part, aggregation allows the adsorption in interstitial places which can be positive for some applications but extremely difficult to be reproduced by simple mechanical packing of the nanomaterial.

Recently a new family of compounds, the so called soft material or gel resulting from the combination of carbon nanotubes with ionic liquids has been described [11]. Soft materials are interesting from the analytical point of view because they combine the properties of ionic liquids and carbon nanotubes. In addition, they present for some properties a synergistic effect, probably due to the special configuration of carbon nanotubes. This soft material has been widely used in analytical chemistry to develop electrochemical sensors [12] and to perform sample treatment [13]. Then, the aim of this work is to study how carbon nanotubes affect the analytical properties of the soft material concretely to their chemical stability and sorption capacity to perform solid phase extraction of organic compounds. PAHs have been selected as target analytes for this study.

2. Materials and methods

2.1. Reagents and standards

The ionic liquid HMIM PF_6 (1-hexyl 3-methylimidazolium hexafluorophosphate) $>99\%$ from MERCK (Darmstadt, Germany)

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* Corresponding author. Tel./fax: +34 957 218616.
E-mail address: qa1vacam@uco.es (M. Valcárcel).

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Table 1
Characteristics of carbon nanotubes and recommended carbon nanotube concentration to prepare the soft material in each case.

	Diameter (nm)	Length (μm)	Functio-nalization (wt%)	Purity	Soft material CNT (%w/w)	Supplier
MWNTs-1	5–20	1–10	–	> 95%	3.7	Bayer (Germany)
MWNTs-2	110–170	2	–	> 90%	4.4	Mer (Arizona, USA)
MWNTs-3	9.5	1.5	–	90%	1.9	Nanocyl (Belgium)
MWNTs-4	10–30	10–30	–	> 90 wt%	3	Cheap-Tubes (USA)
MWNTs-5	10–30	10–30	–OH 2.5	> 90 wt%	2.6	Cheap-Tubes (Vermont, USA)
MWNTs-6	10–30	10–30	–COOH 1.6	> 90 wt%	3.7	Cheap-Tubes (Vermont, USA)
MWNTs-7[a]	10–20	5–15	–	> 95%	2.6	NTP Ltd. (China)
SWNTs	< 2	5–15	–	SW: 50% CNT > 90%	7.5	NTP Ltd. (China)

[a] Aligned-CNT.

and eight different types of carbon nanotubes were used to prepare the bucky gels. Table 1 summarizes the main characteristics of the carbon nanotubes used in this work.

Individual standard stock solution containing 1000 mg L^{-1} of fluoranthene (Sigma-Aldrich) was prepared in methanol. Working solution of fluoranthene was made by using purified water (18 MΩ) from a Milli-Q water purified system (Millipore, Bedford, MA, USA). Hexane, methanol, acetonitrile and ethyl acetate from Panreac (HPLC-grade) were used as solvents. Acetonitrile for fluorescence measurements was from Fluka.

Ammonium acetate, formic acid (Sigma-Aldrich) and HPLC-grade methanol (Panreac Química, S.A.; Barcelona, Spain) were used to prepare the BGE. Potassium hydroxide (MERCK; Darmstadt, Germany) was used for capillary conditioning.

2.2. Instrumentation

Fluorescence emission spectra were measured on a PTIQuantaMasterTM Spectrofluorometer (Photon Technology International) equipped with a 75 W xenon short arc lamp and the model 814 PTM detection system. Felix 32 software was used for fluorescence data collection and analysis, which also controlled the whole instrument. All optical measurements were carried out in 10-mm quartz microcuvettes at room temperature under ambient conditions.

Raman spectra were measured on a Confocal Raman Microscope (CRM) (alpha500 R) equipped with a frequency doubled NdYAG laser with 532 nm excitation. For the analysis using the alpha500 R, a WITec UHTS 300 spectrometer and a DU970N-BV (EMCCD) (16×16 μm pixel size, 1600×200 pixels) camera are additionally connected to the system. WITec Project Plus software was used for advanced data evaluation for Confocal Raman Microscopy.

Capillary electrophoresis was performed on a Beckman Coulter (Palo Alto, CA, USA) MDQ instrument equipped with an on-column UV detector and a diode array detector (DAD). The uncoated fused-silica capillary used was 50 μm I.D., and 375 mm O.D. The instrumental setup was controlled, and data acquired and processed using a 32 Karat software.

2.3. Preparation of the soft materials

The soft material was prepared by mixing appropriate amount of carbon nanotubes with 200 μL of IL. The suspension formed was then ground in an agate mortar with a pestle. After that the suspension turned viscous, affording a soft material like a gel. The concentration selected for each nanotube to prepare the soft material is indicated in Table 1. This concentration, close to the critical gel concentration, was determined experimentally adding increased amount of carbon nanotubes to the ionic liquid until the absence of free ionic liquid was observed as a second phase.

2.4. Raman characterization of soft material

The Raman spectra of the soft material and carbon nanotubes were measured with a $20 \times /0.4$, $\infty/0.17$, WD 3.8 mm objective. For measurements, the soft material was placed into 1 mm hole in a stainless steel plate.

2.5. Determination of solubility of ionic liquid from the soft material. Stability

The solubility measurement was carried out putting in contact 5 mg of soft material immobilized on cotton fibers with 1 mL of the organic solvent. After 5 min, the organic solvent was collected and removed with an air stream. Finally the ionic liquid was reconstituted in 1 ml methanol. The methanolic solution of solubilized ionic liquid was diluted and analyzed by CE. For CE analysis the BGE consisted of 100 mM ammonium acetate pH=7.7 in methanol. The samples were injected in the hydrodynamic mode at 0.5 psi for 15 s. Tests were carried out in the positive polarity mode, a constant voltage of 10 kV and an overimposed pressure of 50 psi in both vials in order to avoid the formation of bubbles which can occur due to the organic dissolvent analysis. Measurement was performed at 210 nm.

2.6. Determination of preconcentration capacity of the soft material

To study the preconcentration capacity of the soft material, fluoranthene was selected as an analyte model. The method used was a modification of [14]. Briefly, fiber cotton having a surface area of 16.3 mm^2 and impregnated with the soft material was immersed in 5 ml of fluoranthene standard of 0.5 mg/L to perform the preconcentration. Afterwards, the fiber was washed with water and dried at room temperature. Finally, the fiber was immersed in 1 mL of acetonitrile to perform the elution of the analytes (5–10 min), and then 300 μL of acetonitrile was added into the microcuvette to measure the fluorescence. The spectra were registered with λ_{exc}=341 nm and λ_{em}=440 nm. The slit widths for excitation and emission were both 3 nm.

3. Results and discussion

This section describes the characterization of carbon nanotubes from their Raman spectrum. Then, considering the properties of carbon nanotubes, the formation of soft material or bucky gel by mixing them with ionic liquid is also presented. Then, the analytical figures of merit resulting from the study of the sorption process of fluoranthene for the different soft materials are determined and compared.

Table 1 summarizes the characteristics of the carbon nanotubes studied in this work and also the information typically provided from suppliers and manufacturers. As can be seen this

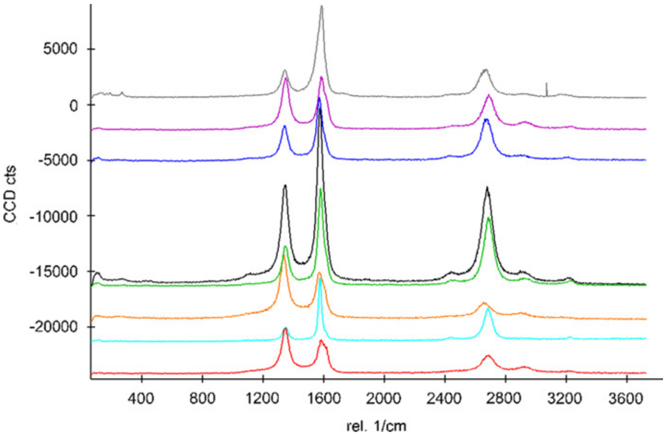

Fig. 1. Raman spectrum of carbon nanotubes. The spectra from bottom to top are MWNTs-1, MWNTs-2, MWNTs-3, MWNTs-4, MWNTs-5, MWNTs-6, MWNTs-7 and SWNTs.

Table 2
Raman spectroscopy analysis of carbon nanotubes.

	Intensity D-band	Bandwidth D-band (cm^{-1})	Intensity G/D ratio	Bandwidth G/D ratio
MWNTs-1	3697	55	0.70	1.30
MWNTs-2	1094	43	5.00	0.51
MWNTs-3	5048	55	0.69	1.20
MWNTs-4	3215	51	2.60	0.80
MWNTs-5	7656	52	1.88	0.90
MWNTs-6	2826	49	1.90	0.94
MWNTs-7	4241	52	1.03	1.20
SWNTs	2053	52	3.80	0.96

information is limited to dimensional information as well as some indications about purity. In this way, it must be remarked that synthesis procedures result in a mixture of carbon nanotubes with different chiralities and purities. In order to characterize carbon nanotubes, the Raman spectrum was recorded. Spectrum is depicted in Fig. 1

Interpretation was based on the following facts: (i) The D-band around 1350 cm^{-1} is sensitive to structural defects in the graphitic sp^2 network, for example it marks the presence of carbonaceous impurities such as amorphous carbon particles [15,16]; (ii) The intensity ratio of the tangential mode in carbon nanotube (G-band) with regard to the D-band can be related with purity [17]. When there are fewer carbon impurities, the G/D ratio can be used as an index related with the presence of defects on the sidewall of the nanotube [18]; (iii) The bandwidth ratio of G and D bands can be related to the presence of defect sp^3 in the structure. Table 2 shows the information obtained for the analysis of the eight types of carbon nanotubes.

The main conclusions of the spectral analysis can be summarized as follows: (i) according to D-band symmetry MWNTs-1, MWNTs-3 and MWNTs-7 are the most pure; (ii) MWNTs-3 presents lower defects on the sidewall; (iii)MWNTs-2 presents the higher content in amorphous organic carbon particles; and (iv) MWNTs-6 compared with MWNTs-4 presents a higher number of defects, probably this defects have been produced during chemical functionalization.

In Table 1 the concentration of CNTs required to form the soft material or gel, the so called critical gel concentration, which has been determined experimentally as the minimum amount of carbon nanotubes required to avoid the presence of free ionic liquid as a second phase is presented. If we relate this information with the characteristics of carbon nanotubes it can be concluded that the formation of the soft material is improved with the purity of carbon nanotubes. The presence of sidewall defects as well as the presence of amorphous carbon material has a negative effect on the formation of the soft material. The results obtained also pointed out that multiwalled carbon nanotubes easily interact with the ionic liquid to form the gel, in other words lower amounts are dispersed and oriented to form the network of the gel.

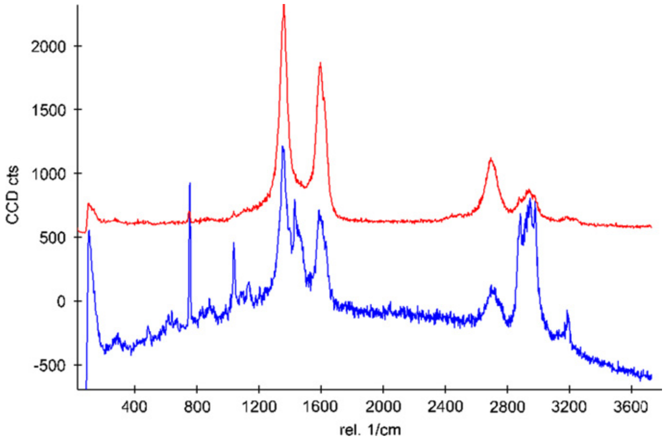

Fig. 2. Raman spectrum of a mixture of IL and an amount of MWNTs-1 lower than that necessary to form the soft material (bottom spectrum) and Raman spectrum of soft material obtained from MWNTs-1 (above spectrum).

As it was indicated before, in the gel the amount of free ionic liquid can be considered negligible. In fact after centrifugation it is not possible to separate the ionic liquid from the gel. This high interaction between the carbon nanotube and the ionic liquid is also observed in the Raman spectra. As a representative example Fig. 2 shows the Raman spectrum obtained for the gel. Raman spectrum of the soft material (above spectrum) is the result of the combination of carbon nanotube and ionic liquid spectra, being possible to distinguish the typical bands of solid MWNTs-1 (D, G and G′), although less intense than solid one, and a small band at 750 cm^{-1} corresponding to the ionic liquid anion (PF_6^-). On the other hand, for the mixture of low concentration of MWNTs-1/IL (bottom spectrum), the Raman spectrum shows a decrease in the CNT bands and an increase in the ionic liquid bands. As can be seen in comparison with the spectrum obtained with a lower amount of carbon nanotubes dissolved in IL, the formation of the gel results in a clear diminution of the fluorescence and stability of the baseline. When the gel is formed the strong interaction of the ionic liquid with the carbon nanotube avoids the fluorescence as well as the intensity of the Raman bands of IL.

From the analytical point of view soft materials are mainly used as components of electrochemical sensors or as sorbents to carry out sample treatment of chemical separation. Then, for analytical applications it is important to know the integrity and stability of the soft material as well as the capacity to absorb chemical compounds.

One important characteristic of the soft material (gel) is the integrity and stability of the system LI/CNTs; thanks to the strong binding among carbon nanotubes and the IL by means of strong π–π interactions. This strong interaction also affects the solubility of the IL, which dramatically decrease when the soft material is formed. The stability of the soft material has been tested as their stability in organic solvents. For that methanol, acetonitrile, ethyl acetate and hexane were tested. Table 3 summarizes the results obtained expressed as reduction of the solubility of the ionic liquid in the solvents with regard to the solubility obtained with

Table 3
Stability of the soft material. Percentages of reduction of the amount of IL in different solvents.

	Methanol (%)	Acetonitrile (%)	Ethyl acetate (%)	Hexane
MWNTs-1	54	64	51	Quantitative reduction signal < LOD
MWNTs-2	38	50	41	
MWNTs-3	51	60	39	
MWNTs-4	49	66	30	
MWNTs-5	56	61	46	
MWNTs-6	55	65	43	
MWNTs-7	56	60	44	
SWNTs	57	59	46	

Table 4
Figures of merit for the preconcentration and fluorescence detection of fluoranthene.

	LOD (μg/L)	Sensibility normalized	RSD (%)	RECOVERY (%)		
				0.5 h	1 h	4 h
MWNTs-1	13.9	45	8.9	29.0	32.8	65.0
MWNTs-2	7.8	80	6.7	51.4	60.1	65.0
MWNTs-3	5.0	100	5.9	64.6	97.5	102.5
MWNTs-4	6.7	93	6.7	60.2	61.9	59.0
MWNTs-5	7.9	79	10.4	51.0	64.2	64.0
MWNTs-6	10.5	59	12.4	38.3	49.7	49.0
MWNTs-7	12.4	50	8.7	32.5	47.8	47.6
SWNTs	19.3	32	9.7	20.9	25.2	29.0

free ionic liquid. Higher reduction means higher gel stability. As can be seen, the stability was good for all the nanotubes; this result demonstrated that it is possible to use organic solvents, for example to elute analyte. The gels obtained from carbon nanotubes of higher purity seem to be more stable (higher diminution of ionic liquid solubility).

To study the sorption capacity of the soft material, taking into account the results obtained in Table 3, acetonitrile was selected as a solvent because it allows the direct fluorescence analysis of fluoranthene. In hexane, fluoranthene was not fluorescent. Table 4 shows the results obtained for the adsorption study. As can be seen, the higher sorption capacity was obtained for MWNTs-3. As can be seen, the limit of detection was four times lower for this carbon nanotubes and the sensitivity expressed as the slope of the calibration graph was three times higher than that obtained for the single walled carbon nanotubes. Although soft materials have mainly been described for single walled carbon nanotubes, the results obtained point out that multiwalled carbon nanotubes are better for this kind of application than single walled carbon nanotube. However, between different multiwalled carbon nanotubes also exists higher differences in the stability and sorption capacity of the soft material. Differences are not only related with the sorption capacity but also with the kinetic. With regards to kinetic, MWNTs-4 shows the highest sorption kinetic (see Table 4) controversy, the kinetic of materials having the higher sorption was clearly lower. Probably this fact was due to the combination of adsorption and absorption processes. Absorption could lead the preconcentration of higher amounts of analyte but required higher equilibration time. Results can be summarized in the following points: (i) MWNTs have better preconcentration values for fluoranthene than SWNTs. (ii) High surface area and purity are related with higher sorption capacity of the gel. (iii) Sorption kinetic in the gel is due to adsorption (faster process) and absorption (slower process). The RSD values for consecutives pre-concentration steps for each gel were between 5.9% and 12.4%. To this end, it must be remarked that significant differences in the precision was not found. This was attributed to the similar stability observed for all the soft materials studied.

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