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Scanning electron microscopy of carbon nanotubes dispersed in ionic liquid: Solvent influence study

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ABSTRACT

In this work we present the results from the use of ionic liquids (ILs) for the sample preparation of carbon nanotubes prior to their characterization by scanning electron microscopy (SEM). Their use implies some advantages such as no damage of the surface of CNTs, the aggregation of the nanoparticles decreases while the number of CNTs individually dispersed increases, therefore, the sample is more representive. The use of ILs avoids the gold sputtering of the sample prior to analysis owing to the conductivity of the ionic liquid medium while increasing the contrast and brightness of the image. A comparative study of the feasibility of three different solvents — namely methanol, surfactant Triton X-100 solution, and imidazolium-based ionic liquid – for the dispersion of MWNTs prior to SEM analysis was carried out. Complementarily, Raman spectroscopy was employed to follow the solubilization of carbon nanotubes within the ionic liquid medium, demonstrating the excellent features of ILs for their use as solvent of CNTs.

1. Introduction

Carbon nanotubes have aroused great attention in many fields owing to their exceptional electrical, optical and mechanical properties. A bottleneck for a more widespread industrial application is the accurate characterization of their properties. CNT dispersions have been characterized by UV-visible absorption spectroscopy [1] and near infrared (NIR) fluorescence spectroscopy [2]. Separation techniques (i.e. electrophoresis) have been also employed for the separation of single-walled carbon nanotubes (SWNTs), based on tube length or diameter-selective CE separation [3]. Raman spectroscopy has also emerged as a powerful technique for the characterization of carbon nanotubes [4–6].

Particle size is an important physical property of the nanomaterials [7–10] as well as size distribution. An essential measure is the aspect ratio determination, based on the measure of the length and outer diameter of the MWNTs by SEM. Scanning electron microscopy is one of the most commonly-used techniques employed for this purpose [11–13].

Microscopy-based techniques provide exact information about type and characteristics (shape, size, etc.), however, they present shortcomings in sample preparation such as the aggregation of the nanoparticles [14]. Thus, sample preparation prior to microscopic analysis is crucial to achieve representative results of the sample. Some procedures for sample preparation show several problems i.e. damage or modification of the surface of the MWNT, due to the metallic coating, chemical attack or their aggregation [15–17].

In the past decade, a variety of strategies have been devised to improve solubility and dispersion of CNT, mainly in strong acids or volatile organic solvents [18,19] or dispersion with the aid of surfactants [5,20,21]. In recent years, ILs have emerged as “green” alternatives to volatile organic solvents for this purpose. In the literature, ILs have been used as media for functionalization reactions or as functionalizing agents for the covalent binding of CNTs [22]. Moreover, the compatibility of ionic liquids for their use in scanning microscopy has been proved since they have been analyzed by SEM [23] as their negligible vapor pressure enables their introduction in the apparatus requiring vacuum conditions [24]. ILs have been also used to improve the SEM observation of wet biological specimens [25,26].

In this paper, a preparation procedure for the dispersion of carbon nanotubes prior to SEM analysis has been developed which involves the use of ionic liquids, in this case 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6). This procedure for dispersion of CNTs has been compared with other preparation methods, namely dispersion in organic solvent — methanol and dispersion with the aid of a surfactant — Triton X-100. Ionic liquid enabled better dispersion of the MWNTs, thus allowing further characterization of the nanomaterial, such as diameter and length measurements. In order to demonstrate the effective dispersion of the carbon nanotubes within the ionic liquid medium, Raman spectroscopy was employed to monitor the process and corroborate that the carbon nanotubes are homogeneously distributed within the ionic liquid medium and the excess of ionic liquid has been effectively removed before SEM analysis.

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2. Materials and method

2.1. Materials

Multiwalled carbon nanotubes (MWNTs) were provided by Bayer Material Science (Germany), with an outer mean diameter between 25 and 70 nm and a length between 1 and 10 μm. The ionic liquid employed for dispersing the carbon nanotubes was 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMIM PF_6) purchased from Sigma-Aldrich. Triton X-100 was provided by Fluka, (Buchs, Switzerland). Methanol was purchased from Sigma-Aldrich.

The membrane filter was acquired from Millipore, Germany (Isopore Membrane, polycarbonate, Hydrophilic, 0.22 μm pore size, 25 mm of diameter). The ultrasonic bath was a Branson model CPX952319R.

2.2. Sample preparation of carbon nanotubes prior to SEM analysis

Carbon nanotube suspensions have been prepared using three different procedures, namely dispersion in organic solvent, in surfactant solution and in an ionic liquid, at the same concentration of 10 $g \cdot L^{-1}$. Then, solutions were homogenized by ultrasonic bath during 15 min at 1800 J/mL. A drop of the suspension was taken and placed on a polycarbonate or cellulose filter.

MWNTs dispersed in an organic solvent or surfactant solution were submitted to the conventional procedure for SEM analysis (Fig. 1a), which comprises four steps: dispersion, separation, drying, and metallic coating. A drop of the solution is firstly placed on a cellulose membrane and the drying is performed under a laminar flux within a hood of the laboratory. Afterwards, a metallic coating (Au) is made by ion sputtering deposition. In this procedure the environment of the sample is continually changing (liquid–air–vacuum), since the separation is on a liquid medium, then is dried into an air medium and, finally, the analysis, once the sample is coated, takes place on a vacuum environment.

On the other hand, Fig. 1b displays a scheme of the proposed procedure employed for the sample dispersed in IL, which involves two steps: dispersion of the MWNTs in the ionic liquid medium and IL excess removal. A drop of the suspension was taken and placed on a polycarbonate membrane into the extraction cartridge. It is important to have a filter with small pores that allow the removal of excess of IL, and, at the same time, prevent the loss of MWNTs during the process. Filtration was carried out using a solid phase extraction manifold (model Whatman). In this case the sample surface possesses a thin film of ionic liquid that increases the conductivity of the sample without needing a further coating with gold. This IL film neither damage the sample surface nor modify the measured dimensions. The membrane is then removed to be analyzed by SEM. The sample remains humid inside the microscope in a vacuum atmosphere.

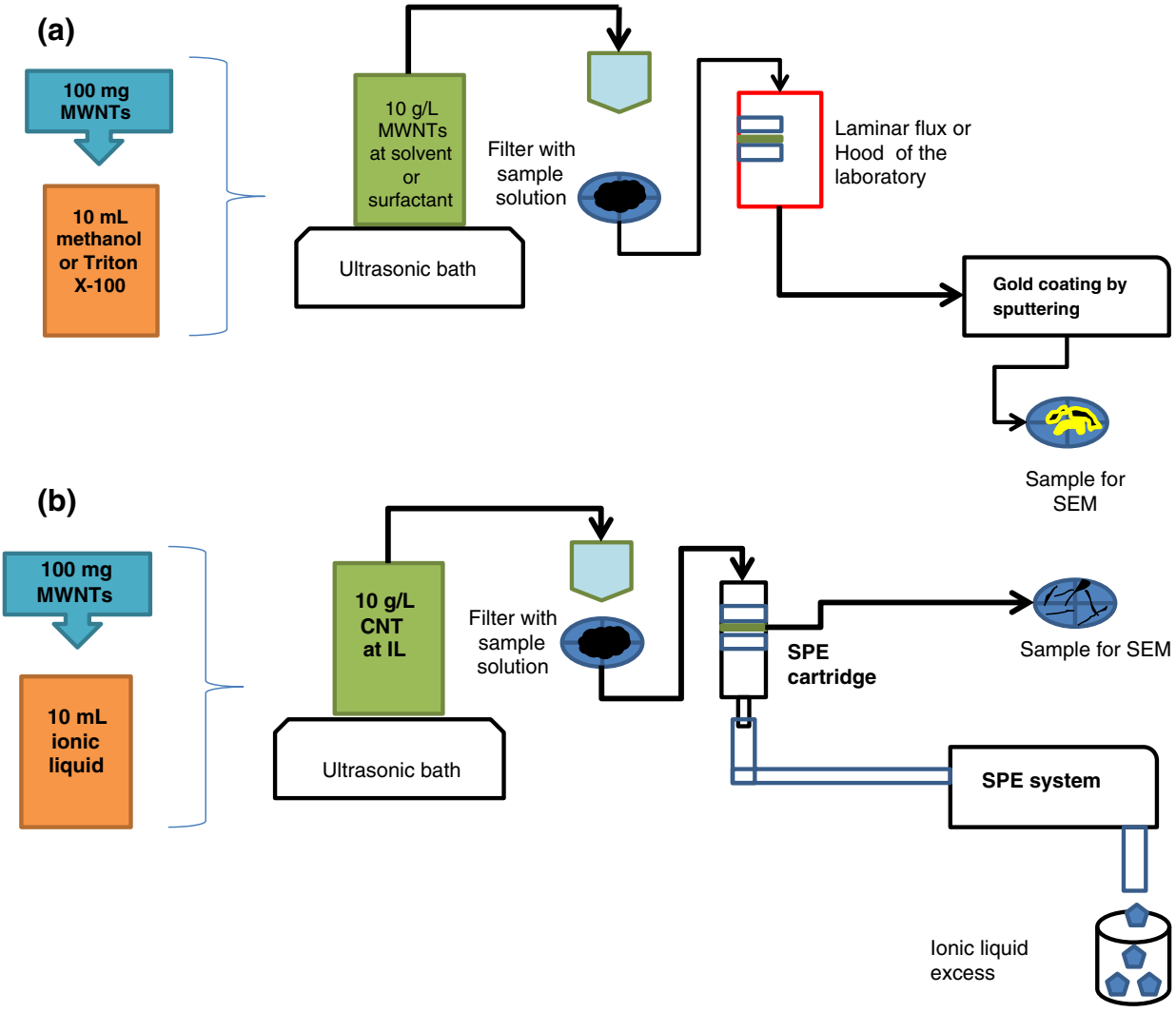

Fig. 1. Schemes of the procedures followed for the preparation of MWNT samples prior to SEM analysis: (a) using methanol and a Triton X-100 solution as dispersing agents, (b) MWNTs dispersed with the aid of ionic liquid BMIM PF_6.