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Review

Recent applications of carbon nanotube sorbents in Analytical Chemistry

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ABSTRACT

Carbon nanotubes (CNTs) are still awakening scientists' interest because of their inherent properties as well as their applications in a wide variety of fields. Regarding Analytical Chemistry, and although they have also been used as stationary phases in chromatography or pseudostationary phases in capillary electrophoresis, they have also found a particular place in sorbent-based extraction techniques. In fact, they are currently used as sorbents in solid-phase extraction, solid-phase microextraction, stir-bar sorptive extraction and matrix solid-phase dispersion, for analyte enrichment or storage, sample fractionation or clean-up as well as support for derivatization reactions. CNT surface is tuneable and, as a result, they can be suitably functionalized, aggregated or linked to other supports which increase their potential use as sorbents. They can also be arranged under different formats (cartridges, fibers, stir bars, disks, etc.) or even combined with magnetic nanoparticles, which clearly enlarge their applications. This review article overviews the most recent applications of CNTs as sorbent materials, covering the period from 2010 to early 2014.

Contents

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1. Introduction

We are currently living in the era of nanotechnology, in which challenging and interesting applications are continuously being proposed. Among new nanomaterials, the nanocarbon-based family, which includes graphene, fullerenes, nanotubes, nanodiamonds and nanohorns [1,2], has highly attracted researchers' attention in many fields. Although all these new materials show interesting properties, carbon nanotubes (CNTs) studies have particularly triggered an exponential growth in nanoscience, being at the forefront of scientific research in physics, chemistry, material sciences, etc.

As it is well known, CNTs are graphene sheet structures rolled up in the shape of a cylinder which can have an *open end* or a *closed end* depending on the synthetic procedure. In this sense, their synthesis and characterization, which are not easy tasks, have been recently reviewed by Liu et al. [3]. At present it is clear that the best methods for CNTs synthesis are still chemical vapor deposition (CVD), arc discharge and laser vaporization or laser ablation, with different variants/improvements (especially in catalyst preparation and new carbon sources). However, explanation for the growth mechanism of CNTs is still under a fair amount of controversy [3].

CNTs show very interesting properties that arise from one key feature: the combination of small size and immense surface area. Some of the most relevant properties are their outstanding tensile strength, high thermal conductivity and stability, high resilience, semiconducting and/or conducting electrical properties, etc. [4–6]. As a result, CNTs have been used in different disciplines. Some recent review articles have covered their specific applications in drug delivery [7,8], reproductive medicine [9], as biosensors [8], as scaffolds for tissue engineering [8], and for decontamination purposes [8], among others.

CNTs are also playing an interesting role in Analytical Chemistry [10], in particular, for sample preparation. In this sense, and as it is well known, the use of sorbent-based techniques has found a very important place in sample preparation as a result of their high extraction capacity and selectivity. In general, solid-based sorbents can be used for different purposes depending on the physicochemical properties of both analyte and stationary phases and therefore, on the extraction mechanism/principle. Analyte enrichment or storage, sample fractioning or clean-up as well as support for derivatization reactions are some of the examples. Essentially, solid-phase extraction (SPE), matrix solid-phase dispersion (MSPD), solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) comprise the sorbent-based techniques most commonly used, in which CNTs have also been applied. In this sense, CNTs are suitable sorbents for the extraction of both organic and inorganic analytes because of the previously mentioned combination of small size and extremely high surface area. On the one hand, they are somehow tuneable and they can be functionalized, aggregated or linked to other supports which may increase their affinity toward target compounds. On the other hand, they can be arranged under different presentations or formats (cartridges, disks, fibers, stir bars, solid suspensions, etc.) or even combined with magnetic-nanoparticles (m-NPs) which enlarge their applications.

In previous articles developed by our group in 2010 [11] and 2012 [12], we reviewed the application of CNTs in SPE [11] as well as their more general application in Separation Science [12]. Following this trajectory, this article aims to overview the most recent and challenging applications of CNTs sorbents, focusing on articles published in the period 2010 until early 2014. First, the different modifications of CNTs that may have an interesting effect on their use as sorbents will be presented, to continue with their most recent applications in the different sorbent-based extraction techniques used for Analytical Chemistry purposes.

2. CNTs modifications

2.1. CNTs functionalization

CNTs functionalization allows the modification of their physical and chemical properties. Very often, CNTs surface is altered for this purpose or to change their selectivity, depending on the final required characteristics. This modification not only enlarges their potential but also enhances their solubility, which is extremely low in most solvents due the strong intertube van der Waals interactions [13,14].

The functionalization process frequently includes an acidic or an oxidative treatment that also reduces the impurities resulting from the synthetic procedure of CNTs. It can be done using either easy or complex methodologies to obtain covalent [15,16] or non-covalent [15,17,18] modified CNTs. On the one hand, covalent functionalization could be carried out by direct covalent sidewall functionalization with the molecule of interest or by indirect covalent functionalization with carboxylic groups previously introduced on their surface [15,16]. On the other hand, CNTs tend to form non-covalent aggregates via van der Waals forces, π–π stacking interactions, hydrogen bonds, electrostatic forces and hydrophobic interactions [15,17,18]. The combination of two or more of these interactions improves the stability and the selectivity of the system. A particular case of non-covalent functionalization is the endohedral filling of CNTs with atoms or small molecules. The encapsulation not only protects small molecules against the external environment and prevent from aggregation but also improves the dispersion stability of core-shell nanomaterials in a wide range of solvents [4]. From a detailed revision of the literature, it is quite clear that a high number of procedures for CNTs sidewall modifications have been published in the period covered by the present review in addition to their later application as sorbents (see Tables 1–5).

With the aim of verifying CNTs functionalization and demonstrating that the sorptive structure has changed, a combination of different structural characterization techniques is frequently used. Among them, electronic microscopy (principally transmission electron microscopy, TEM), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and X-Ray photoelectron spectroscopy (XPS) are the most widely used. Electronic microscopy not only provides a 3D image of the material but also allows a semi-quantitative study of the elemental composition, depending on the instrument. FTIR and Raman are complementary techniques that allow confirmation of the molecular structure of liquid, solid or gas inorganic and organic samples through their covalent bonds. XRD supplies information about the crystal structure of compounds and imperfections or defects in the materials, while TGA allows deducing the introduction of changes in a compound by measuring the variation of decomposition temperatures. Finally, XPS provides information about the chemistry composition of CNTs surface. This set of