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Carbon nanotools as sorbents and sensors of nanosized objects: The third way of analytical nanoscience and nanotechnology

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A B S T R A C T

This review describes the current state and the challenges of Analytical Nanoscience and Nanotechnology (AN&N) regarding the use of carbon nanomaterials as nanotools for nanoparticle characterization and determination, which is included in the "Third Way" of AN&N. Therein, this review article attempts to provide a systematic comparison of the recent analytical methodologies involving carbon nanoparticles as analytical tools in this context, which focuses, on the one hand, on the preconcentration and capture of nanoanalytes and, on the other hand, on the sensing and detection of other nanoparticles.

Contents

1. Introduction

Engineering nanoparticles hold promise as novel materials in a wide range of applications owing to their exceptional properties by virtue of their reduced size. In the last years, the extensively production of engineering nanomaterials and their recently incorporation into a variety of industrial processes, in commercial products and even in medicine have experienced an exponential growth, entailing potential risks and great concerns about their impact on the environment and human health [1].

Although many toxicological investigations on nanoparticles have been carried out using different cell lines and living organisms, their potential harmful effect is still unclear and sometimes even contradictory by the lack of standardised toxicological procedures for nanomaterials. Nanoparticles are naturally or intentionally be present

Abbreviations: AN&N, Analytical Nanoscience and Nanotechnology; AuNPs, gold nanoparticles; AgNPs, silver nanoparticles; C NPs, carbonaceous nanoparticles; CAPS, 3-(cyclohexylamino)-1-propanesulfonic acid; CE-UV, capillary electrophoresis with ultraviolet-diode array detection; CNDs, carbon nanodots; CQDs, carbon quantum dots; C_{60}, Buckminsterfullerene; CNTs, carbon nanotubes; c-CNTs, carboxylic carbon nanotubes; c-MWCNTs, carboxylated multi-walled carbon nanotubes; c-SWCNTs, carboxylated single-walled carbon nanotubes; NC, nanocellulose; CTAC, hexadecyltrimethylammonium chloride; cit-AgNPs, citrate coated silver nanoparticles; FRET, fluorescence resonance energy transfer; Ksv, Stern-Volmer quenching constant; MEF, metal-enhanced fluorescence; PAH, poly(allylamine hydrochloride); GO, graphene oxide; GQDs, graphene quantum dots; IFE, inner filter effect; LSPR, localized surface plasmon resonance; M NPs, metallic nanoparticles; MET, metal enhanced fluorescence; MWCNTs, multi-walled carbon nanotubes; N-GQDs, N-doped graphene quantum dots; PAMAM, polyamidoamine dendrimers; PVP, polyvinyl pyrrolidone; SDS, sodium dodecyl sulfate; SQDs, semiconductor quantum dots; SWCNTs, single-walled carbon nanotubes; TA, thioctic acid; TiO_2 NPs, titanium oxide nanoparticles.

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in the environment [2] and afterwards entered in living organisms through direct routes. In biological systems, the unexpected toxicity of nanomaterials related to the cellular uptake, biodistribution, possible transformations over time or with biomolecules is influenced by a variety of factors such as the nanoparticle nature and size, surface-to-volume ratio, colloidal stability and surface reactivity [3–5]. Taking into account that some of these nanomaterials are considered as human life threatening, emerging analytical methodologies are recently reported to provide innovative detection strategies towards nanoparticles in a wide variety of scenarios (simple and complex matrices) [1,6].

In this context, a substantial progress in the use of nanoparticles as nanotools for analytical applications was accomplished in the last decades as a consequence of their outstanding adsorption capacities as well as their optical and magnetic properties by virtue of their large surface areas, chemical reactivity and composition, and quantum effects. Such fascinating properties, which are different from other materials, take the lead to improve and simplify available analytical methods in terms of sensitivity and specificity as well as help us to gain a better understanding and controlling of the nanoworld.

2. Third way of analytical nanoscience and nanotechnology

The particular interest of analytical chemistry in nanostructured materials has ended up in a new Era of Nanotechnology, the Analytical Nanoscience and Nanotechnology (AN&N) [7]. Thus, nanoparticles provide valuable benefits which address the diverse needs of the analytical community in improving any of the steps of the analytical process, from the sample treatment to the detection stage. Many reports about their usefulness as analytical tools [8–13] gave rise to the development of new analytical methodologies and improvement of the well established analytical processes, methods and techniques.

This first classical facet of the AN&N is based on the sorption and sensing capabilities of a wide variety of nanoparticles. The most exploited nanomaterials are magnetic and carbon-based nanostructures used as sorbent materials in the pretreatment step for the extraction, preconcentration and isolation of the target analyte [10–11], and metallic nanoparticles (M NPs) and semiconductor quantum dots (SQDs) mainly used as sensing probes because of their fascinating optical properties [12–13]. Thus, the specific affinity of the surface ligands of carbon nanostructures as well as their aromatic character afford the determination of a wide variety of analytes, from metallic ions to biomolecules, in the environmental and clinical fields [8].

The second classical role of the nanoparticles in an analytical process is to be considered as the target analyte. The determination of nanomaterials requires methods capable of detecting and quantifying traces of the nanoparticles in a variety of complex matrices. This role is of great importance since it allows the nanomatter characterization gathering relevant information about the nanoworld. However, few of such methods have been reported to date, about 30–35 % of the published articles related to AN&N, meanwhile the use of nanomatter as nanotool supposes the 65–70 % of published works within AN&N.

A combination of these two classical roles has recently appeared as a new concept in the AN&N, which has been named as the "Third Way" [14]. In this new outlook the nanomatter acts simultaneously as the tool and as the object of analysis within the same analytical process. This concept arises from the need to improve and establish new methodologies for the extraction of chemical information and accurate determination of such nanostructures. A crucial factor in this point of view lies in the possible synergies between the nanomaterials involved in the same process, giving rise to the improvement of their individual or combined properties [8,15].

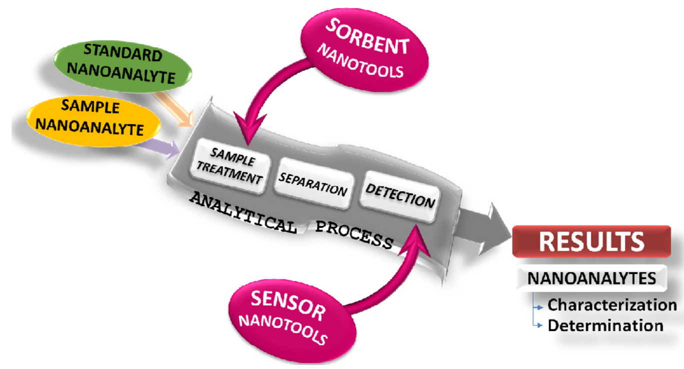

Fig. 1. Roles of nanoparticles as objects – analytes- and as analytical tools in the same analytical process, being considered as the "Third Way" AN&N.

In this new vision of the AN&N, nanostructures of same or different nature which are involved as tool and analyte can give rise to hybrid nanomaterials with excellent properties to improve the top, basic and productive analytical features. The roles played by nanoparticles in the same analytical process are summarized in Fig. 1.

As regards carbon nanostructures, this review focuses on the relatively new developments of sorbents and sensors based on carbonaceous nanoparticles (C NPs) for the determination of other nanostructures of same or different nature (metallic or non-metallic nanoparticles), with special emphasis on the nanoanalyte-nanotool interactions and sensing mechanisms amongst others (Fig. 2). Recent noteworthy applications illustrating the so-called "the Third Way" of AN&N are summarized in Table 1.

3. Carbonaceous nanomaterials

In this review, two different families of C NPs depending on the content of carbon atoms are addressed. On the one hand, a first group is composed by nanostructures of low-carbon content involving a variety of polymeric and molecular nanoparticles as well as nanocellulose (NC). Herein we only address NC for being involved in the context of the review. Those nanosized cellulose fibrils bearing multiple hydroxyl groups display a strong tendency to intramolecular hydrogen bonds. On the other hand, a second group of high carbon-content nanostructures is discussed; according to their structure and carbon hybridation, a new family of carbon nanoallotropes can be classified into fullerenes, spherical nanodots, carbon nanotubes, graphene nanoparticles and other nanostructures (nanodiamonds, nano-onions, nanohorns, nanocones amongst others). Those carbon nanoparticles exhibit particular electrical, mechanical, optical and chemical properties by virtue of the variety of sizes and shapes achieved depending on the carbon arrangement in sp^2 and/or sp^3 hybrid networks. Nowadays, despite the fascinating properties of such carbon nanostructures, only few applications have been discovered so far; we just scarcely scrapped along the iceberg of opportunities.

Interestingly, carbon nanostructures have recently been paid great attention in analytical applications since they allow obtaining more sensitive methods to determine a wide variety of analytes, being involved in any of the steps of the analytical process. Furthermore, many methods have been described by combining different carbon nanostructures or even by mixing of nanoparticles of different nature.

This review covers the uses of carbon nanostructures to determine other nanoparticles being classified by the role of the analytical nanotool, as sorbent materials or as sensing systems, as well as categorized depending on the nature of the nanoanalyte (carbon nanostructures, M NPs and metal oxide nanoparticles).