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Differences in Iron Removal from Carbon Nanoonions and Multiwall Carbon Nanotubes for Analytical Purpose

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The paper describes the differences between wet iron removal from carbon nanoonions and from multiwall carbon nanotubes for analytical purpose. Nowadays, both carbon nanoonions and multiwall carbon nanotubes are one of the most interesting materials with applicability in electronics, medicine and biotechnology. Medical applications of those nanomaterials require not only recognition of their structure but also measurement of metal impurities concentration. Inductively coupled plasma optical emission spectrometry as a method for Fe-determination requires liquid samples. Hence, we propose various protocols for leaching of iron from studied materials. Our results proved that structure of nanomaterials have an impact on the efficiency of iron removal.

Keywords: Multiwall carbon nanotubes, Carbon nanoonions, Iron, ICP-OES.

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1. INTRODUCTION

Multiwall carbon nanotubes (MWCNTs) since their discovery have been one of the most interesting materials in science. This is due to their unique properties (chemical, mechanical, magnetic and electronic) [1–3]. Another interesting material which exhibits similar to MWCNTs properties are carbon nanoonions (CNOs). Both MWCNTs and CNOs can be used in optics and electronics but also in biotechnology and medicine [4,5].

Synthesis of CNTs and CNOs often requires metal catalyst (e.g. Fe, Mo, Co, Ni and others) which usually remain in the products as impurities. But also, some elements are deliberately introduced into the nanomaterials structure in order to add to them special properties [6]. The presence of metal nanoparticles in CNTs and CNOs – both as contaminants and modifiers – should be conveniently monitored, especially as for medical application.

There were a few methods already proposed for iron content determination in MWCNTs: instrumental neutron activation analysis (INAA) [1], inductively coupled plasma mass spectrometry (ICP-MS) [7], thermogravimetric analysis (TGA) [8,9], X-ray photoelectron spectroscopy (XPS) [9], scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDX) [8,9], transmission electron microscopy/ energy-dispersive X-ray spectrometry (TEM/EDX) [9], inductively coupled plasma optical emission spectrometry ICP-OES [10] whereas for CNOs only three: TEM, XRD and TGA [11,12]. Most of these methods are only qualitative or semi-quantitative and they do not provide information about concentration or the results are only estimated. In methods such as ICP-OES or ICP-MS, which could give full information on particular elements concentration, liquid samples are required. However, because of the extreme difficulties in destruction of carbon nanomaterials structure – procedures of sample pretreatment constitute the most obstacle step in such analysis. Dry ashing coupled with acid extraction, wet digestion, combination of dry ashing with acid digestion and microwave-assisted digestion as a MWCNTs sample pretreatment protocol for ICP-MS were already proposed [7]. These methods are time-consuming, laborious, and multistage. They also require the use of aggressive chemicals and conditions and depend on the type and structure of materials. In addition, they not always ensure complete extraction of the interesting element. This behavior can cause some mistakes in the further analysis. A use of MWCNTs or CNOs certified reference materials would be the most appropriate procedure to estimate the efficiency of iron removal. Unfortunately, such materials have not been yet available since a huge variety of molecular architectures of these carbon nanostructures were synthesized under a range of different conditions.

In this paper we propose a method of removing iron from the CNOs as an sample pretreatment protocol for the ICP-OES analysis. In addition, the same experiments were conducted for MWCNTs to present similarities and differences in the behavior of these materials under different conditions.

2. EXPERIMENTAL

2.1 Materials and reagents

MWCNTs and CNOs were synthesized via catalytic chemical vapor deposition (c-CVD). MWCNTs were obtained according to a procedure previously described, briefly at 760 °C using $FeCp_2$ as iron precursor, toluene as carbon source and Ar as carrier gas [13]. In turn, CNOs were obtained from hydrogen pre-treated iron oxides nanoparticles as catalyst, acetylene as carbon source and Ar as carrier gas (800 °C).

To remove iron from examined material nitric acid (65%, Suprapur, Merck), sulfuric acid (98%, Suprapur, Merck) were used. For calibration stock standard solutions of Fe (1mg mL-1 in 2% HNO_3, CPI International)

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was used. All solution and samples were prepared with using ultrapure water (MilliporeElix 10 System).

2.2 Instrumentation

Scanning electron microscope (Phenom Pro Desktop SEM) was used to obtain the micrographs of MWCNTs and CNOs.

All determination of Fe concentrations were performed utilizing Varian 710-ES spectrometer equipped with an OneNeb nebulizer (Varian, Australia). Operating parameters are described in Table 1.

Table 1 – The operating parameters of ICP-OES analysis

RF power, kW	1
Ar plasma flow rate, L min^{-1}	15
Ar carrier flow rate, L min^{-1}	1.5
Nebulizer pressure, kPa	210
Pump rate, rpm	15
Viewing	axial
Fe wavelength, nm	234.350, 261.187, 261.382

2.3 Sample pretratment

Five different conditions were chosen to examine the extractability of iron from CNOs and MWCNTs: water, diluted HNO_3, concentrated HNO_3, mixture of concentrated HNO_3 and H_2SO_4 (4:1) and microwave digestion (MARS 5 CEM Corp. 200°C, ramp time 15 min., hold time 15 min.) in mixture of concentrated HNO_3 and H_2SO_4 (4:1). All the samples, with the exception of samples for mineralization, were shaken with the solution for 12 hours at room temperature using the laboratory shaker. After that samples were filtered and the obtained solutions were analyzed using ICP-OES.

3. RESULTS AND DISCUSION

3.1 Structure

Firstly, SEM micrographs of examined materials were prepared to compare their structures (see Fig. 1).

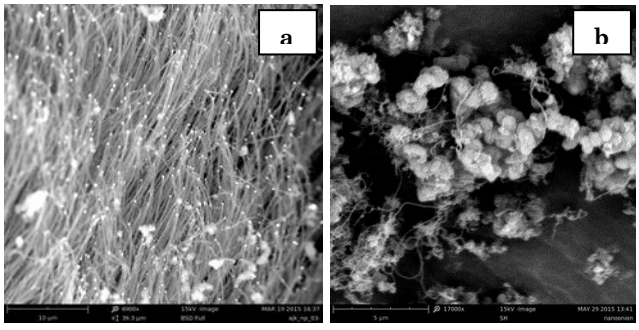

Fig. 1 – SEM image (a), MWCNTs with encapsulated Fe catalyst (b), CNOs with encapsulated Fe catalyst

The differences in structure of carbon nanotubes and carbon nanoonions are clearly visible. CNOs have a spherical shape with smooth surface in contract to the MWCNTs that have the needle-like fiber shape. This difference was also visible in product of mineralization. CNOs after mineralization get slurry of small particles evenly dispersed in a solution whereas MWCNTs gets a slurry of puffed up bundles of a significantly greater volume (see. Fig. 2).

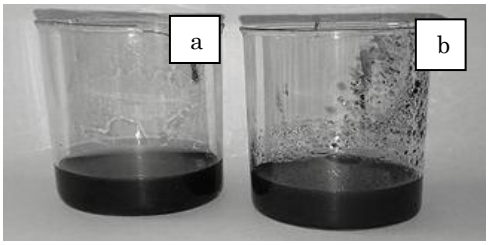

Fig. 2 – Slurries after mineralization (a), CNOs (b), MWCNTs

3.2 Determination of iron content in leachate by ICP-OES analysis

Iron content in studied CNOs and MWCNTs obtained after leaching with nitric and sulfuric acid in a few conditions are presented in Fig. 3a and 3b. Results obtained from water solution were omitted because iron wasn't being removed under these conditions.

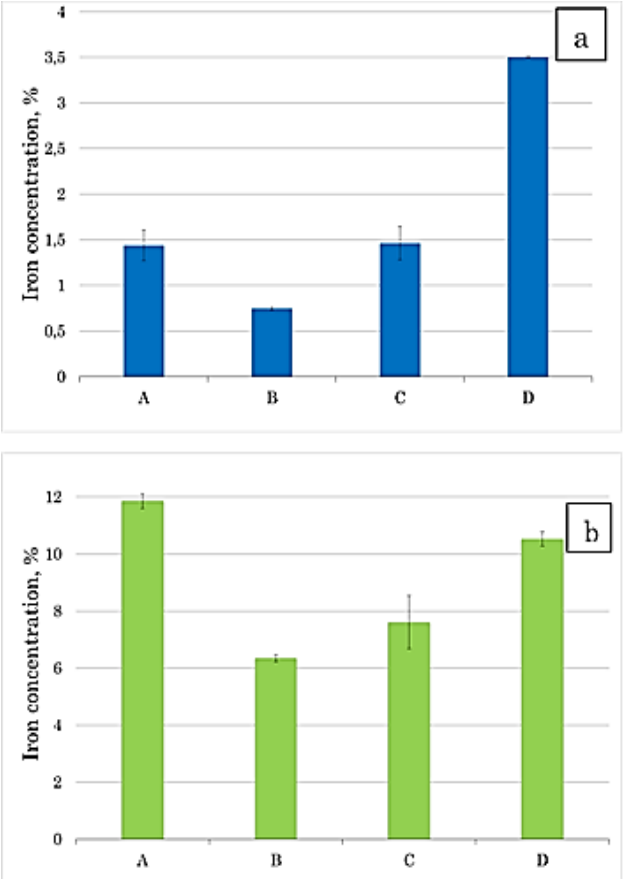

Fig. 3 – Iron concentration (ICP-OES) in (a), CNOs (b), MWCNTs obtained after using different sample pretreatment: A – 5% HNO_3, B – conc. HNO_3, C – mixture of conc. HNO_3 and conc. H_2SO_4 (4:1), D - mixture of conc. HNO_3 and conc. H_2SO_4 (4:1) and mineralization

The best results for CNOs and MWCNTs were measured if diluted nitric acid and microwave mineralization in mixture of concentrated nitric and sulfuric

acid were used respectively. When concentrated nitric acid was used the obtained results were about half lower than when diluted acid was used. It could be due to the fact that in concentrated acid iron is rendered passive. If 5% HNO_3 and mineralization in conc. HNO_3 and H_2SO_4 were used the highest content of iron was removed from CNOs (there is only a 12% difference). Otherwise, in the case of MWCNTs difference in obtained results, in mentioned condition, was about 40%. This fact may be related to differences in the structure of the CNOs and the MWCNTs. Fiber like structure in which iron is encapsulated makes MWCNTs less susceptible for acid treatment.

The result obtained shows the differences between the removal of iron from MWCNTs and CNOs. This fact proves that before carrying out the analysis of any others carbon-based nanomaterials, protocols of sample pretreatment should be carefully studied as the first step.

4. CONCLUSIONS

In this paper we proved that the sample pretreatment protocol is crucial step in analysis. We present that different leaching media, used to remove iron, lead to different results. The differences in structure of the MWCNTs and CNOs have also an impact to the iron removal. Moreover, the obtained results could be useful in the development of method for CNOs purification or direct fast and simple analytical method for determination of metal content in such nanomaterials.

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