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Removal of metal particles from carbon nanotubes using conventional and microwave methods

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ABSTRACT

A removal of different metals using both acid reflux and the microwave assisted digestion method was investigated. As a carbon material multi-walled carbon nanotubes synthetized on iron, cobalt and iron–cobalt catalysts without support were applied. The amount of metal particles after purification was determined using a thermobalance and it was found that microwave heating improved the efficiency of purification, especially at elevated pressure. Similar removal degrees of catalyst particles were achieved using the acid reflux method for 24 h and microwave heating for 15 min at 20 at regardless of the kind of metal. Raman measurements indicate that all the obtained samples were characterized with a high ratio of peak IG/ID intensities which confirms a good quality of the materials.

1. Introduction

Carbon nanotubes (CNTs) are nanocrystalline carbon materials with unique properties: mechanical, thermal and electronic, which make them suitable for use in field emission devices, molecular electronics, aeronautics, fillers to polymers and many other applications [1–3].

A number of methods for the synthesis of carbon nanotubes (CNTs), including: chemical vapor deposition (CVD), electric arc discharge or laser sputtering of graphite have been developed. One of the most commonly used methods is chemical vapor deposition, which is simple, cheap and very attractive for mass production. The final product contains various contaminants in the form of catalyst particles and by-products of synthesis. A sample can be composed of amorphous carbon, carbon nanofibers or encapsulates, which have a metal core surrounded by graphite layers. Therefore, after synthesis the purification of carbon nanotubes is usually necessary.

The available papers describe many CNTs purification techniques but the most popular one is the oxidation of carbon nanotubes in the liquid phase, which is usually conducted using nitric acid (HNO_3), nitric acid and sulfuric acid (H_2SO_4), perchloric acid ($HClO_4$), sulfuric acid and potassium dichromate (K_2CrO_7), sulfuric acid and potassium permanganate ($KMnO_4$) or hydrogen peroxide (H_2O_2). This method enables effective removal of metal catalyst or catalyst support [4,5]. Oxidative processes are used also for the modification of carbon nanotube surface which results in an increase of CNTs solubility in water [6], and which provides a method to conjugate them with biomolecules such as proteins [7], to open their ends and to fill them with various materials [8].

The efficiency of oxidation treatment, which can be combined with physical methods, e.g. filtration, depends on nanotube morphology (single-walled SWCNTs or multi-walled MWCNTs), their growth process and contamination of carbon material with metal catalyst. For example, the purification of non-supported CNTs from metal particles and carbonaceous impurities reported by Ando et al. [9] required 69 h of refluxing. In another report [10], SWCNTs were heated in air at 300 °C for 12 h to remove amorphous carbon. Then, a sample was stirred in concentrated nitric acid at 60 °C for 24 h in order to dissolve nickel nanoparticles. Next, the sample was heated in a furnace at 1200 °C, in flowing hydrogen for 2 h, and again was stirred in concentrated nitric acid at 60 °C for 3 h and heated in flowing hydrogen for 2 h. The TGA analysis of this SWCNTs sample showed that it contained only a negligible amount of impurities after the second hydrogen treatment. In another paper [11], MWCNTs were treated in boiling concentrated nitric acid under reflux at 120 °C for 50 h in order to remove amorphous carbon and traces of Fe/Al_2O_3 catalysts. All impurities (traces of Al, Fe and amorphous carbon) are effectively removed in the reaction with almost one hundred percent efficiency.

A purification of MWCNTs [12] was performed by sample calcination in the furnace at 450 °C for 60 min under oxygen atmosphere at ambient pressure. Next, the material was immersed in

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3 M solutions of different acids of HNO_3, H_2SO_4, HCl and HF for 24 h at room temperature. The removal of Fe–Ni/MgO metal particles required more than 24 h. The degree of removal of the catalyst was the lowest for MWCNTs treated with HF (approximately 50%). The best results were obtained for material purified using HNO_3, H_2SO_4 and HCl (above 80%).

Summarizing, the acid reflux method cannot be successfully applied to CNTs produced using the CVD method because it is often unable to remove catalyst particles and other impurities. Additionally, the method is time-consuming.

An alternative route to the purification of carbon nanotubes can be a microwave assisted acid method. It is a promising technology for large-scale purification, avoiding long processing time or multiple stages, utilizing minimal acid volumes and achieving high purity of carbon material. The microwave assisted purification generates high temperatures in metal catalyst particle impurities which either burst any carbon overcoats or preferentially oxidize carbon surrounding the particle in order to increase the accessibility of metal particles for subsequent acid treatments [13]. A high temperature (above the boiling point of the reactant) might activate the reactivity of CNTs, permitting their modification in new kinds of reactions that do not occur under classical reflux heating.

The available papers concern microwave treatments requiring a two-stage acid wash/reflux, leading to increased handling and processing costs for any commercial operation. Subsequent research demonstrated that incorporating acid during microwave irradiation improved purification (>90% efficiency) while simultaneously reducing processing and handling requirements. For example in the paper [14] the efficient purification of MWCNTs proceeded in the temperature of 210 °C for 30 min and then kept for 10, 20, 30 to 120 min with nitric acid treatment in the microwave digestion system to dissolve the metal catalyst. After the treatment the total amount of catalyst dropped from 10.39% to 1.75% during a 10-min digestion and to 1.03% in a 120-min treatment. In another case [15] the purification of MWCNTs on Fe/Al_2O_3 catalyst was carried out using the microwave digestion at 230 °C for 30 min using sulfuric acid. The total amount of catalyst dropped to 1.9%. In the paper [16] MWCNTs on Co/SiO_2 catalysts were purified. The first digestion step was run at 210 °C for 20 min with a 1:1 mixture of 5 M HNO_3 and 5 M HCl. The microwave power was set at 100 W. The second digestion step was carried out at 210 °C for 30 min. After purification, the amounts of residual catalyst metals in the samples were reduced from 30 to 5 wt%. These examples clearly show that the microwave purification process is inherently more amenable to industrial scale-up purification, orders of magnitude higher than other approaches [9].

In this work the possibility of the removal of different kind of metals using the microwave assisted digestion method was investigated. As a carbon material multi-walled carbon nanotubes synthetized on the iron, cobalt and iron–cobalt catalysts without support were applied. The results were compared with those obtained with the nitric acid reflux technique. Morphological, structural and spectroscopic analysis was performed for catalysts and obtained carbon materials, both before and after the purification.

2. Experimental

2.1. Catalysts preparation

Nanocrystalline catalysts based on iron, cobalt and both metals were obtained from cobalt (II) and iron (III) nitrates together with a small amount of calcium and aluminum nitrates. The salts were dissolved in distilled water and 20% NH_4OH was added as a precipitating agent continuously, to obtain a pH of 8. Metal hydroxides were precipitated from the solution and the deposit was washed with water, filtered and dried at 110 °C. The next step was the calcination at 500 °C for 1 h to obtain the precursors of nanocrystalline metals – cobalt and iron oxides with a small amount of structural promoters – CaO and Al_2O_3. In the last stage of preparation the precursors of nanocrystalline metals were reduced under hydrogen atmosphere polythermally at the temperature rising from 20 °C to 600 °C. For all the catalysts, reduction processes were conducted until the mass was stabilized within 90 min.

2.2. Carbon nanotube growth

The synthesis of nanocarbon materials was carried out in a high-temperature furnace (HST 12/400 Carbolite). The catalyst samples were placed in a quartz boat inside a ceramic tube (diameter 70 mm, length 120 mm) of the furnace. After reduction of the catalyst at 600 °C, the temperature was increased to 700 °C. When the temperature was stable, ethylene – as a carbon source – together with argon was introduced into the chamber. The processes were performed under atmospheric pressure for 1 h.

2.3. Purification of MWCNTs

The purification of carbon nanotubes was performed in two ways. The first approach involved the traditional acid reflux method, the second – microwave assisted heating. Microwave heating was conducted under atmospheric pressure in the open system and under elevated pressure of 20 at.

Before purification, carbon nanotubes were oxidized in order to remove amorphous carbon from their surface. Oxidation was carried out in a high-temperature furnace in the air atmosphere at 400 °C for 1 h. Next, the samples were placed into a flask. The process was conducted under reflux in the presence of 5 M HNO_3 (5 g of MWCNTs per 100 ml of HNO_3) for 0.5 or 24 h. The residue was collected by vacuum filtration through a 0.2 μm PC membrane, carefully washed with distilled water until a pH value of about 7 was reached and at the end washed with acetone. The samples were dried overnight in an oven at 110 °C.

In the second, case multi walled carbon nanotubes directly after their growth were used. A sample of approximately 1.0 g with 50 ml of 5 M nitric acid was placed into a Teflon vessel and next in a microwave reactor (Ertec Magnum II). The process was conducted for 30 min under a pressure of 20 at. Optionally the purification of carbon nanotubes was carried out in the microwave reactor but under atmospheric pressure. After cooling down of the reactor the sample was collected by vacuum filtration through a 0.2 μm PC membrane, carefully washed with distilled water until a pH value of about 7 was reached and at the end washed with acetone. The samples were dried overnight in an oven at 110 °C.

2.4. Characterization

The phase composition of the as-synthesized samples and the samples after purification step was characterized by X-ray diffraction method. Before measurement the samples were triturated in an agate mortar and pressed into the ring. The rings were placed in a holder of the diffractometer. Analysis was performed on the X'Pert PRO Philips diffractometer using a Cu Kα radiation.

The quality of the carbonaceous material was determined using Raman spectroscopy. Raman spectroscopy can verify the integrity of MWCNTs because the method is sensitive to variations of structural disorder in carbon nanotubes. The important bands of RS are the D band (1350 cm^{-1}), the G band (1580 cm^{-1}) and the 2D band (2700 cm^{-1}) [17,18]. Raman spectra were obtained using excitation laser lines 785 nm (1.58 eV) with a Renishaw InVia Raman