

Purification of multiwall carbon nanotubes obtained by AC arc discharge method

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In this paper we report several different methods that can be used for the purification of multiwall carbon nanotubes (MWCNT) obtained by the AC arc discharge method. The purification of multiwall carbon nanotubes is required in order to eliminate the metal catalyst and amorphous carbon. The removal of the metal catalyst was carried out by treatment with different acids. Subsequently, we have applied two different methods for removing also the amorphous carbon. The first approach for the purifying of the MWCNT was the weak oxidation performed by refluxing the MWCNTs in strong acid for 6 h and the second method was the oxidation with air for 10 minutes. The samples were analyzed using FE-SEM (Field Emission Scanning Electron Microscope), powder X-Ray diffraction (XRD) and Raman spectroscopy and the results were discussed.

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1. Introduction

It is well known from a long time that the elemental carbon exists only in three forms - amorphous, graphite and diamond. Different types of carbon in the sp^2 hybridization can form a variety of amazing structures. One of these amazing structures was discovered by Kroto et al. and was called fullerene [1]. Fullerenes are similar in structure with graphite and are composed by a sheet of linked hexagonal rings, but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. In a very short period of time after the discovery of fullerenes, new forms of carbon were identified.

In 1991 Iijima [2] observed for the first time tubular carbon structures which consisted of up to several tens of graphitic shells (so called multi-walled carbon nanotubes (MWCNT)). Two years later, Iijima and Ichihashi [3] and Bethune et al. synthesized single-walled carbon nanotubes (SWNT).

No matter of the method used for the synthesis of multiwall carbon nanotubes (MWCNT), the product obtained presents in its composition, carbon nanostructures, graphitic sheets, amorphous carbon, metal catalyst and small amount of fullerenes.

Before the use of carbon nanotubes in different applications [4-9] it is necessary to be purified. Purification of carbon nanotubes must be performed for the impurities and unreacted reagents removal. The most common purification methods are the oxidation by different techniques, treatment with different acids, calcinations etc.

In this paper we present the researches carried out to get new purification methods of carbon nanotubes which

consist in weak oxidation by refluxing the samples in acid and the oxidation in air.

2. Experimental

2.1 Multiwall carbon nanotubes synthesis

Multiwall carbon nanotubes were synthesized by AC arc discharge method in argon ambient with the pressure of 250 mbar using pure graphite electrodes with different diameter 12 mm and 3 mm, and iron catalyst [10].

2.2 Purification procedure

Multiwall carbon nanotubes were purified applying two different methods. One method was used in order to eliminate the metal catalyst from multiwall carbon nanotubes and the other one for the removing of amorphous carbon. The removal of the metal catalyst was carried out by refluxing the carbon nanotubes in nitric acid (63%) for 6 h at 118°C and in hydrochloric acid (37%) for 6 h at 105°C. The purification procedure is presented in Fig. 1, (a). The method for removing amorphous carbon from multiwall carbon nanotubes was air oxidation for 10 minutes at 550°C. The heating regime is presented in Fig. 1, (b). The sample with MWCNT purified by treatment with nitric acid was noted as MWNT_HNO₃ and the sample with MWCNT purified by treatment with hydrochloric acid was noted as MWNT_HCl.

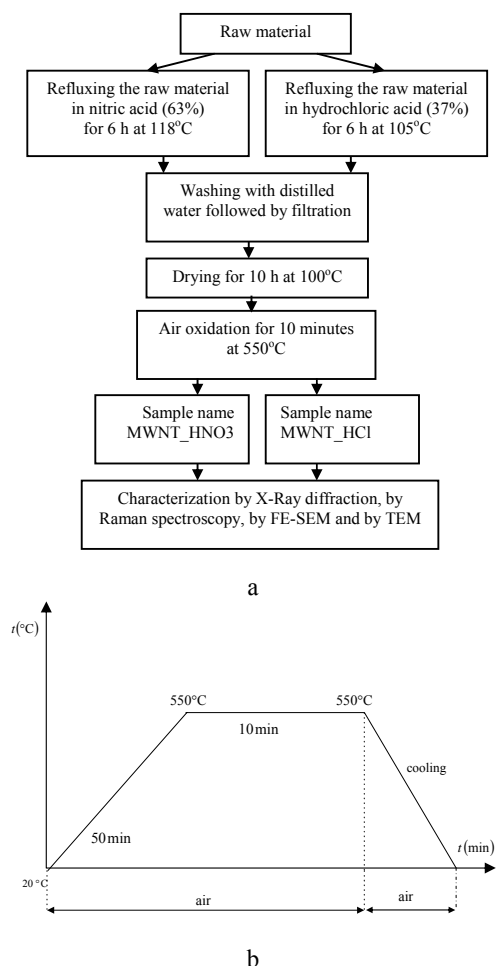


Fig. 1. (a) Schematic of the purification procedure; (b) Heating regime.

2.3. Structural analysis

The materials obtained before and after purification were characterized by powder X-Ray diffraction (XRD), by FE-SEM (Field Emission Scanning Electron Microscope), by Raman spectroscopy and by TEM (Transmission Electron Microscopy).

Diffraction patterns were recorded on a D8 ADVANCE Nova diffractometer using the characteristic radiation $K\alpha$ of copper, at a voltage of 40 kV and 5 mA intensity.

The quality, but also the major modifications of the multiwall carbon nanotubes caused by this purification procedure were investigated by Field Emission Scanning Electron Microscopy (FE-SEM). The equipment used was Nova NanoSEM 630.

Raman spectra of the multiwall carbon nanotubes produced were recorded using one excitation wavelength (532 nm) on a NRS-3000 Raman equipment from Jasco.

The TEM investigations were performed using a TECNAI/FEI F20 instrument equipped with a 200 kV electron gun.

3. Results and discussion

Fig. 2 shows the X-ray diffractograms of the MWNT_HNO₃, MWNT_HCl and raw material samples for 2θ from 1 to 60°.

Intrinsic peak of raw material is observed at ca. 26° and all spectra have that peak at the same position. This peak corresponds for the typical structure for MWCNT [11].

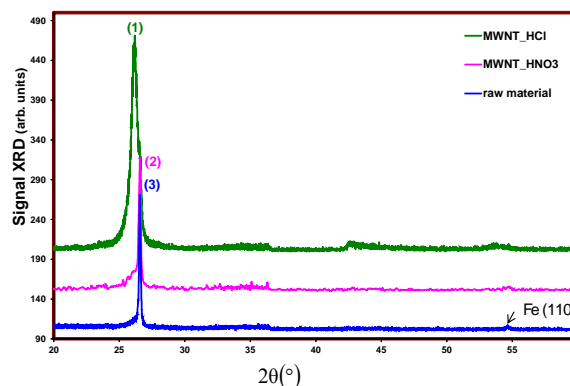


Fig. 2. X-ray diffractograms of the MWNT_HNO₃, MWNT_HCl and raw material samples

The concentrations of nitric acid and hydrochloric acid used for purification of carbon nanotubes don't affect the position of this peak. Crystallite size was calculated by Scherrer's equation using the data of integral breadth of the peaks (Table 1). In conclusion, the reflux with nitric acid and hydrochloric acid make no change of crystallinity in carbon nanotubes, but make change of the crystallite size of the nanopowders.

The diffractogram of the raw material sample shows a peak diffraction of Fe catalysts at ca. 54.6°. After purification treatment, the diffraction intensity of the Fe (110) peak is reduced. We concluded that reduction of Fe content due to the chemical treatment.

Table 1. Indexing of diffraction lines.

Sample name	D. lines	2θ (°)	d (Å)	FWHM (°)	D(nm)
MWNT HCl	1	26.19	3.402	0.586	13.76
MWNT HNO ₃	2	26.6	3.404	0.574	14.06
Raw material	3	26.58	3.353	0.186	43.38

Fig. 3 a presents SEM image of the unpurified sample, hereinafter called raw material and the Figs. 3 b and c present SEM images of the purified samples.

In SEM image of the raw material sample are observed large bundles of carbon nanotubes and carbonaceous impurities. The raw material sample has three components: microcrystalline graphitic component, nanotubular component and granular component with the size estimated at 20 nm. In Fig. 3c the granular component

has a spheroidal shape but also has an ellipsoid shape [12] and can be found located in particular aggregates.

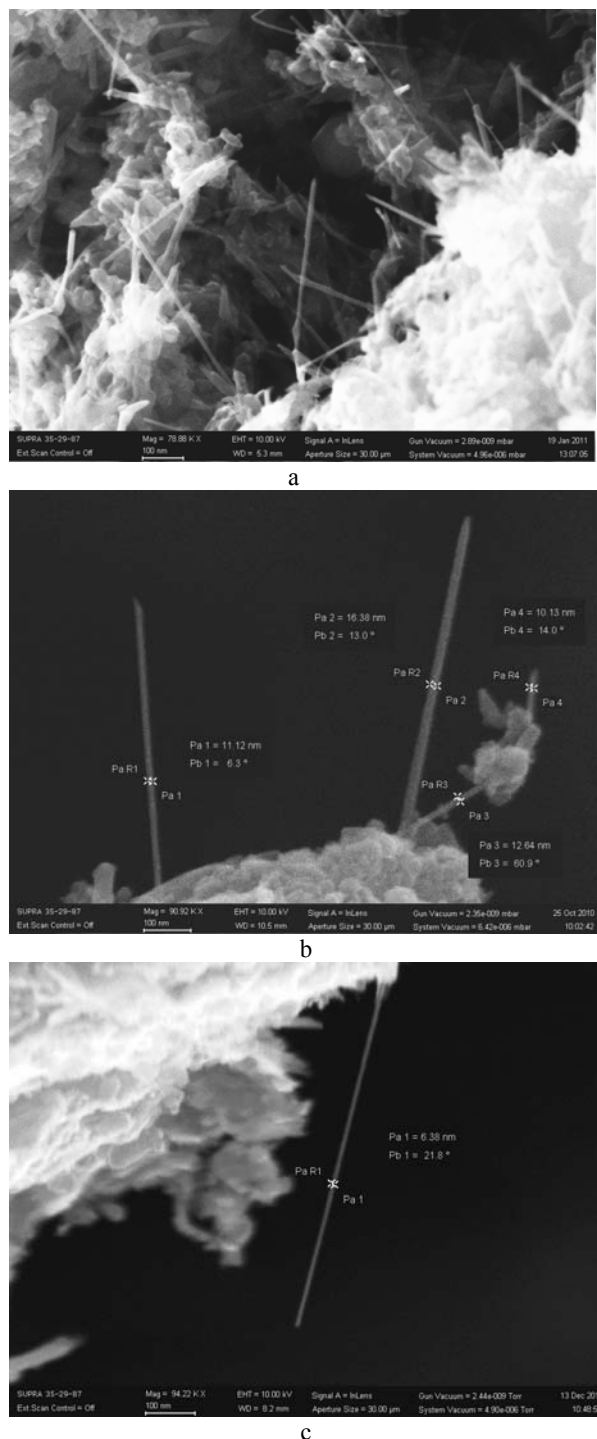


Fig. 3. SEM images of raw material sample (a), MWCNT sample treated with HNO₃ (b) and MWCNT sample treated with HCl (c).

Fig. 3 shows that the diameters of the multiwall carbon nanotubes are from range 6 to 20 nm. As a result of purification, the purity of the multiwall carbon nanotubes,

as is apparent in Fig. 3 b and c, is improved, though some granular components remained in the sample.

Fig. 4 shows the Raman spectra recorded using the 532 nm laser wavelength for MWNT_HNO₃, MWNT_HCl and raw material samples.

The use of Raman spectroscopy allows the observation of many aspects of carbon materials, especially carbon nanotubes. The Fig. 4 shows the positions for the most intense components corresponding to the D, G, and G' bands. The first and second order Raman spectra of the samples produced are compared. In Fig. 4, we can observe the presence of the so-called G-band at around 1580 cm⁻¹ for all the samples. Also, in Fig. 4, we can observed, the D band around 1335 cm⁻¹ (D peak is assigned to disordered or defective structures of the material) and the second order of the G and D bands. The most prominent second-order Raman peak historically named G' [13], is located at ~2700 cm⁻¹. The presence of the second order of Raman spectra is an additional proof of the high order degree of the samples [13].

The D band shift and the G band shift of the raw material sample are strongly shifted after the treatment with acids.

Therefore, in the samples treated with acids, the D band shifts from 1357 to 1350 cm⁻¹ and the G band shifts from 1585 to 1580 cm⁻¹. These shifts are related to a direct electron charge transfer process from the carbon nanotubes to the acceptor molecule [14, 15].

The frequencies of the various G-band peaks exhibit a clear and well-established dependence on diameter, as well as a dependence on whether the nanotube is metallic or semiconducting [16].

The intensity ratio of the G-band to the D-band can be employed to assess the quality of the MWCNT samples.

For the investigated samples the following values of G/D peak intensity ratios were found: $I_G / I_D = 1.32$ for raw material sample, $I_G / I_D = 1.19$ for MWNT_HNO₃ sample and $I_G / I_D = 1.07$ for MWNT_HCl sample.

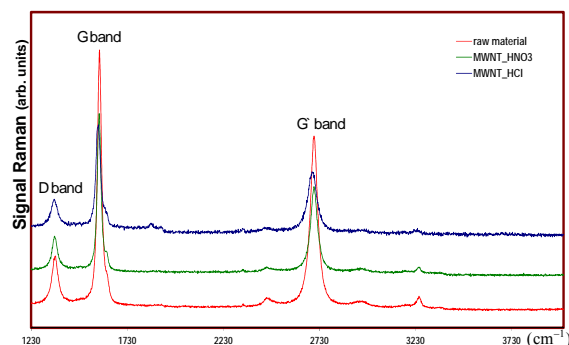


Fig. 4. Raman spectra for MWNT_HNO₃, MWNT_HCl and raw material samples.

From that it values we conclude that the raw material sample shows has a graphitic component concentration more pronounced than amorphous component. The result

is that after each chemical attack, the graphitic component in the each sample was reduced compared with the graphitic component from the raw material sample. The graphitic component from each samples are found as tiny crystals and as the form of graphitic nanostructured material (multiwall carbon nanotubes or small nanostructured forms considered as evolutionary phases of multiwall carbon nanotubes).

The treatment with acids shows a decrease of the I_G/I_D ratio. This was due to presence of the guest molecule can either intercalate the walls [17] or react with the defects in the surface creating attached functional groups [18].

We can conclude that the acid treatment strongly affects the number of defects in the MWCNT surface.

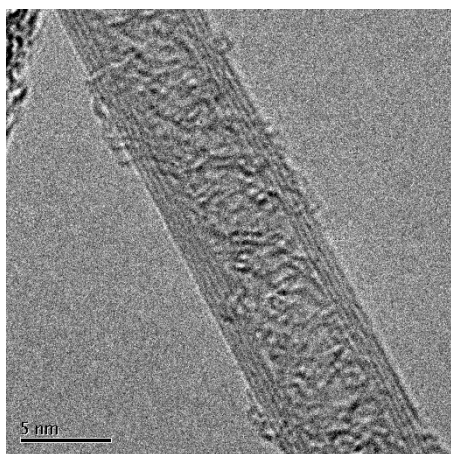
In Fig. 4 shows diverse G' band peaks for the samples purified with different acids and can be explained by the different molecular composition of the guest molecules. The relative purity of the treated MWCNT was also influenced by the introduction of the guest molecules.

Fig. 5 presents TEM images of the raw material MWNT_HNO₃, and MWNT_HCl samples. This figure shows the presence of MWCNT.

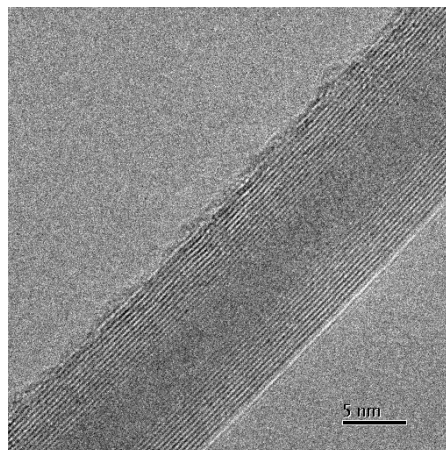
In Fig. 5 a can be observed that the amorphous aggregates appear distributed on the axis of MWCNT more than on its walls. The multiwall carbon nanotube from Fig. 5 a, has outer diameter 7.1 nm.

The multiwall carbon nanotube from Fig. 5 b has outer diameter ~13 nm and the multiwall carbon nanotube from Fig. 5 c has outer diameter ~7 nm. In Fig. 5 b and c can be observed that the MWCNT which was treated with acids were purified. Therefore, the metal catalyst and the amorphous carbon were removed.

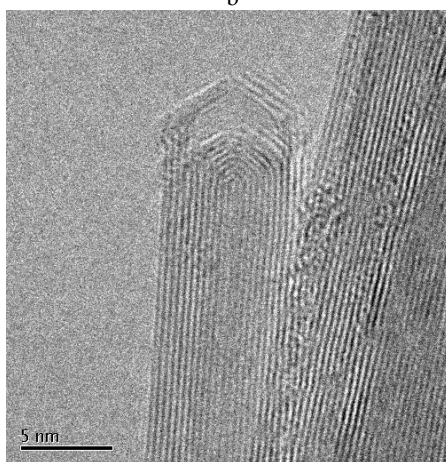
According to the TEM observations, the best quality of MWCNT (neither containing many defects nor any amorphous carbon deposit) was obtained after treatment with acids.



a



b



c

Fig. 5. TEM images of raw material sample (a), MWCNT sample treated with HNO₃ (b) and MWCNT sample treated with HCl (c).

4. Conclusions

The purification procedure is dependent on the method of synthesis of carbon nanotubes. In this paper we report a simple procedure to purify multiwall carbon nanotubes obtained by the AC arc discharge method. Metal catalyst and also amorphous carbon were oxidized by refluxing in acids including hydrochloric acid and nitric acid. Oxidation in air at 550°C removes disordered carbon, but does not eliminate the D-band. The purification procedure consisted in refluxing in different acids followed by air oxidation to obtain highly pure MWCNT samples.

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