Article

The importance of water for purification of longer carbon nanotubes for nanocomposite applications

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Abstract: Ultralong carbon nanotubes (UCNTs) are highly demanded for nanocomposites applications because of their magnificent physical and chemical properties. UCNTs are synthesized by catalytic chemical vapor deposition (CCVD) method and, before using as fillers in nanocomposites, should be purified from residual catalyst and non-CNT particles without significant destruction or scissoring of UCNTs. The role of water vapor for purification of UCNTs is investigated, the importance of water assistance in this process is confirmed. It was shown that wet air treatment of products of UCNTs CCVD synthesis under mild conditions can be used to decrease sufficiently residual catalyst content without significant carbon losses in comparison with the results obtained with dry air, while the residual iron content was shown to influence heavily on the subsequent oxidation of different forms of carbons, including UCNTs. The increasing of D/G ratio of Raman spectra after wet air treatment of products of UCNTs CCVD synthesis makes it possible to conclude that iron catalyst particles transform into iron oxides and hydroxides that caused inner structural strains and destruction of carbon shells improving removal of the catalyst particles by subsequent acid treatment. UCNTs purification with water assistance can be used to develop economically and ecologically friendly methods for obtaining fillers for nanocomposites of different applications.

Keywords: nanocomposites; ultralong carbon nanotubes; catalytic chemical vapor deposition; purification; catalyst removal; water vapor treatment; thermal analysis; Raman spectroscopy;

1. Introduction

Outstanding physical and chemical properties of carbon nanotubes (CNTs) open prospects for using them in different nanocomposites for various industrial applications such as biosensors, supercapacitors, solar cells, EMC shielding, corrosion protection materials, etc. [1]. On the other hand, some properties of nanocomposites, for example, mechanical or electrical ones, are highly dependable on the aspect ratio of CNTs and the longer the nanotubes, the better are the properties of nanocomposites [2, 3], so ultralong CNTs are in urgent need for many responsible applications. There are two main methods of synthesis of ultralong CNTs, one of which is carried out on flat substrate [4,5] and the other one is performed in fluidized-bed reactor with floating catalyst and aerogel [6]. Unfortunately, since both of these methods are based on catalytic chemical vapor deposition (CCVD) non-CNT and residual catalyst particles [7] are formed in synthesis products besides ultralong CNTs. It should be noted that purity of CNTs or low content of non-CNT and catalyst particles often represent crucial demand for better properties of nanocomposites, for example, mechanical properties such as Young's Modulus and toughness, which get increased in polymer nanocomposites when purified CNTs are used in comparison with raw CNTs [8]. There are many purification methods of CNTs including chemical methods, physical methods and combination of both [9]. Among them, the gas phase oxidative purification by air is the most popular in the community due to its convenience, economic and ecological reasons. This method is based on the fact that non-CNTs have usually higher oxidation activity in comparison with CNTs, - for example, non-CNTs are easily

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oxidized at 480 - 500°C, while single wall CNTs (SWCNTs) begin to oxidize at higher temperatures [10]. However, some metals such as iron or their compounds being the catalyst of carbon oxygen oxidation [3] can level out these differences between oxidation activity of CNTs and non-CNTs resulting in very low yield of pure carbon nanotubes. So, to minimize the undesired oxidation of CNTs and increase the yield of final product before air oxidation it is necessary to remove the residual catalyst particles. According to [11] SWCNTs can be purified from iron catalyst by wet air treatment under mild conditions excluding carbon oxidation (at 225-425°C) followed by acid treatment, and the mechanism of this purification is based on density changes of iron under oxidation, which are 7.86 and 5.13 cm^3/g for iron and iron (III) oxide, respectively. The decreasing of iron density resulting from oxidation causes swelling of encapsulated iron, destruction of carbon shell and exposing of iron for the following acid treatment. It should be noted that this method was discussed for using only for purification of SWCNTs [11], while there are no publications on ultralong multiwall CNTs (UCNTs) purification by this method, despite the fact that UCNTs are quite perspective for using in nanocomposites [12,13].

This work is devoted to study of water influence on purification of ultralong CNTs, obtained by water-assisted CVD method [7].

2. Materials and Methods

CNTs were synthesized as mentioned earlier by water-assisted CCVD from ethanol, ferrocene and thiophene as carbon source, catalyst and CNTs growth activator, respectively [7]. The mild oxidation was carried out in quartz tube reactor at 400°C for 6 or 12 hours under dynamic (50 ml/min) synthetic air atmosphere. Before dynamic synthetic air was entered into reactor with CNTs, it was bubbled through distilled water at 50 or 80°C. After mild oxidation, the samples were treated with 18 wt.% hydrochloric acid at 70°C for 4 hours (2 times for 2 hours), rinsed with distilled water after acid treatment until pH of water was higher than 4 and dried at 110°C for 1 hours. The heat treatment was carried out at muffle furnace under static air atmosphere at 480°C for 2 or 6 hours.

Thermogravimetry was carried out using NETZSCH STA 449 F1 device in alumina crucible with the heating rate of 10 K/min under dynamic synthetic air atmosphere (50 ml/min). Raman spectroscopy was carried out using Renishaw inVia Raman Microscope device. Scanning electron microscopy (SEM) with energy dispersive X-Ray analysis (EDX) was carried out using TESCAN VEGA 3 SEM device. To calculate Fe residual content in samples, the mass, remaining after thermogravimetry, was multiplied by 0.7 in accordance with approximation that all metallic Fe in samples converts to Fe_2O_3 during oxidation.

The marking of samples treatment and their treatment conditions are presented in Table 1.

Table 1. Marking of samples and conditions of their treatment

Sample	Description
INI	Initial CNTs synthesis product
AT	INI after acid treatment
MO_0	INI after mild oxidation without water at T_{CNT}^{*}=400°C and t_{MO}^{**}=6 hours and acid treatment
MO_W1	INI after mild oxidation with water at T_{CNT}^{*}=400°C, T_{H2O}^{***}=50°C, t_{MO}^{**}=6 hours and acid treatment
MO_W2	INI after mild oxidation with water at T_{CNT}^{*}=365°C, T_{H2O}^{***}=50°C, t_{MO}^{**}=6 hours and acid treatment
MO_W3	INI after mild oxidation with water at T_{CNT}^{*}=400°C, T_{H2O}^{***}=80°C, t_{MO}^{**}=12 hours and acid treatment

*T_{CNT} - temperature of mild oxidation, **t_{MO} – time of mild oxidation, ***T_{H2O} – temperature of water bath during bubbling of purge gas,

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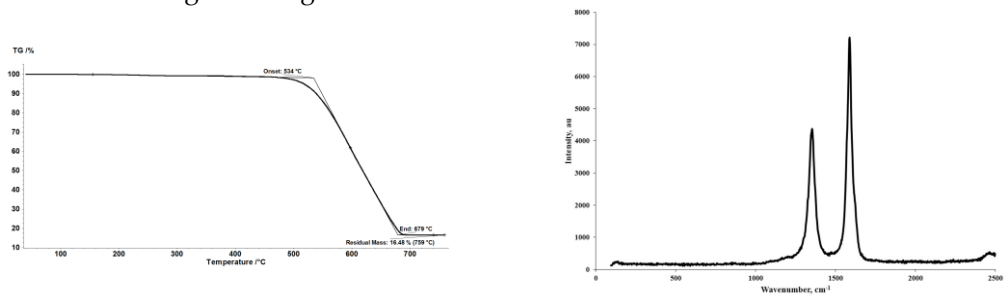
3. Results

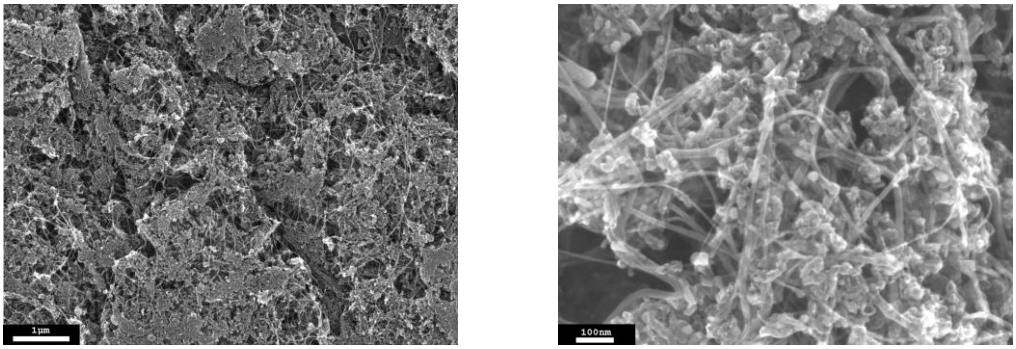
3.1. Free or unbound iron

To find out the quantity of free or unbound iron in CNTs synthesis products, they were treated by hydrochloric acid at 70°C for 4 hours, then rinsed with distilled water until pH was higher 4 and dried at 110°C. Thermogravimetry, Raman spectroscopy and scanning electron microscopy results of initial CNTs synthesis products are presented in Fig.1 and Fig.2.



(**a**) (**b**)

Figure 1. Thermogravimetry curve (a) and Raman spectrum (b) of initial CNTs synthesis products.



(**a**) (**b**)

Figure 2. SEM images of initial CNTs synthesis product.

Thermogravimetry and Raman spectroscopy results of initial and acid treated samples are presented in Table 2.

Table 2. Thermogravimetry and Raman spectroscopy results of initial, acid treated samples and samples after mild oxidation with subsequent acid treatments

Sample	T_{ONSET}, °C	T_{ENDSET}, °C	m(Fe), wt.%	D/G
INI	534	679	11.54	0.66
AT	528	682	10.65	0.77
MO_0	524	678	11.17	0.816
MO_W1	523	684	8.60	0.867
MO_W2	531	703	6.52	0.821
MO_W3	550	767	3.80	1.181

3.2. Water influence at the stage of mild oxidation

To find out the importance of water presence in purging gas during mild oxidation, two experiments were carried out with and without bubbling purging synthetic air through distilled water. Thermogravimetry and Raman spectroscopy results of acid

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treated and rinsed samples after mild oxidation with and without water are presented in Table 2.

3.3. Influence of intensity of mild oxidation with water

To find out the influence of mild oxidation intensity on the residual catalyst content, two experiments with different temperature of mild oxidation (365°C and 400°C), different time of mild oxidation (6 and 12 hours) and different water saturation of purging gas (50°C and 80°C water bath temperature) were carried out. Thermogravimetry and Raman spectroscopy results of samples after mild oxidation with different degree of water saturation of purging gas, mild oxidation time and temperature are presented in Table 2.

3.4. Oxidative heat treatment after mild oxidation

To investigate the influence of previous mild oxidation on the subsequent oxidation with oxygen the samples were heat treated at 480°C for 2 hours under static synthetic air atmosphere at muffle furnace with subsequent acid treatment. Thermogravimetry and weight losses results of heat treated at 480°C for 2 hours samples are presented in Table 3.

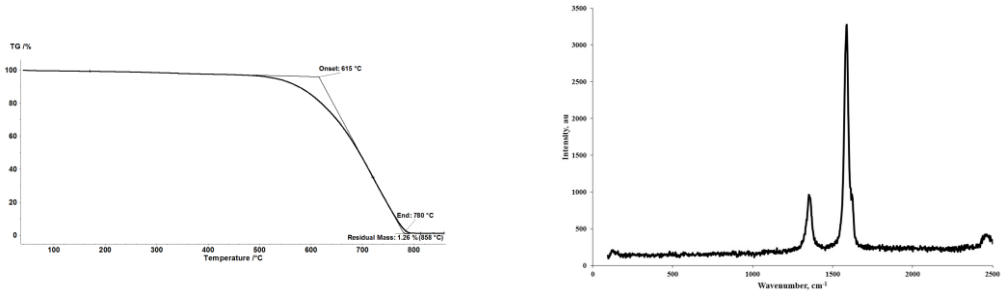
Table 3. Thermogravimetry and weight losses results of heat treated at 480°C for 2 hours samples

Sample	T_{ONSET}, °C	T_{ENDSET}, °C	Δm_{TO}**, %	m(Fe), wt.%
INI_HT	547	715	-34.5	4.62
MO_0_HT	542	674	-30.9	3.08
MO_W1_HT	549	710	-19.4	2.15
MO_W2_HT	547	731	-20.7	2.02
MO_W3_HT	550	746	-4.60	1.88

* Weight losses after mild oxidation and acid treatment, ** Weight losses after heat treatment at 480°C for 2 hours and acid treatment

3.5. Oxidative heat treatment after mild oxidation

To burn out all non-CNTs particles form CNTs synthesis products, the rinsed and dried sample after mild oxidation with water were heat treated under static air atmosphere at 480°C for 6 hours, then acid treated and dried. Thermogravimetry, Raman spectroscopy and scanning electron microscopy results of acid treated and rinsed heat treated sample after mild oxidation are presented in Fig.3 and Fig.4.



(**a**) (**b**)

Figure 3. Thermogravimetry (a) and Raman spectrum (b) of acid treated and rinsed heat treated at 480°C for 6 hours sample after mild oxidation.

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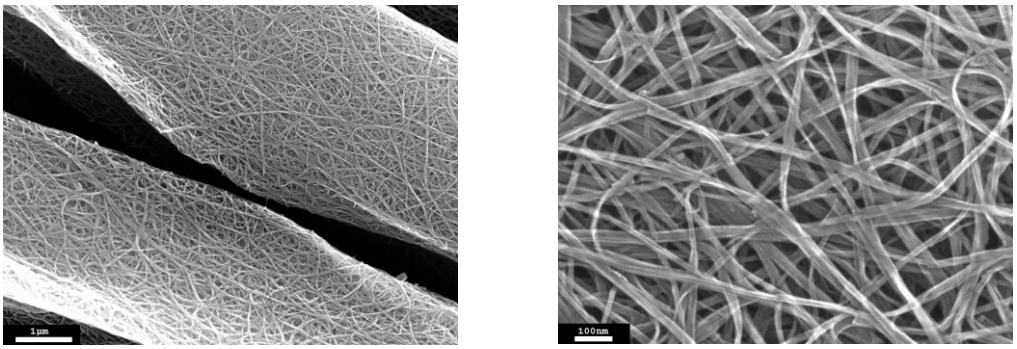

(**a**) (**b**)

Figure 4. SEM images of acid treated and rinsed heat treated at 480°C for 6 hours sample after mild oxidation.

4. Discussion

As one can see from Table 2, the hydrochloric acid treatment of initial synthesis products leads to insignificant decrease of iron content in the sample. On the other hand, according to Fig.1, acid treatment does not cause significant structural changes, but in accordance with Table 2 results in slight increase of D/G ratio of Raman spectra. It is known [14] that Raman spectroscopy is a powerful method for investigation of nanostructured carbon materials including CNTs and can be used for estimation of UCNTs purity relatively rough from D/G ratio of Raman spectra [15], where G band is related to absorbance at ~1584 cm^{-1} and D band – at 1300-1400 cm^{-1}. For example, the increasing of D/G ratio of Raman spectra can be related to the increasing of edge defects of nanotubes [15] which can be created after partial removal of catalyst particles.

All mentioned findings probably show that only small part of residual iron catalyst is unbound and accessible to acid, but the main part of the residual iron catalyst is encapsulated inside CNTs or non-CNTs particles and cannot be removed from the sample by simple acid treatment without additional high temperature treatment. Mild oxidation by wet air can be used to remove iron catalyst particles from UCNTs as suggested by successful application of similar technique for SWCNTs [11. The importance of water during mild oxidation for UCNTs synthesis products can be seen from Table 2, where the results of two experiments carried out at 400°C with and without water in purging oxidative gas are presented.

As can be seen from Table 2 the presence of water in purging oxidative gas causes a removal of more iron catalyst from the sample after sequential acid treatment in comparison with the sample without water in purging oxidative gas. On the other hand, presence of water in purging oxidative gas does not result in significant changes in sample structure, but causes the increasing of D/G ratio of Raman spectra (Table 2). The increasing of D/G ratio due to water presence in purging gas can be related with appearance of more CNT edge defects [15] after catalyst removal as well as a result of inner structural strain formation inside carbon matrix [16]. It is known that during oxidation of iron, the density is changed by about 35 % when iron transforms to iron (III) oxide [10] and this changing can result in inner structural stain formation in the case if iron is located inside carbon shells, for example, inside carbon nanotubes. In the case if iron is not oxidized completely and there are many carbon shells enveloping these iron particles, the structural strain formed during iron oxidation does not cause the destruction of carbon shells, so prevents encapsulated iron particles from removal by subsequent acid treatment. It can be concluded that depth of iron oxidation can be dependable on mild oxidation conditions such as temperature and time of mild oxidation as well as degree of purging oxidative gas saturation by water molecules. To show this, additional two experiments with different intensity of mild oxidation were carried out.

As can be seen from Table 2 the increasing of mild oxidation intensity results in enhancing of iron catalyst particles removal from the samples that can be related with more complete oxidation of iron and consequently more complete destructions of carbon shells,

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which enveloping iron catalyst particles. One can note that intensity of mild oxidation correlates proportionally with intensity of D/G ratio on Raman spectra (Table 2), which can be related with more intensive formation of CNT edge carbons [15] after iron catalyst removal or enhancing of inner structural strain formation due to oxidation of encapsulated iron [16].

It should be noted that mild oxidation with wet air allows to remove iron catalyst without significant losses of different forms of carbon due to carbon oxidation. For example, as one can see from Table 4, heat treatment with dry air allows reaching the same level of residual iron content only with more than twice weight losses in comparison with mild oxidation using wet air.

Table 4. Weight losses during purification using wet and dry air with subsequent acid treatment

Sample	m(Fe), wt.%	Δm, %
MO_400-12*	3.8	-17.3
HT_480-2**	4.6	-34.5
HT_480-6***	3.1	-83.0

* mild oxidation with wet air at 400°C for 12 hours, ** Heat treatment with dry air at 480°C for 2 hours, *** Heat treatment with dry air at 480°C for 6 hours,

In other words, lower level of iron content before heat treatment is necessary to increase the yield of CNTs, because during heat treatment iron particles catalyzes carbon oxidation [3] and results in besides non-CNTs oxidation, the oxidation of useful CNTs. For example, as can be seen from Fig.5 the weight losses during heat treatment under static air atmosphere at 480°C for 2 hours are proportional to residual iron content in the samples undependably previous treatment.

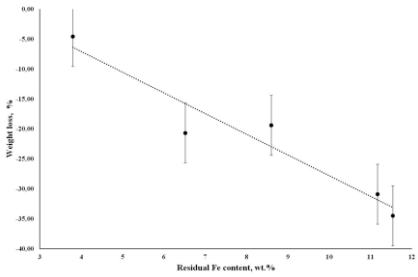

Figure 5. Dependence of weight losses during heat treatment of samples under static air atmosphere on residual iron content.

It should be noted that wet air mild oxidation results in lowering of residual iron content by more than 140 % in comparison with the sample without mild oxidation and by more than 63 % in comparison with sample with dry air mild oxidation. Moreover, the more intensive conditions of wet air mild oxidation, the less residual iron is the sample (Table 3).

Additional high temperature treatment with sequential acid treatment of samples after mild oxidation and acid treatment allows to obtain ultralong CNTs without significant content of non-CNTs and as low residual iron content as 0.9 wt.% and as low D/G ratio as 0.26 (Fig.3, Fig.4).

The results obtained allow to conclude that mild oxidation with wet air at the initial stage of purification makes it possible to remove the main part of iron catalyst without significant carbon losses and increase the yield of CNTs after heat treatment for non-CNTs removal.

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5. Conclusions

The importance of water during purification of ultralong CNTs obtained by catalytic CVD method is shown. The presence of water in the purging oxidative gas during mild oxidation at 400° allows to oxidize the majority of encapsulated iron particles without significant oxidation of different forms of carbon. The oxidation of encapsulated iron particles causes density decreasing and inner structural strain formation that results in destruction of carbon shells enveloping iron particles and allows them to be removed after subsequent acid treatment. Such factors as temperature and time of mild oxidation as well as degree of saturation of purging oxidative gas with water vapor can be used to intensify the process of iron removal. The purification of CNTs synthesis products under mild oxidation with the assistance of water vapor can be used to develop economic and ecologically friendly methods for purification of ultralong carbon nanotubes obtained by catalytic chemical vapor deposition.

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