

# The effects of liquid-phase oxidation of multiwall carbon nanotubes on their surface characteristics

I N Burmistrov<sup>1</sup>, D S Muratov<sup>1</sup>, I A Ilinykh<sup>1</sup>, E A Kolesnikov<sup>1</sup>, A Yu Godymchuk<sup>1,2</sup>, D V Kuznetsov<sup>1</sup>

<sup>1</sup> National University of Science and Technology “MISiS”, 4, Leninsky Prospekt, Moscow, 119049, Russia

<sup>2</sup> National Research Tomsk Polytechnic University, 30, Lenina Ave., Tomsk, 634050, Russia

E-mail: [glas101@yandex.ru](mailto:glas101@yandex.ru)

**Abstract.** The development of new sorbents based on nanostructured carbon materials recently became a perspective field of research. Main topic of current study is to investigate the effect of different regimes of multiwall carbon nanotubes (MWCNT) surface modification process on their structural characteristics. MWCNT samples were treated with nitric acid at high temperature. Structural properties were studied using low temperature nitrogen adsorption and acid-base back titration methods. The study showed that diluted nitric acid does not affect MWCNT structure. Concentrated nitric acid treatment leads to formation of 2.8 carboxylic groups per 1 nm<sup>2</sup> of the sample surface.

## 1. Introduction

Intensive development of new science-driven technologies of rare-earth metal extraction is one of the strategic goals of today's industry. Main focus of research in this field is concentrated on the separation of so called allied substances. The problems of allied substances separation and purification are typically solved by ion-selective and ion-exchange processing. Ion-exchange technique shows good results when used for extraction and collection of low quantities of rare-earth metal contaminations. On the other hand the increasing amount of non-traditional mineral raw materials leads to development of new more efficient techniques and methods [1-3].

Promising perspectives in the field has been shown with carbon nanotubes [4-7]. Carbon nanotubes are known to have good sorption properties due to the high specific surface area which goes up to 2000 m<sup>2</sup>/g for single walled carbon nanotubes. MWCNTs have lower values of specific surface area varying from 150 to 600 m<sup>2</sup>/g but even this is quite high compared to other traditional sorbents. Graphene is also considered good sorption agent with specific surface area of 200-700 m<sup>2</sup>/g and in some cases even up to 1000 m<sup>2</sup>/g.

Ion-exchange activity of carbon nanomaterials could be achieved by surface functionalization which involves covalent and van der Waals bonding of different substances to MWCNT structure. Generally non-covalent bonding of different agents with the surface of MWCNT is not considered as functionalization process and is studied separately. MWCNT surface functionalization is usually done in stages. The first stage is oxidation which leads to formation of carboxyl surface groups. The second one is grafting of oxidized surface with various functional groups to obtain more specific surface reaction.



MWCNT surface oxidation is the most typical functionalization treatment and is also used for surface cleaning [8-10]. As the result of such cleaning various oxygen-containing surface groups are formed. Functionalization effectiveness is often evaluated by functional group content relative to the sample weight.

There are two generally used oxidation techniques: gas-phase thermal oxidation in oxygen or ozone atmosphere; and liquid-phase oxidation in nitric acid or in mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . Present study is focused on effect of MWCNT functionalization on their surface characteristics.

## 2. Materials and methods

Present study involved MWCNT Taunit-M and polygraphene materials provided by Ltd. "NanoTechCenter" (Tambov, Russia). MWCNT oxidation treatment was done by boiling of MWCNTs in concentrated and diluted nitric acid ( $\text{HNO}_3$ ) for 1–8 hours with MWCNT/acid ratio equal to 1/20. Oxidation process was carried out in two-necked flask with backflow condenser and a thermometer to control the reaction temperature between 100 and 105 °C Next the reaction products were rinsed with distilled water until neutral pH. Reaction products separation was done by decantation with subsequent vacuum filtering and drying at 60 °C for 48 hours.

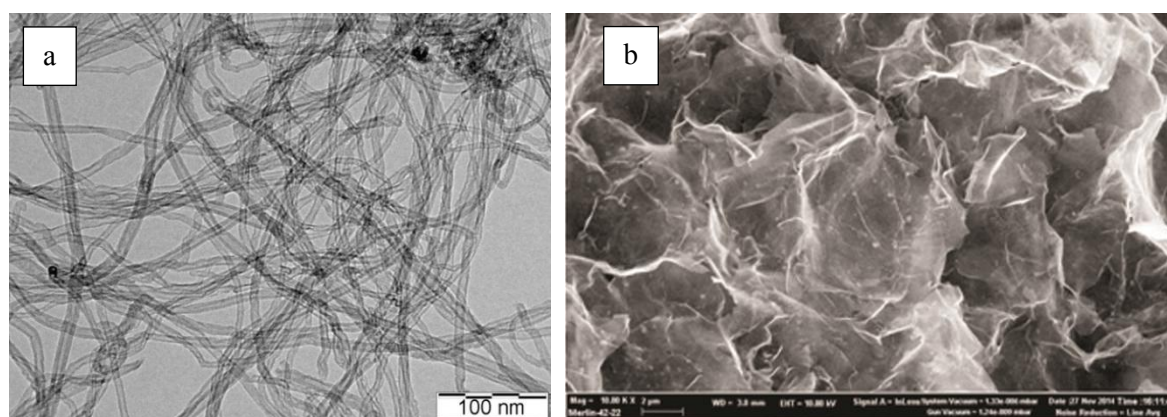
Surface oxygen-containing group count was measured by acid-base back-titration. MWCNTs were then covered with sodium hydroxide solution of the known concentration and left for 24 hours. The precipitate was filtered on the paper filter, and then the aliquot was mixed with hydrogen chloride solution with subsequent titration with sodium hydroxide. The pH value was measured by "Anion-4100" with absolute error of  $\pm 0.02$ . Specific surface measurements were done according to ASTM D3663 and BET method using Quantachrome Nova 1200 instrument.

## 3. Results and discussions

Specific surface measurement results are shown in the Table 1. SEM and TEM images are shown on the Figure 1.

**Table 1.** Specific surface for MWCNT and graphene samples

Sample	Material	Specific surface area, $\text{m}^2/\text{g}$
1	MWCNTs	$170 \pm 7$
2	Graphene	$90 \pm 5$



**Figure 1.** Microphotography of the materials: a) TEM image of MWCNT Taunit-M, b) SEM image of graphene sample

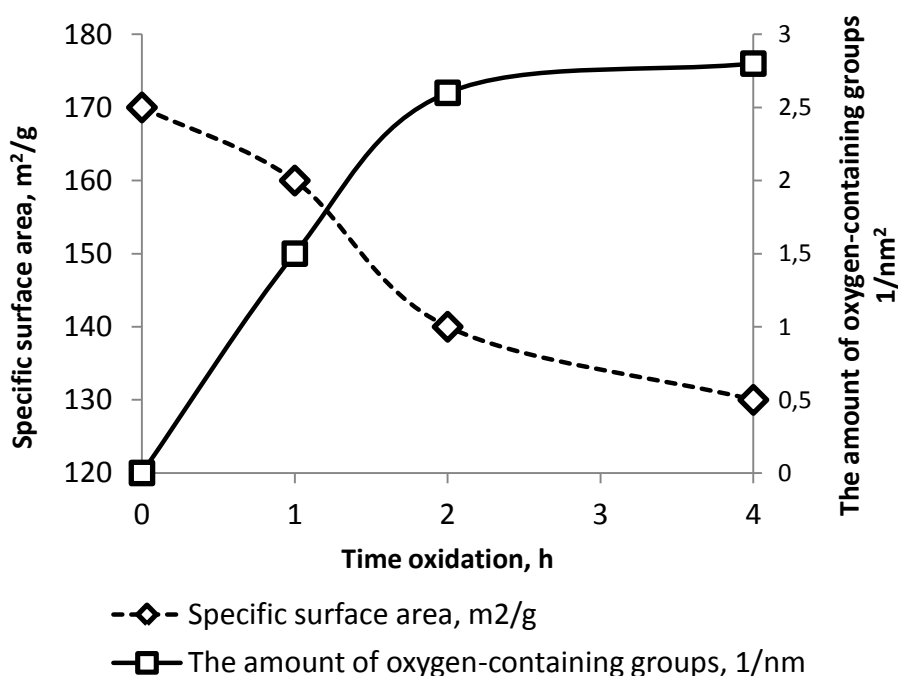
Specific surface area for MWCNT sample (table 1) correlates with nanotube diameter measured from TEM (fig. 1A). It should be noted that nanotubes in sample 1 are entangled and it is quite difficult to obtain good suspension for those samples without additional intensive processing.

The evaluation of surface oxidation processing is shown in the Table 2.

**Table 2.** Titration results for MWCNT samples

#	Treatment time, hours	Treatment type	Temperature, °C	Specific surface area, m <sup>2</sup> /g	Amount of oxygen-containing groups, nm <sup>-2</sup>
1	1	HNO <sub>3</sub> concentrated	100–105	160	1.5
		Diluted HNO <sub>3</sub>	130–140	Sample degraded	
2	2	HNO <sub>3</sub> concentrated	100–105	170	0
		Diluted HNO <sub>3</sub>	130–140	140	2.6
3	4	HNO <sub>3</sub> concentrated	100–105	170	0
		Diluted HNO <sub>3</sub>	130–140	130	2.8
4	8	HNO <sub>3</sub> concentrated	100–105	170	0
		Diluted HNO <sub>3</sub>	130–140	Sample degraded	

The specific surface area does not change at the treatment with a nitric acid and decreases in the case of treatment with concentrated nitric. According to table 2 data it is clear that diluted HNO<sub>3</sub> does not affect MWCNT surface characteristics even when the treatment time is 8 hours. In those cases the treatment just dissolves metal catalyst from the sample. In the treatment of a concentrated acid for 8 hours CNTs degraded and the specific surface area cannot be measured.



**Figure 2.** Specific surface area and amount of oxygen-containing surface groups for MWCNT sample against treatment time

Specific surface area and the amount of oxygen-containing groups are plotted against treatment time on the Figure 2. The specific surface area is significantly reduced during the first two hours of treatment. The content of carboxyl groups is also increased within this range treatment time. According to the Figure 2 the optimal treatment time is 2.5-3 hours.

On the other hand concentrated nitric acid treatment leads to formation of oxygen-containing groups with simultaneous decrease in specific surface area values. This is probably caused by decrease of highly reactive amorphous carbon amount due to treatment process. Amorphous carbon is present in the sample volume due to incomplete nanotube formation process at the synthesis stage.

With longer treatment times the oxygenated group amount per nm<sup>2</sup> steadily increases. When treatment time is longer than 8 hours surface of all the samples is considered to be oxygenated and yields a clear homogeneous solution.

#### 4. Conclusions

The research of functionalization process effect on the structural properties of carbon nanomaterials showed that diluted nitric acid does not affect MWCNT structure even when treated for 8 hours. In those cases the treatment just dissolves mal catalyst from the sample.

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