

STUDIES OF SURFACE PROPERTIES AND FRACTAL DIMENSIONS OF CARBON NANOTUBES USING COMPLEX METHODS

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Abstract. Physicochemical properties of carbon nanotube surfaces by means of the special thermogravimetry (Q-TG), sorptometry and atomic force microscopy (AFM) methods were investigated. A numerical and analytical procedure for the evaluation of total heterogeneous properties (desorption energy distribution and pore-size distribution functions) on the basis of liquid thermodesorption from the sample surfaces under the quasi-equilibrium conditions and sorptometry techniques are presented. The desorption energy distribution was derived from the mass loss Q-TG and the differential mass loss Q-DTG curves of thermodesorption of pre-adsorbed polar and apolar liquid films. For the first time, the evaluation of the fractal dimensions of nanotubes using the sorptometry, Q-TG and AFM data are presented.

1. INTRODUCTION

Recently, nanotechnology has become key technologies with significant effect on the development of new products and production methods [1]. Due to their enormous potential for new applications nanotechnologies in the future will increasingly affect our every day life with an impact comparable to that of the industrial revolution and developments in microelectronics in the New Millennium [2].

A great number of physical and chemical processes take place and/or are initiated at the solid surface/gas or solid surface/liquid interfaces. The knowledge of the phenomena occurring there is of importance because in many cases they result in changes of the physicochemical properties of the material. One of the most striking properties of a solid surface is its capability of adsorption of vapours and gases [3,4]. Adsorption behaviour, properties of the heterostructure and, in particular, the fractal dimensions are necessary for understanding sorp-

tion and diffusion the mechanism in solid surfaces. Recently, a new model for the evaluation of fractal dimensions from the programmed liquid thermodesorption in quasi-isothermal conditions (Q-TG) have been proposed and discussed [5].

The carbon nanotubes are used in many branches of science, industry and technology as e.g. novel components of mechanically strong composites. Carbon nanotubes are nanoobjects built from rolled graphene planes [6]. These are fascinating materials that have been the subject of intensive research due to their extraordinary physical (structural, mechanical, electronic) properties and potential technological applications [7,8]. Applications include, but are not limited to, quantum wires and transistors [9], field emission devices [10], sensors based on chemical functionalization [11], hydrogen storage [12] and polymer matrix composites [13]. Carbon nanotubes in particular because of their size and large surface area are being considered as prime materials for gas adsorption or molecular filtering.

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Specific surface area, pore size distribution and pore volume of above aggregates play an important role in gas sorption and various properties.

Adsorption and total heterogeneous properties are necessary for understanding unique physico-chemical properties of nanotubes, e.g. surface layers, porosity, semiconducting, superconducting or metallic behaviour depending on their geometrical parameters and surface structure. For that reason, in this paper the possibilities to study physicochemical properties of nanotubes by means of thermogravimetry Q-TG, sorptometry and atomic force microscopy (AFM) techniques are presented and discussed.

2. EXPERIMENTAL

Materials. The carbon nanotube samples which were grown in a horizontal quartz tube reactor placed in a furnace by the reaction technique using xylene-ferrocene mixture by means of a method described in details in papers [14, 15] were examined. In our investigations of adsorbed liquids and surface porosity parameters of nanotubes we used carbon products obtained by two methods: DC electric arc generated between graphite electrodes and thermal decomposition of hydrocarbon vapour in the presence of catalyst (N-1 sample). This material was sonicated in the water/ethanol mixture for 30 min (N-2 sample). The fraction that precipitated on the bottom included nanotubes but there were mainly clusters. The N-3 sample was prepared by catalytic decomposition of xylene C_8H_{10} used as a carbon source and ferrocene $Fe(C_5H_5)_2$ as a catalyst precursor [16, 17].

Methods. Thickness of the adsorbed liquid layers on the surface can be assessed by means of immersion mode of the solid samples. Adsorption of apolar (benzene and n-octane) and polar (water and n-butanol) liquid layers was measured using the derivatograph Q-1500 D (MOM, Hungary) [18]. The samples were saturated with liquid vapors in the vacuum desiccator at $p/p_0 = 1$. The Q-TG mass loss and Q-DTG differential mass loss curves were measured under the quasi-isothermal conditions [19, 20] in the temperature range 20–250 °C at a heating rate of 6 °C/min. Porosity properties e.g. specific surface areas, pore size distribution and pore volume were calculated from low-temperature nitrogen adsorption-desorption isotherms measured by means of the Sorptomat ASAP 2405 V1.01 (Micrometrics Co., USA). The adsorption and porosity properties of tested samples are presented in Table 1. In order to characterize fully the structural changes caused by modification, atomic force microscopy photos were also obtained by means of the AFM apparatus NanoScope III type (Digital Instruments, USA) and are presented in Figs. 1-3.

3. RESULTS AND DISCUSSION

The Q-TG mass loss and the Q-DTG differential mass loss curves of water as a function of temperature from the N-2 nanotube sample surfaces are presented in Fig. 4a. The characteristic inflections in the Q-DTG curves correspond to the individual stages of thermodesorption of the selected liquids from nanotube surfaces. It can be considered as a certain type of spectrum of thermodesorption process describing an energetic state of polar water mol-

Table 1. Pore structure parameters of the samples calculated from nitrogen adsorption-desorption isotherms using the sorptometry method.

PARAMETERS:	SAMPLES:		
	N-1	N-2	N-3
Single point surface area at $p/p_0=0.2$, m^2/g	75.71	30.00	78.75
BET surface area, m^2/g	87.05	36.74	87.85
Langmuir surface area, m^2/g	119.96	53.21	119.33
BJH adsorption cumulative surface area, m^2/g	102.54	48.25	106.87
BJH desorption cumulative surface area, m^2/g	96.18	49.30	123.97
Single point total pore volume, cm^3/g	0.17	0.10	0.23
BJH adsorption cumulative pore volume, cm^3/g	0.30	0.12	0.30
BJH desorption cumulative pore volume, cm^3/g	0.19	0.11	0.30
Average pore radius (4V/A by BET), nm	7.73	10.88	10.59
BJH adsorption average pore diameter (4V/A), nm	11.79	9.69	11.27
BJH desorption average pore diameter (4V/A), nm	8.00	9.17	9.70

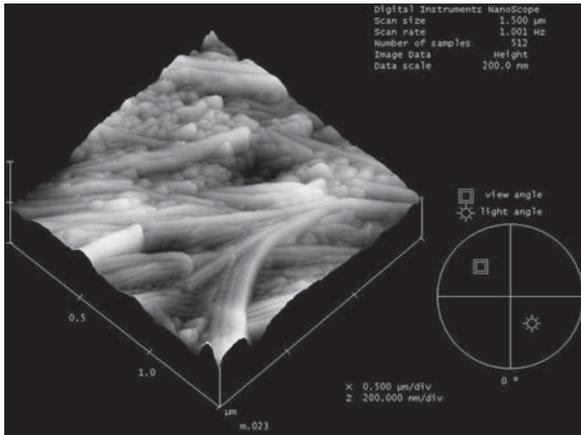


Fig. 1. AFM photo of N-1 sample.

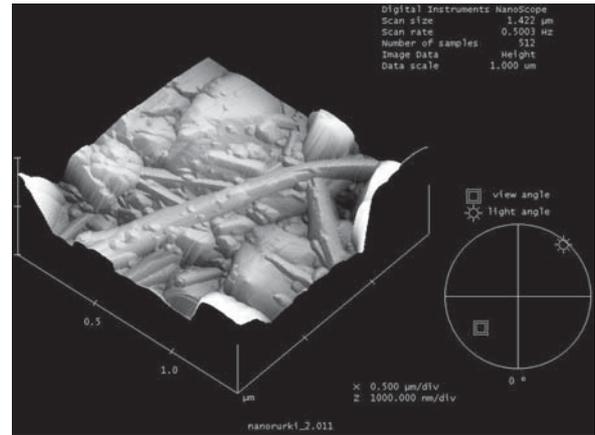


Fig. 2. AFM photo of N-2 sample.

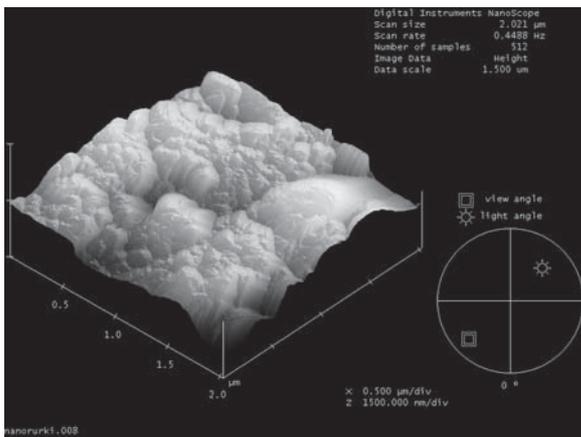


Fig. 3. AFM photo of N-3 sample.

ecules on surface. The Q-DTG spectrum indicates long wide peaks with the minimum near 100 °C and a few other small peaks. It is shown from the obtained data that the N-2 sample is highly sensitive to water vapour because the mechanism of molecule adsorption depends largely on the activated surface centres.

The energetic heterogeneity of materials is conditioned by the differences in topology of adsorption centres, dispersion of pore size and other factors. This paper presents the estimation of the energetic heterogeneity of carbon nanotubes making use of the results of the programmed thermodesorption of liquids from the solid surfaces. The desorption energy distribution from the Q-TG and Q-DTG curves was derived using an equation for the desorption kinetics characterised by a constant value of the desorption energy [21].

The desorption energy distributions, $\rho(E)$, from the pores for each temperature T_i in the Q-TG and Q-DTG curves were calculated. The results for n-butanol, water and benzene desorption from the N-1, N-2 and N-3 sample surfaces within the tempera-

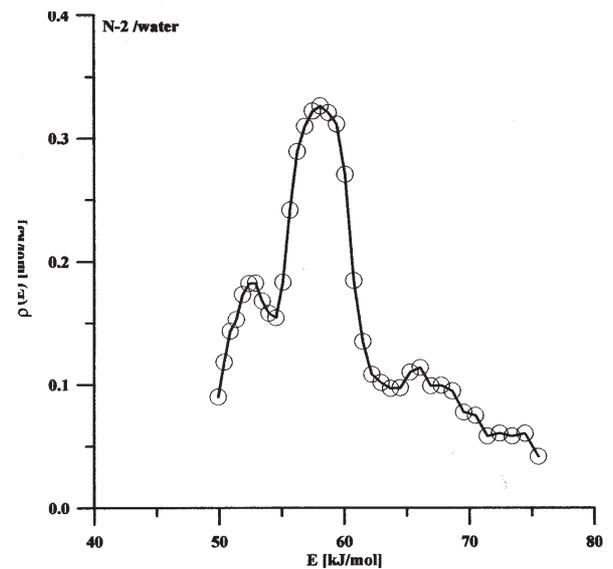
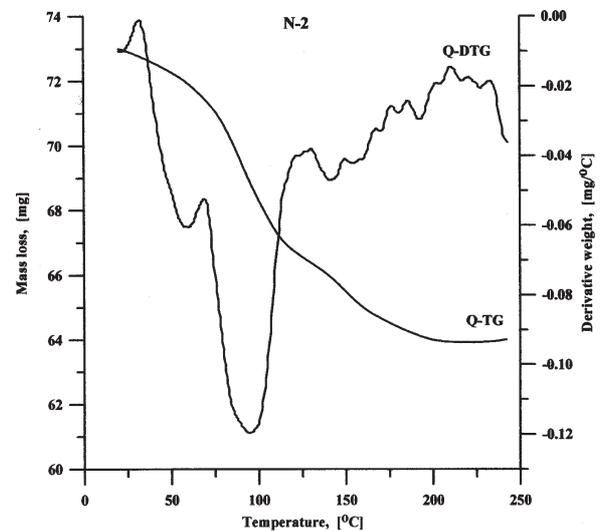


Fig. 4. (a). The Q-TG and Q-DTG curves of water thermodesorption from N-2 sample. (b). Desorption energy distribution functions for N-2/water system.

Table 2. Fractal dimensions calculated from the sorptometry, Q-TG thermogravimetry and AFM methods.

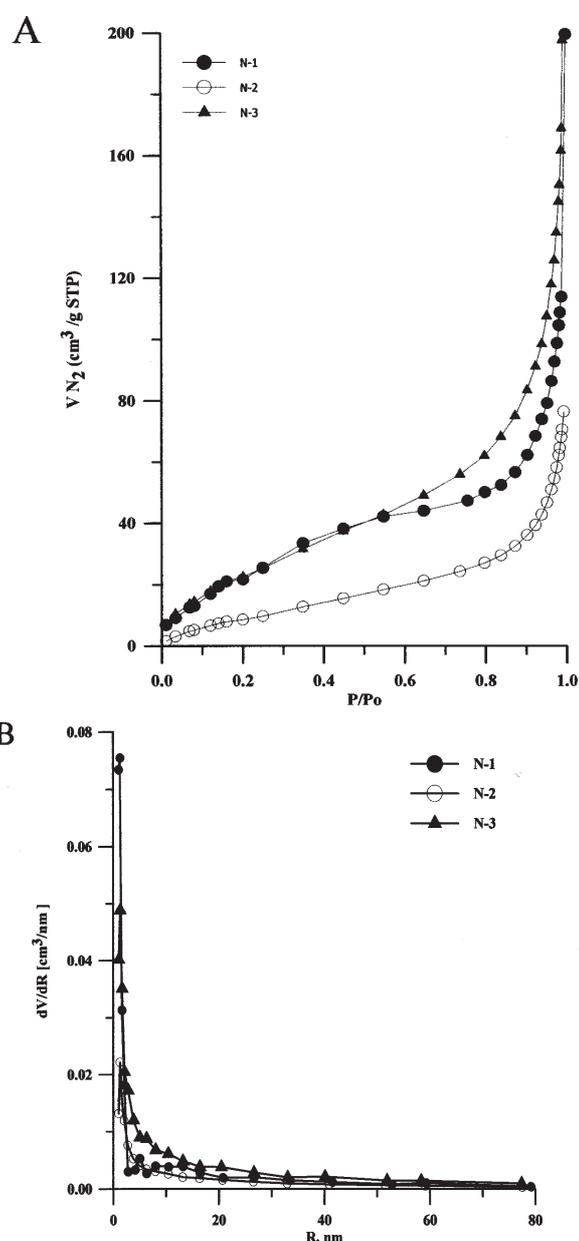
Samples	Sorptometry method (average)	Thermogravimetry method (average)	AFM method
N-1	2.49	2.50	2.33
N-2	2.64	2.52	2.54
N-3	2.54	2.49	2.34

ture range $T = 50\text{--}180\text{ }^{\circ}\text{C}$ are presented in the paper [22]. The E values range of 28–82 kJ/mol (benzene), 38–75 kJ/mol (n-butanol), 32–73 (n-octane) and 26–76 kJ/mol (water) were obtained. In the case of benzene, the high value of desorption energy indicates great influence of the surface on adsorbed molecules. For aromatic hydrocarbons, a considerable increase of energy desorption value occurred in creation of high-energy adsorption sites for benzene molecules [22]. The thermodesorption of the above liquids shows that the investigated materials have non-polar surface properties. The typical Gauss and bimodal shapes presented in Fig. 4b of the adsorption site distribution associated with the desorption of water from the surface may be observed for the modified N-2 sample. However, changes in the distribution of adsorption sites which occur as a result of mechanical and chemical treatment appear somewhat complicated. The above treatment resulted in creation of low energy adsorption sites for the adsorbed molecules. On water/N-2 material curve (Fig. 4b) exhibits three maxima which suggests the presence of 3 types of active site for the sample under examination.

It follows, therefore, that mechanical and chemical modifications of N-2 nanotube sample causes not only an decrease in its porosity (Table 1) but also significant changes in its adsorption properties with respect to the adsorption of polar and apolar liquids. The decrease in the specific surface area and pore volume of the modified N-2 surface may be attributed to the presence of the newly created pores and/or to an internal reorganization of the crystal network. The studied phenomenon is very complicated but the obtained results seem to be very promising for future investigations.

Nitrogen adsorption isotherms measured at $-196\text{ }^{\circ}\text{C}$ for the nanotube samples were determined and presented in Fig. 5a. According to the BET classification, isotherms of this kind belong to the isotherms of type II describing the process of physical adsorption of nitrogen. The specific surface areas were calculated using the BET method and the pore volume and pore-size distribution were calculated

using the BJH method. The pore-size distribution PSD functions (i.e. dV/dR in relation to R , where V is the pore volume and R is the pore radius) which reflect geometrical heterogeneity for nanotube

**Fig. 5.** The nitrogen adsorption isotherms (a) and pore-size distribution functions (b) for nanotubes.

samples were calculated and presented in Fig. 5b. The pores with a radius near 10 nm (Table 1) have the highest value on these curves. The concentration of micropores decreases with the increase of the radius. The observed shapes of the pore-size distribution curves are typical of most industrial mesoporous materials. For example, this shape is similar to that evaluated from the low-temperature nitrogen adsorption-desorption isotherms for activated carbons [23] using Dollimore-Heal method [24].

The low-temperature nitrogen adsorption and desorption isotherms were used for calculation of fractal dimensions on the basis of a method presented in papers [5,22]. The fractal dimension characterizes the nature of sorbents and heterogeneity of pores. This method is based on the surface of the adsorbed layer calculated using the Frenkel-Halsey-Hill theory and Kiselev equation [25,26,27]. The average values of fractal dimensions were calculated and given in Table 2. The fractal dimensions on the basis of Q-TG data presented in Table 2 were made using new method [5].

On the basis of AFM data the fractal dimensions were calculated for different angles by analysing the Fourier amplitude spectrum [28,29]. For different angles the Fourier profile is extracted and the logarithm of the frequency and amplitude coordinates was calculated using analytical method from AFM apparatus. The fractal dimension for each direction was then calculated as 2.0 minus the slope of log-log curves and presented in Table 2. The obtained average fractal dimension values calculated from the Q-TG thermodesorption measurements of polar (water and n-butanol) and apolar (n-octane and benzene) liquids are in a good agreement with those calculated from the sorptometry and AFM data (Table 2) and those given in papers [26,30].

4. CONCLUSIONS

Special applications of Q-TG thermal analysis for the investigation of adsorbed liquid layers and porosity parameters used for the quantitative characterisation of the energetic and geometrical (e.g. total) heterogeneities of carbon nanotubes have been discussed. The presented method is very useful to investigate physicochemical properties of surface liquid films, adsorbate-adsorbent interactions and total nanotube surfaces heterogeneity. The thermodesorption process of liquids depends on the surface wetting phenomenon and surface properties of the solid surfaces. Comparison of the complex Q-TG, sorptometry and AFM data provide new information about the adsorption and structure of

the studied materials. The N-1 and N-3 samples possess micropores with homogeneous structure because the fractal dimensions are close to 2.5. The modified N-2 sample was characterized by larger heterogeneity of the pores (fractal coefficients are higher than 2.5).

The new method for determination of the fractal dimension of nanotube surfaces using the Q-TG technique is presented and discussed. It is in good agreement with the results from sorptometry and AFM techniques. The presented results show that the above Q-TG method for determination of the fractal dimensions on the basis of thermodesorption of liquids under the quasi-isothermal conditions is reliable, simple and practicable.

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