WORLD OF NANOSTRUCTURES – NANOTECHNOLOGY
SURFACE PROPERTIES OF CHOSEN NANOMATERIALS
Determined by adsorption, Q-TG, AFM and SEM methods

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The paper presents the basic information on nanotechnology and the recent results of studies of physicochemical properties of chosen nanomaterial surfaces (montmorillonites, carbon nanotubes, smart surfaces) by means of complex measuring methods. Physicochemical properties of nanomaterial surfaces by means of the special thermogravimetry Q-TG, sorptometry, porosimetry, atomic force microscopy (AFM) and scanning electron micrograph (SEM) 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 evaluation of the fractal dimensions of nanotubes using the sorptometry, porosimetry, thermogravimetry Q-TG and AFM data are presented. The comparison of fractal coefficients calculated based on them with the results from Q-TG, sorptometry, porosimetry and AFM gave good agreement.

Keywords: nanomaterials, nanotechnology, Q-DTG, Q-TG, thermogravimetry, total (energetical and geometrical) heterogeneity

Introduction

At present main interest of interdisciplinary studies are focused on development of theoretical and experimental papers concerning nanomaterials and their practical applications [1]. Interest in the nanoworld is enormous and nanotechnology is at present the most dynamically developing discipline of science and technology e.g. over 30 nanotechnological research centres exist at universities. Nanotechnology deals with production and studies of properties of very small objects which can be applied in practice in future [2]. The nanotechnology term was given by Norio Taniguchi in 1974 to determine processing with the accuracy smaller that \(10^{-9}\) m but its quick development and diminution of objects in practice as well as manipulation of molecules on a small scale were predicted by Richard Feynman in 1957 [3].

The subject of nanotechnology is search and synthesis, characteristics, making use and practical application of new materials of advanced technology which possesses the sizes of nanometers. Such nanostructures are the bridge between individual atoms and molecules where quantum mechanics laws are applied and vast volume phase in which most properties result from collective behaviour of billion atoms. Individual nanostructures are clusters, nanomolecules, nanocrystals so called quantum points nanowires and nanotubes which possess orderly structures and they can be large molecules in single nanostructures [4]. Quantum size and shape of nanomolecules affect mechanical, chemical, electrical properties, nuclear-electronic, electric-optical and dynamic levels of structure. That promotes disclosure of new, unique physicochemical phenomena and more profitable than large structures such as quantitative differences in properties compared with the volume phase. This leads to possible control of action and application of nanostructures.

Nanotechnology must satisfy three criteria:

• Studied structures should have at least one size not larger than 100 nm. Thus nanotechnology is not technology in many cases.
• In the nanomaterial process production physicochemical properties should be controllable.
• There must be a possibility of building larger objects from the produced advanced materials.

The modern nanotechnology devices are scanning microscopes, mainly scanning tunnel microscope and atomic force microscope. Using these apparatus it is possible to obtain pictures of even single atoms and their dislocation on the surface.

Nanomaterials can be obtained using the methods from top to bottom and from bottom to top. The from top to bottom method consists in modelling of the surface by addition or removal of some amount of substance. In this way there are formed self-contained systems of the paths slightly broader than 100 nm.

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However, in the from bottom to top method self-ar-
rangement in formation of large structures is used. Under suitable conditions atoms or molecules form orderly systems spontaneously. In this way nanotubes are formed. The survey of typical nanostructures and their size are given in Table 1.

So far, advanced materials have found some application in practice. Fullerenes of a 1 nm diameter prepared for the first time in 1985 can be used as superconductors [6]. Carbon nanotubes discovered in 1991 were used in 1998 to build diode transistors, transmitters, logical gates but in 2003 in France to produce indestructible tights [7]. Moreover, they can be used as superconductors [8]. In 1999 single organic molecules and intersecting nanowires were used as catalysts for production of petrol. Non-magnetic layers of a thickness smaller than 1 nm placed between magnetic layers form computer hard discs of very large sensitivity and capacity. Drugs placed in lipid bags of a 100 nm diameter act longer because they circulate longer in the blood circulatory system. The biological tests for the presence and activity of searched substances are quicker, more sensitive and elastic when nanomolecules are used as markers [9]. Crystalline nanopowders improve properties of materials like chemical, mechanical, optical and magnetic ones. Harder ceramic materials, solar filters and catalysts used in the environmental protection are obtained. It is believed that in the near future microscopic ro-
bots will revolutionize the industrial production [10–12] and will be used in the interplanetary travels [13].

Studies of typical nanomaterials (soil mineral components adsorbents, silica gels with deposited proteins – so called smart surfaces, latexes, synthetic zeolites modified by ions, MCM-41 molecular sieves) were made earlier by author of this paper and pub-
lished [14–20]. At present our research focuses on studies of surface properties (e.g. adsorption capacity), total heterogeneity (energetical and geometrical), surface layers as well as structure and phase transformation of fullerenes, carbon nanotubes, active car-

### Table 1 Typical nanostructures given in [5]

<table>
<thead>
<tr>
<th>Nanostructure</th>
<th>Size</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>clusters, nanocrystals, quantum dots</td>
<td>radius: 1–10 nm</td>
<td>insulators, semiconductors, metals, magnetic</td>
</tr>
<tr>
<td>other nanoparticles</td>
<td>radius: 1–100 nm</td>
<td>ceramic oxides</td>
</tr>
<tr>
<td>nanobiomaterials, photosynthetic reaction center</td>
<td>radius: 5–10 nm</td>
<td>membrane protein</td>
</tr>
<tr>
<td>nanowires</td>
<td>diameter: 1–100 nm</td>
<td>metals, semiconductors, oxides, sulphides,</td>
</tr>
<tr>
<td>nanotubes</td>
<td>diameter: 1–100 nm</td>
<td>carbon, layered chalcogenides</td>
</tr>
<tr>
<td>nanobiorods</td>
<td>diameter: 5 nm</td>
<td>DANN</td>
</tr>
<tr>
<td>2D arrays of nanoparticles</td>
<td>area: several nm²/µm²</td>
<td>metals, semiconductors, magnetic materials</td>
</tr>
<tr>
<td>surfaces and thin films</td>
<td>thickness: 1–1000 nm</td>
<td>insulators, semiconductors, metals, DNA</td>
</tr>
<tr>
<td>3D superlattices of nanoparticles</td>
<td>radius: several nm</td>
<td>metals, semiconductors, magnetic materials</td>
</tr>
</tbody>
</table>

bions, semiconductors, high-temperature supercon-
ductors, modified zeolites and adsorbents with depos-
ited proteins [21–28]. In this paper recent results are presented and discussed.

### Experimental

#### Materials

The tested materials were Na- and La-montmoril-
lonites from Lago Pellegrini (Argentina) [29, 30]. The substituted samples were obtained by saturation of the ion exchange capacities of the water-saturated clay samples with sodium and/or lanthanium chloride (0.5 M). Finally, the Na- and La-samples were air dried. Moreover, thermodesorption of liquids from natural zeolite–clinoptilolite and zeolite–mordenite (from Ukrainian Transcarpathian region) were made.

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 pa-
ers [26, 28] 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 de-
composition of xylene C₈H₁₀ used as a carbon source and ferrocene Fe(C₅H₅)₂ as a catalyst precursor.

Bovine serum albumin (BSA, Fraction V, mini-
mum 98%) was purchased from Sigma. Silica gel Davisol 653XWP (Z-300) was obtained from Supelco. Synthesis of ZS-300 (silica gel covered with chemically bonded triaminopropyltriethoxysilane) and ZB-300 (sil-