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N.O. Oliinyk [1], G.D. Ilnytska [1], G.A. Bazaliy [1], I.M. Zaitseva [1], M.A. Marinich [1], O.M. Sizonenko [2], A.S. Torpakov [2]

SPECIAL FEATURES FOR FUNCTIONALIZATION OF CARBON NANOTUBES NANOPOWDERS

[1] N. Bakul Institute for Superhard Materials of National Academy of Sciences of Ukraine
2 Avtozavodska Str., Kyiv, 04074, Ukraine, E-mail: oleynik_nonna@ukr.net
[2] Institute of Pulse Processes and Technologies of National Academy of Sciences of Ukraine
43a Bohoavlensky (Zhovtnevy) Ave., Mykolaiv, 54018, Ukraine

Physical and mechanical properties of carbon nanotube (CNT) powders depend on the method of their synthesis and chemical refinement. In order to create new composite materials that contain CNT powders as a filler, it is necessary to achieve functionalization of powder surface.

Functionalization of MWCNT-A brand CNT powder surface using pulse processing by high voltage electric discharges (HVED) in liquid leads to changes in distribution of its particles by size, a decrease in amorphous carbon content and in powder thermostability. Sedimentation separation of powder after HVED processing leads to formation of powder in three size ranges (0.118–0.139, 2.639–20.895 and 2.44–33.701 μm). Thermochemical modification of CNT powders leads to an increase in specific surface area, total volume of pores and micropores, their mean radii, a decrease in impurities content, changes in distribution of its particles by size, a decrease in amorphous carbon content and in powder thermostability. Electrochemical reconstruction of the surface of specimens of initial MWCNT-A brand CNT powder allows decreasing impurities content, free energy of surface saturation by water vapor, specific magnetic susceptibility, electrokinetic potential as well as increasing specific surface area, pores total volume and hydrogen adsorption.

Consecutive application of these methods leads to a decrease in impurities content in MWCNT-A brand CNT powder and to changes of its physical and chemical characteristics. Mass share of impurities decreases 3.7 times, mass share of soluble impurities decreases 7 times, specific magnetic susceptibility increases 5.2 times, electrokinetic potential increases 7.8 times. Specific electric resistivity increases 1.3 times, which leads to changes of adsorption and structural characteristics of powder: specific surface area increases 1.4 times and free energy of surface saturation by water vapor decreases by 11.9 %, which means that surface becomes more hydrophobic. As a result of such changes, rate of hydrogen adsorption on powders surface increases by 46 % and the current density at the potential of –0.6 V increases by 50 %.

***Keywords**: carbon nanotube powders, powder modification, physicochemical characteristics*

Currently the interest to nanosized materials in the world is growing. Carbon nanotubes (CNT) are of special interest among such materials. Scientific progress promotes intensification of nanomaterials production, including carbon nanotubes, which can be used in technical areas connected with biology, medicine, ecology.

During the synthesis of carbon nanotubes, thread-like structures of cylindrical shape are formed, which can be multilayered or single-layered with diameter of 0.8–5.0 nanometers and length up to hundreds of micrometers. Impurities that consist of catalytic metals, that are used in CNT production, as well as of amorphous carbon in form of carbon black and graphitized inclusions, fullerenes and other nanoparticles can be situated inside carbon nanotubes and on their outer surfaces.

Physical and chemical properties of carbon nanotubes depend on the method of their synthesis and chemical refinement. Creation of new materials with the use of CNT often demands functionalization of their surface, which can be performed in different ways:

– filling the inner space of CNT with media that change their electric, magnetic and mechanical properties;
– attachment of different functional groups to the ends of nanotubes;
– substitution of portion of carbon atoms by atoms of different elements;
– opening of double bonds on the surface of nanotubes by attachment of different reagents.

Determining the regularities of the impact of methods of CNT nanopowders functionalization on their physical and mechanical properties is an urgent task for creation of new composite materials.

High strength of 2–3.5 GPa, elastic modulus of 220–700 GPa [1] and developed specific surface area open prospective for application of CNT as a filler for composite materials [2], adsorbents [3] *etc*.

A wide range of CNT powders brands is developed in Ukraine for application in different areas. However, values of physical and chemical characteristics of CNT powder can vary in vide range so they do not reflect the range of powder particles size, its homogeneity by size and energetic condition of its surface (see Table 1).

Table 1. Basic physical and chemical characteristics of MWCNT-A brand CNT powder, which is produced according to regulatory acts of Ukraine

Indicator	Nanopowder MWCNT - A
Specific surface area (*BET*), m^2/g	110–200
Total pores volume, ml/g	0.2–0.4
Average pore radius, Å	60–100
Mass fraction of impurities, %	1.5
Mass fraction of soluble (Ni, Mg, Fe) impurities, %	0.70
Mass fraction of amorphous carbon impurities, %	0.50
Specific electric resistance, Ω·m	0.0006
Specific magnetic susceptibility, 10^{-8} m^3/kg	100.0

It is known that modification of powders can be performed in gaseous or liquid medium. Chemical and energetic condition of CNT powders surface can be changed using physical and chemical methods, which leads to changes of powders physical and chemical characteristics, first of all their specific surface area, adsorption capability and hydrophilic-hydrophobic balance of their surface [4-6]. Functionalization of CNT powders surface must be performed in order to make them suitable for efficient application. Functionalization leads to obtainment of fine nanotubes powders, which are homogeneous by their size and have given energetic state of surface [3].

The goal of present work is to determine the regularities of the impact of different methods of CNT powders surface modification, that are performed in liquid medium, on physical and chemical characteristics of treated powders.

METHODOLOGY

Studies were performed using specimens of CNT powders, produced at V.N. Bakul ISM of NAS of Ukraine from the product of pyrolysis of CVD-synthesis, performed by "Alit" company (Zhytomyr, Ukraine). Specimens of powder of MWCNT-A brand before and after their modification by pulse processing by high voltage electric discharges (HVED) in liquid, sedimentation separation, thermochemical processing and a full cycle of powder surface modification, which includes all of the above treatments and ends with an electrochemical treatment were studied.

High voltage electric discharge processing of specimens was performed at the Institute of Pulse Processes and Technologies of NAS of Ukraine (Mykolaiv). Processing parameters were as follows: integral energy of 0.6 MJ, working voltage of 50 kV, discharge circuit inductance of 0.6 μH, concentration of solid phase in liquid (distilled water) 1:50 [6].

Sedimentation separation of powders on three fractions of suspension after their HVED processing was performed during 48 h. Separation was performed under static conditions. Hereinafter modification and studies were performed using the powder of medium fraction, content of which was 60 % of initial specimen mass.

Thermochemical modification was performed using the mixture of chromic acid and sulfuric acid (method No. 3), mixture of nitric acid and sulfuric acid (method No. 2) and alkali melt (method No.1) by heating and subsequent normalization of surface by washing with distilled water at boiling temperature until washing water shows neutral reaction.

Cathode electrochemical processing was performed in a cell with platinum reticulate electrodes and a membrane in the electrolyte (0.1 N sulfuric acid solution). Polarization current was 0.5 A.

Specimens of powders were studied using a complex of common experimental methods. Mass share of impurities according to SSTU 3292-95 [7], specific magnetic susceptibility [8], free energy of surface saturation by water vapor [9], and specific electric resistivity [10] were determined. Electrokinetic potential was determined using method of electrophoresis with "Dzeta-potential-analyzer" device, made by Micromeritics company [11]. Adsorption and structure characteristics of powder (specific surface area, specific pores volume and mean pores radius) were determined using method of adsorption and structure analysis (ASA) with a "NOVA 2200" (Quantachrome, USA) gas adsorption analyzer [12, 13]. The structure of specimens was studied with the use of a PEM-UM transmission electron microscope and a NeoScope JCM-600 scanning electron microscope. Distribution of powder particles by size and powders homogeneity were determined with a "SEISHIN LMS-30" device, made in Japan.

Studies of the process of hydrogen adsorption of powder surface were performed using a P-5848 potentiostat and 0.1 N solution of sulfuric acid [14].

Thermal stability of powder was determined according to derivatograms obtained using a "Q1500" derivatograph.

RESULTS AND DISCUSSION

Results of studies of the impact of HVED processing and sedimentation separation of studied specimens on the characteristics of CNT powder are given in Figs. 1–4.

Fig. 1 shows that the mean diameter of powder particles before processing was 40.188 μm and 90 % of its mass was concentrated in size range of 11.84–115.7 μm. After HVED processing mean size of CNT powder decreases to 8.41 μm and the largest share of its mass is concentrated in the size range of 4.07–40.5 μm.

The data represented in Fig. 2 indicate that sedimentation separation of material after its HVED treatment leads to significant changes in the particles distribution by their size, namely to concentration of particles (5 % of total mass) with the size range of 0.118–0.139 μm in the upper layer (Fig. 2 *b*), while in the middle layer 60 % of total particles mass with the size range of 2.639 to 20.895 μm is concentrated (Fig. 2 *c*) and in the lower layer 35 % of particles total mass is concentrated with the size range of 2.44–33.701 μm (Fig. 2 *d*).

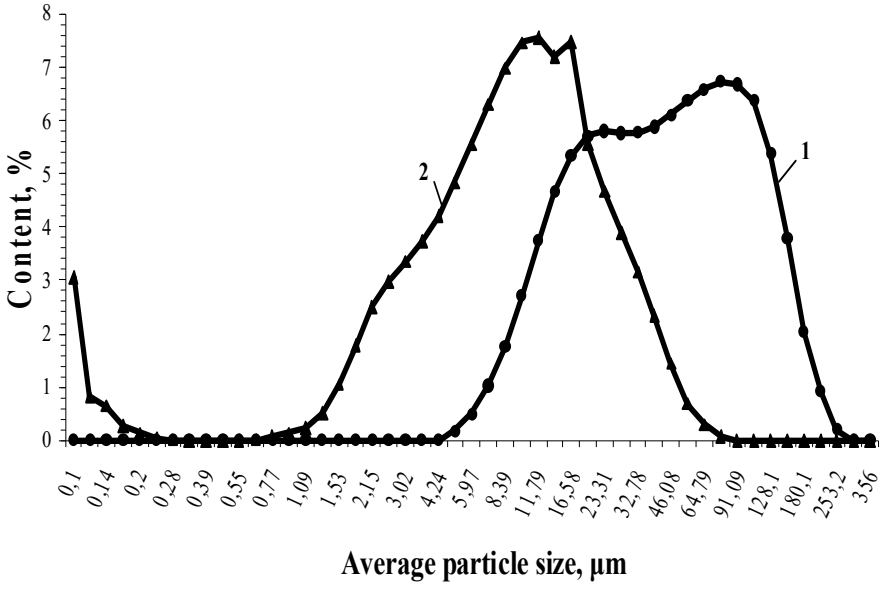


Fig. 1. Granulometric characteristics of the sample of initial CNT powder (*1*) and of that after HVED processing (*2*)

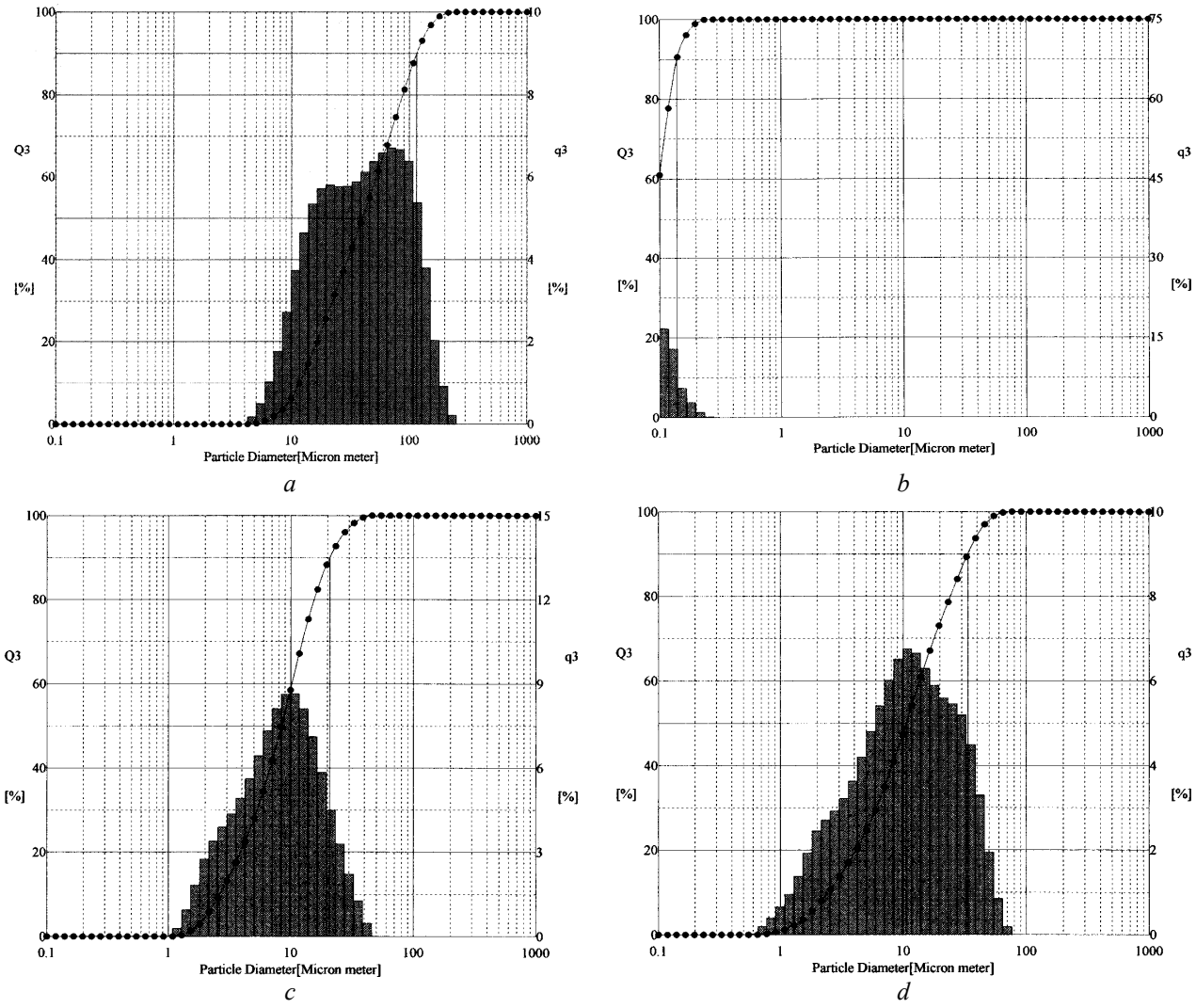


Fig. 2. Granulometric characteristics of the original sample of CNT (*a*), sample of CNT after HVED processing and sedimentation separation: upper layer (*b*), middle layer (*c*), lower layer (*d*)

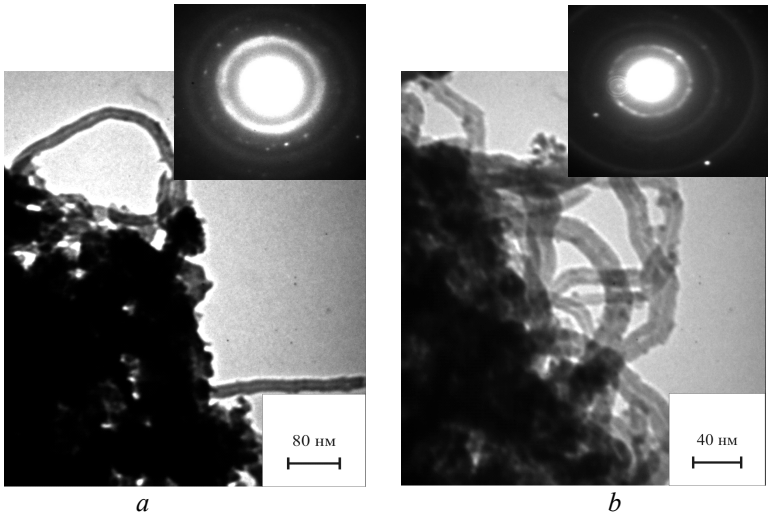


Fig. 3. Microstructure and electron diffraction of the initial sample (*a*) and of the sample after HVED processing and sedimentation separation (middle layer) (*b*)

Electron diffraction patterns of MWCNT–A brand initial powder (Fig. 3 *a*) contain circular reflexes of carbon nanotubes, intensive halo of amorphous carbon and a lot of impurities. Electron diffraction patterns of CNT powder after HVED processing indicate that the content of amorphous carbon is decreased (intensity of amorphous carbon halo is decreased), while the intensity of CNT circular reflexes increases (Fig. 3 *b*).

TG curves of studied specimens indicate that resistance to oxidation by air oxygen is different for initial and processed powder. The temperature of the oxidation initiation of parent material is 560 °C while for material after HVED processing it decreases to 370 °C (Fig. 4).

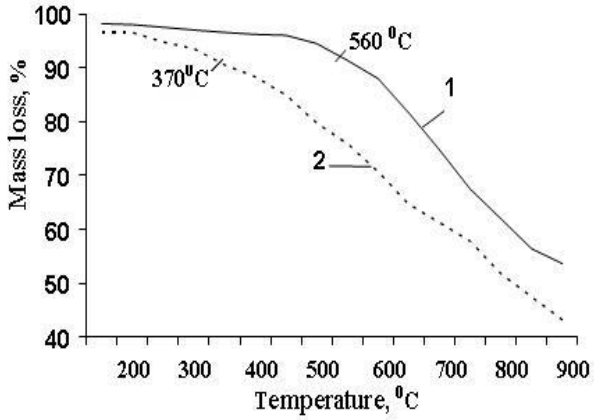
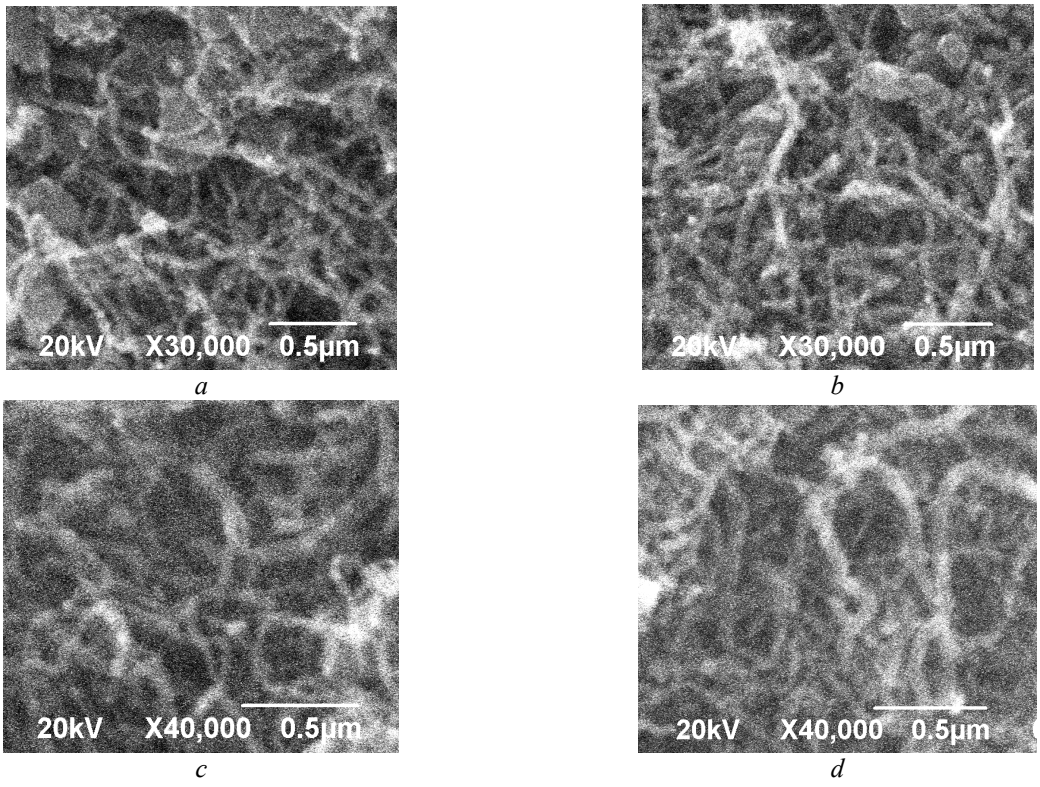


Fig. 4. Thermograms (TG curve) of the CNT samples before (*1*) and after HVED processing (*2*)



a *b* *c* *d*

Fig. 5. General view of carbon nanotube powders (results of electron microscopic studies) obtained with a NeoScope JCM-600 scanning microscope: *a* – MWCNT-A powder before modification; powders after modification *b* – MWCNT-1; *c* – MWCNT-2; *d* – MWCNT-3

Thus it is experimentally found out that HVED processing leads to changes in powder particles distribution by size, a decrease in amorphous carbon content and a decrease in powders thermal stability. Sedimentation separation after HVED processing leads to formation of powder of three different size ranges (0.118–0.139, 2.639–20.895, and 2.44–33.701 μm).

Results of studies on the impact of thermochemical modification on the characteristics of studied powders are shown in Fig. 5 and Table 2.

Table 2. Adsorption-structural characteristics of carbon nanotube powders: MWCNT-A before modification powder and after its modification: MWCNT-1, MWCNT-2, MWCNT-3

Indicator	Meaning			
	Nanopowder MWCNT–A before modification	Modified nanopowder MWCNT–A		
		MWCNT-1	MWCNT-2	MWCNT-3
The method of thermochemical modification		**No. 1**	**No. 2**	**No. 3**
Content of amorphous carbon, %	7.2	5.0	2.0	0.0
Specific surface area (BET), m^2/g	136.0	138.4	147.3	153.8
Volume of micropores, ml/g	0.5954	0.6756	0.7265	0.6539
Total pores volume (DFT), ml/g	0.3088	–	0.3610	–
Total volume of cylindrical pores (DFT), ml/g	0.3150	0.3190	0.3670	0.3230
Average pore radius, Å	87.57	97.63	98.67	85.01
Microporus radius (DR), Å	93.39	27.12	86.08	28.36
Pore radius (DFT), Å	6.739	–	16.92	–
Radius of cylindrical pores (DFT), Å	25.510	25.510	25.510	11.410
Adsorption energy, kJ/mol	13.920	9.587	15.103	9.166
Free energy of saturation of the surface by water vapor, J/mol·g	37.0	40.5	48.9	52.4

As a result of thermochemical modification of the specimens of brand MWCNT–A initial powder, which was performed according to methods No 1, 2, 3, three different powder modifications were obtained: MWCNT–1 obtained by method No. 1, MWCNT–2 obtained by method No. 2 and MWCNT–3 obtained by method No. 3.

Fig. 5 indicates that the powder after modification is visually different from the initial powder, as it has different quantity of nanotubes "clews" with knots and thickenings as well as different number of scattered homogeneous tubes.

The data given in Table 2 indicate that a decrease in X-ray-amorphous carbon content leads to an increase in specific surface area of powders by 1.8–11.5 % as well as to increase in total pores area and volume of cylindrical pores while radii of cylindrical pores decrease and free energy of surface saturation by water vapor increases.

Results of studies on physical and chemical characteristics of powders have shown that, if compared to initial brand MWCNT-A powder, 1.5, 3.6 and 7.2-times decrease in X-ray-amorphous carbon content in different modified powders leads to a decrease in total impurities content (as an incombustible residue) by 20.9, 27.3, and 40.9 % respectively, 1.7, 2, and 3 times decrease in soluble impurities content respectively and, to 1.2, 1.5, and 3.1 times decrease in nickel content respectively while specific magnetic susceptibility decreases 2, 2.4, and 5 times respectively and specific surface are increases by 1.8, 4.8, and 11.5 % respectively.

Thus, it has been experimentally found out that thermochemical modification of CNT powder leads to an increase in specific surface area, total pores volume, micropores, and their mean radii as well as to a decrease in impurities content.

The results of the study on the effect of surface modification of the sample of the original MUNT-A powder on its characteristics (Fig. 6) are represented by the cathodic potentiodynamic curves of hydrogen adsorption on the surface of the original powder (curve 1), after the modification of HVED treatment by

treatment and sedimentation separation (curve 2), a complete cycle of modification (curve 3), in which thermochemical treatment is carried out according to method 3.

As it follows from the data shown in Fig. 6, adsorption of hydrogen on powders surface takes place in the range of negative potentials of 0.1 to 0.6 V. At the potential of – 0.6 V the process of hydrogen adsorption transforms to process of its excretion. After this value only excretion of hydrogen takes place. At the potential of –0.6 V current density of hydrogen adsorption on initial MWCNT–A brand powder (Fig. 6, curve 1) is 2 mA/cm^2, which is significantly lower than the value of current density of hydrogen adsorption for powder after sequential processing: HVED processing and sedimentation sedimentation separation, which is 2.8 mA/cm^2 (Fig. 6, curve 2) and also much lower than the value of current density of hydrogen adsorption for powder after full modification cycle which is 3 mA/cm^2 (Fig. 6, curve 3). The rate of hydrogen adsorption on the surface of modified powder is higher by 46.4 % as compared to the value characteristic for initial powder.

Table 3 shows the physico-chemical characteristics of the powder MWCNT-A before and after the full cycle of modification, in which the thermochemical treatment was carried according to method 3.

Table 3. Physical and chemical characteristics of carbon nanotube powder MWCNT–A before and after full cycle of powder surface modification

Indicator	Meaning	
	Nanopowder MWCNT–A after modification	**Nanopowder MWCNT–A before modification**
Average particle diameter, μm	8.409	40.18
Specific surface area(BET), m^2/g	156.7	136.0
Total pores volume, ml/g	0.462	0.3088
Average pore radius, Å	87.0	87.57
Mass fraction of impurities, %	0.4	1.5
Mass fraction of soluble (Ni, Mg, Fe) impurities, %	0.1	0.70
Specific electric resistance, Ω·m	0.0008	0.0006
Specific magnetic susceptibility, $10^{-8,}$ m^3/kg	20.0	100.0
Electrokinetic potential, V	0.105	–0.817
Free energy of surface saturation by water vapor, J/mol·g	35.7	37.0

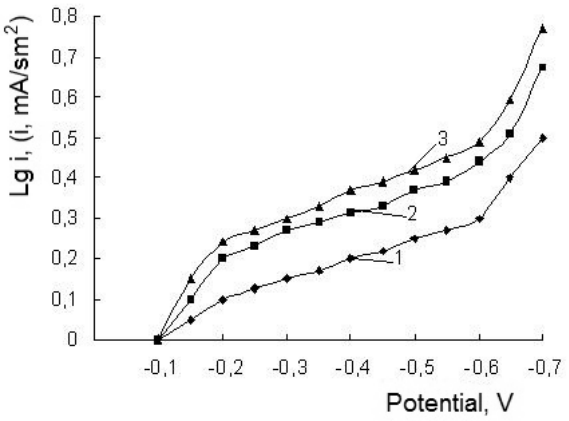


Fig. 6. Potentiodynamic cathode polarization curves of adsorption and hydrogen removal from a 0.1N solution of H_2SO_4 on the surface of carbon nanotube powder MWCNT-A (*1*) and sequential processing: HVED processing and sedimentation (*2*) and after sequential application of HVED processing, sedimentation, chemical modification and after electrochemical reconstruction of the surface (*3*)

As it follows from the data shown in Table 3, full cycle of CNT powders surface modification, which is considered in present work, leads to a decrease in impurities content, free energy of surface saturation by water vapor, specific magnetic susceptibility and electrokinetic potential as well as to increase in specific surface area, pores total volume and specific electric resistivity. Besides, such a modification of powders leads to an increase in hydrogen adsorption.

CONCLUSIONS

Comparative analysis of physical and chemical characteristics of specimens of initial MWCNT–A brand powder and powder after modification using pulse processing with high voltage electric discharges in liquid, sedimentation separation, thermochemical and electrochemical processing have shown that:

1. HVED processing leads to changes of powders particles size distribution, a decrease in amorphous carbon content and powder thermal stability. Sedimentation separation of powders after HVED processing leads to formation of a powder of three different size ranges, namely – 0.118–0.139, 2.639–20.895 and 2.44–33.701 μm.
2. Thermochemical modification of powders leads to an increase in specific surface area, total pores volume, micropores, their mean radius as well as to a decrease in impurities content.
3. Electrochemical reconstruction of specimens surface of initial MWCNT–A brand powder leads to a decrease in impurities content, free energy of surface saturation by water vapor, specific magnetic susceptibility and electrokinetic potential as well as to an increase in specific surface area, pores total volume, and hydrogen adsorption.

Consecutive application of pulse processing with high voltage electric discharges in liquid, sedimentation separation, thermochemical modification and electrochemical reconstruction of surface promotes refinement of impurities and changes of physical and chemical characteristics of specimens of initial MWCNT–A brand powder. Mass share of impurities decreases 3.7 times, mass share of soluble impurities decreases 7 times, specific magnetic susceptibility decreases 5.2 times and electrokinetic potential increases 7.8 times. A 1.3 times increase of specific electric resistivity occurs, which leads to changes of adsorption and structure characteristics of powder: specific area of powder surface increases 1.4 times and free energy of surface saturation by water vapor decreases by 11.9 %, which means that surface becomes more hydrophobic. As a result of such changes, an increase takes place in hydrogen adsorption of powders surface rate by 46 % as well as an increase of current density at potential of – 0.6 V by 50 %.

Consecutive application of pulse processing with high voltage electric discharges in liquid, sedimentation separation, thermochemical and electrochemical processing of CNT ensures obtainment of fine powders, homogeneous by their size, with low content of impurities and hydrophobic energetically active surface.

Особливості функціоналізації нанопорошків вуглецевих нанотрубок

Н.О. Олійник, Г.Д. Ільницька, Г.А. Базалій, І.М. Зайцева, М.А. Марініч, О.М. Сизоненко, А.С. Торпаков

Інститут надтвердих матеріалів ім. В.М. Бакуля Національної академії наук України
вул. Автозаводська, 2, Київ, 04074, Україна, oleynik_nonna@ukr.net
Інститут імпульсних процесів та технологій Національної академії наук України
просп. Богоявленський 43а, Миколаїв, 54018, Україна

Фізичні і фізико-хімічні властивості порошків вуглецевих нанотрубок (ВНТ) залежать від способу синтезу і хімічного очищення. Для створення нових композиційних матеріалів, до складу яких входять порошки УНТ як наповнювачі, необхідна функціоналізація поверхні порошків. Виконання функціоналіації поверхні порошків ВНТ марки МУНТ-А із застосуванням імпульсної обробки високовольтними електричними розрядами (ВЕР) в рідині призводить до зміни розподілу часток порошку за розмірами, зменшення вмісту аморфного вуглецю, зниження термостійкості порошку. Седиментаційний поділ порошку після ВЕР

обробки призводить до утворення порошку трьох діапазонів розмірів (0.118–0.139, 2.639–20.895, 2.44–33.701 мкм). Термохімічне модифікування порошку ВНТ призводить до збільшення питомої площі поверхні, сумарного об'єму пор, мікропор, їхнього середнього радіусу, зниження вмісту домішок, до зміни розподілу частинок порошку за розмірами, зменшення вмісту аморфного вуглецю, зниження термостійкості порошку. Електрохімічна реконструкція поверхні зразка вихідного порошку марки МУНТ-А призводить до зниження вмісту домішок, вільної енергії насичення поверхні парами води, питомої магнітної сприйнятливості, електрокінетичного потенціалу; зростанню питомої площі поверхні, об'єму пор, адсорбції водню.

Послідовне застосування цих методів сприяє очищенню від домішок і зміні фізико-хімічних характеристик зразка вихідного порошку марки МУНТ-А. Зменшується масова частка домішок в 3.7 рази, масова частка розчинних домішок в 7 разів, питома магнітна сприйнятливість в 5.2 рази, електрокінетичний потенціал в 7.8 рази. Відбувається зростання питомого електроопору в 1.3 рази, що призводить до зміни адсорбційно-структурних характеристик порошку: питома площа поверхні порошку зростає в 1.4 рази, вільна енергія насичення поверхні парами води знижується на 11.9 %, тобто поверхня стає більш гідрофобною. В результаті відбувається зростання швидкості адсорбції водню на поверхні порошку на 46 % і зростання густини струму на 50 % при потенціалі –0.6 В.

***Ключові слова**: порошки вуглецевих нанотрубок, модифікування порошку, фізико-хімічні характеристики*

Особенности функционализации нанопорошков углеродных нанотрубок

Н.А. Олейник, Г.Д. Ильницкая, Г.А. Базалий, И.Н. Зайцева, М.А. Маринич, О.Н. Сизоненко, А.С. Торпаков

Институт сверхтвердых материалов им. В.Н. Бакуля Национальной академии наук Украины
ул. Автозаводская, 2, Киев, 04074, Украина, oleynik_nonna@ukr.net
Институт импульсных процессов и технологий Национальной академии наук Украины
просп. Богоявленский 43а, Николаев, 54018, Украина

Физические и физико-химические свойства порошков углеродных нанотрубок (УНТ) зависят от способа синтеза и химической очистки. Для создания новых композиционных материалов, в состав которых входят порошки УНТ в качестве наполнителей, необходима функционализация поверхности порошков.

Выполнение функционализации поверхности порошков УНТ марки МУНТ-А с применением импульсной обработки высоковольтными электрическими разрядами (ВЭР) в жидкости, приводит к изменению распределения частиц порошка по размерам, уменьшению содержания аморфного углерода, снижению термостойкости порошка. Седиментационное разделение порошка после ВЭР обработки приводит к образованию порошка трех диапазонов размеров (0.118−0.139, 2.639−20.895, 2.44−33.701 мкм). Термохимическое модифицирование порошка УНТ приводит к увеличению удельной площади поверхности, суммарного объема пор, микропор, их среднего радиуса, снижению содержания примесей, к изменению распределения частиц порошка по размерам, уменьшению содержания аморфного углерода, снижению термостойкости порошка. Электрохимическая реконструкция поверхности образца исходного порошка марки МУНТ-А позволяет снизить содержание примесей, свободную энергию насыщения поверхности парами води, удельную магнитную восприимчивость, электрокинетический потенциал; повысить удельную площадь поверхности, объем пор, адсорбцию водорода.

Последовательное применение этих методов способствует очищению от примесей и изменению физико-химических характеристик образца исходного порошка марки МУНТ-А. Уменьшается массовая доля примесей в 3.7 раза, массовая доля растворимых примесей в 7 раз, удельная магнитная восприимчивость в 5.2 раза, электрокинетический потенциал в 7.8 раза. Происходит возрастание удельного электросопротивления в 1.3 раза, что приводит к изменению адсорбционно-структурных характеристик порошка: удельная площадь поверхности порошка возрастает в 1.4 раза, свободная энергия насыщения поверхности парами воды снижается на 11.9 %, то есть поверхность становится более гидрофобной. В результате чего происходит возрастание скорости адсорбции водовода на поверхности порошка на 46 % и возрастание плотности тока на 50 % при потенциале –0.6 В.

***Ключевые слова**: порошки углеродных нанотрубок, модифицирование порошка, физико-химические характеристики*

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