

Synthesis of the Carbon Nanomaterials Based on Renewable Bioresources

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The effectiveness and feasibility of producing nanoscale carbon materials from renewable bioresources were shown as an example marsh mass. The mechanisms of synthesis of amorphous organic carbon from sphagnum moss species modified by a liquid peat phase of humic nature are discussed. A fundamentally new way of producing carbon nanotubes by mechanical activation of amorphous organic carbon is described.

Keywords: Biological resources, Sphagnum mosses, Sorption capacity, Amorphous carbon, Carbon nanotubes, Functional materials.

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1. INTRODUCTION

In addition to traditional raw material for synthesis of nanocarbon materials that are based on the use of natural graphite or natural gas, in connection with the problem of their inevitable depletion renewable bioresources, in particular organic products such as peat one of components of which are Sphagnum mosses [1], can be promising products for their synthesis. Sphagnum mosses unlike higher plants do not root system which dictates almost complete absence of mineral substances in products of their decomposition. These mosses are among the fast renewable vegetable resources whose reserve on the planet, in particular in Russia, can completely meet the annual requirements of world processors of raw materials for many centuries. Therefore, carbonaceous raw materials on the basis of Sphagnum mosses have dramatically high carbon concentration and accordingly very low ash content. Another source of renewable resources of marshland ecosystems are easily solvable organic substances of humic nature, which consist, along with carboxyl functional groups, of hydroxyl and aromatic fragments. Owing to this fact amphiphilic properties characteristic of the substances provide a means for them to intensively interact with both various metals and organic compounds. Depending on the concentration of humic substances in water solutions the latter can play a role of both inhibitors and stimulators of various including physiological, processes [2, 3].

2. EXPERIMENTAL RESULTS AND DISCUSSIONS

To establish the optimum concentration of humic substances in water solution for reaching its maximum reactivity we have conducted an experiment. Its aim was to obtain and analyze the size, shape, structure and elemental composition of dendroid images of humic substances that are in peat hydrolyzate with a 5, 10, 15 and 20% in distilled water [4, 5].

To obtain exact local qualitative and quantitative characteristics of the elemental composition in peat hydrolyzate (see Table 1) energy dispersive spectrometer (EDX) "INCA-ENERGY", which was a part of scanning electron microscope (SEM) EVO 60 XVP (firm "Carl Zeiss", Germany), was utilized. The sensitivity of the technique was ~ 0,1 %, the width of electron beam ~ 20-30 nm. Specimen in extremely thin layer was put onto the aluminum table of the device or put between two cover glasses. After water evaporation at the table or one inner surface of the glasses their surface was processed with spattering of gold layer.

Table 1 – Elemental composition of carbon compounds from peat hydrolyzate

Element	Specimen onto aluminum table				Specimen onto cover glasses			
	Results of analysis		Results of analysis with background distracted		Results of analysis		Results of analysis with background distracted	
	Wt. %	At. %	Wt. %	At. %	Wt. %	At. %	Wt. %	At. %
C	23	35	25	31	21	31	28	34
O	29	34	74	68	46	51	72	66
Na	2.8	2.2			4	3		
Al	42	28						
Cu	2.5	0.7						
Mg					1	0.7		
Si					14	8.8		
cA					13	5.7		

As seen from the Table 1 oxygen and carbon are the basis of samples analyzed, which as a whole correlates with the elemental composition of humic substances [6, 7].

The major experiment was conducted with scanning electron microscopy (SEM), atomic-force and confocal microscopy (AFM, CM) and also Raman scattering, IR Fourier spectroscopy, and small angle X-ray scattering technique. As a result topology and chemical structure

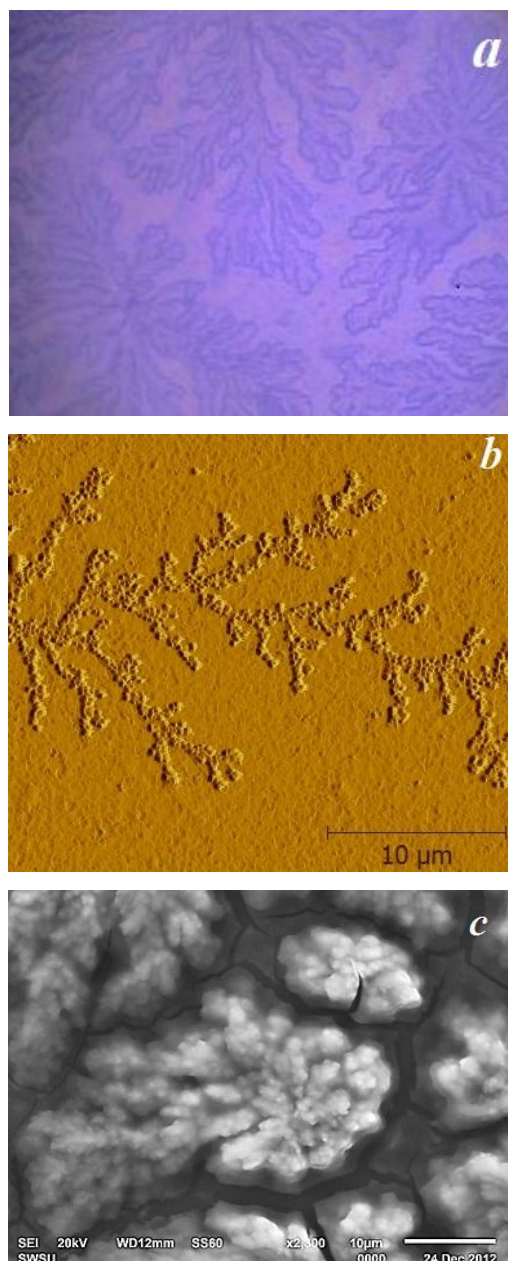


Fig. 1 – Microphase stratification in the form of fractal structures according to a) – AFM, b) – CM, c) – SEM

of fractal formations were studied and a number of plane and out-of-plane deformation vibrations responsible for their manifestation were found (Fig. 1).

Characteristic features of self-organizing structures according to CM, AFM, and Raman scattering microscopy given in Fig. 1 a-c show a decrease in size of all fragments of fractal structures as the solution concentration is reduces. Especially graphically it is seen with transversal size of individual elements. For example, if for the concentration of 20 % it was of order 15 μm in magnitude then for 10 % – 7-8 μm , and for 5 % – 2-3 μm (Fig. 2). It was established that the reduction of transversal size of fractal branches was linearly dependent on the concentration of the solution studied. In doing so, optimum concentration must be equal to 6 %, and the length and width of the fractal branch of the dendroid shape must amount to 3 μm .

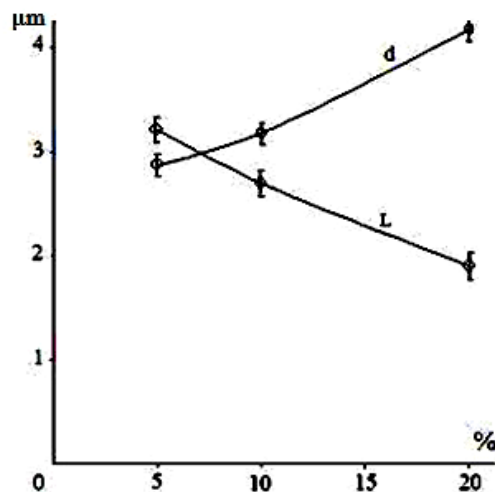


Fig. 2 – The trend of width and length dependence of dendroid structures for organic carbon of humic nature (d – width and L – length, in μm) according to CM data

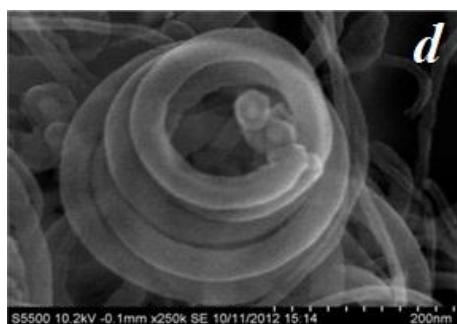
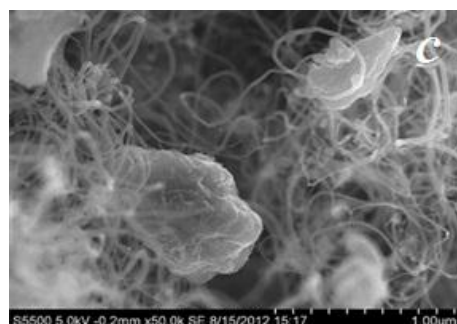
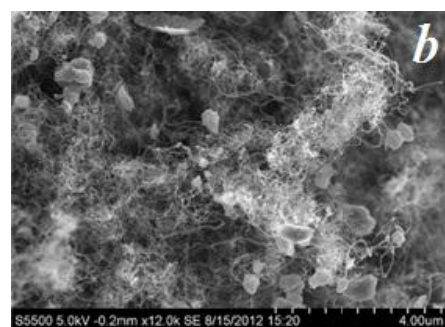
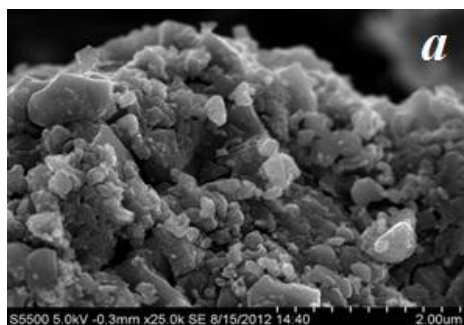
Thereafter the experiment was conducted further to implement synthesis of amorphous carbon on the basis of sphagnum mosses modified by peat hydrolyzate with the desired concentration of humic substances. As a source material Sphagnum fuscum was used. It was pre-dried out thoroughly and sifted to remove admixtures. After that it underwent pyrolysis with the help of an advanced technology at 950 $^{\circ}\text{C}$ in a vacuum furnace with a uniform heating chamber. Then obtained raw material underwent disintegration for reaching dispersion 100-150 μm and was activated mechanically in the reactor of vario-planetary mill Pulverisette 4 (firm “Fritsch”, Germany). Balls from hard alloy of VK 6 type with a diameter of 16 mm were grinding bodies in the vario-planetary mill. The reactor of the mill presented an airtight container from corrosion-resistant steel with an insert from VK 6 steel. In conducting experiments the following mode was used: the rotational speed of the major disk – 400 min^{-1} , the rotational speed of satellites – 800 min^{-1} , intensity (the ratio of the source material mass to the grinding ball mass) 1 : 27, and as a protective atmosphere argon was used. As a result of this stage of the experiment powder material was synthesized with a particle size of less than 50 μm , pore size of 200-1100 nm, and specific surface of 220 m^2/g (single-point BET’s technique). The material structure, its **sorption** and electrochemical properties made it possible to use it in various areas of economic activity: from removing unsanctioned inflow of hydrocarbons into the environment to fabrication on its basis of electrodes for Li-ion batteries [8].

Elemental composition of the synthesized material indicated the high purity of carbon that is comparable with one of its allotropic form – graphite (see Table 2).

The experiment was conducted further to enhance dispersivity of amorphous carbon by mechanochemical method in order to increase specific surface values to 400-500 m^2/g and consequently to increase its sorption capacity. As a result, fibrous material from carbon nanotubes appeared among lamellar structures of carbon (Fig. 3).

Table 2 – Content of chemical elements in amorphous carbon

Content of chemical elements (mass %)	Spectra			
	Spect. 1	Spect. 2	Spect. 3	Spect. 4
O	0.25	0.24	0.27	0.23
C	99.1	99.0	99.1	99.2
W	0.12	0.11	0.10	0.8
Ni	0.005	0.004	0.008	0.004
Cu	0.007	0.011	0.010	0.009
Co	0.12	0.15	0.14	0.12
Fe	0.09	0.07	0.05	0.03
Ti	0.017	0.011	0.005	0.029

**Fig. 3** – Kinetics of forming carbon nanotubes from amorphous carbon on the basis of Sphagnum mosses: a, b – topograms of organic carbon for 7-8 hours of mechanoactivation; c, d – topograms of organic carbon for 8-10 hours of mechanoactivation.

As a result it was established that by the end of 10th hour of mechanoactivation the volume of nanotubes in activated material had been 100 % whereas by the end of 8th hour their part had not surpassed 70 %. In accord with the proprietary method of obtaining carbon material mechanoactivation was done with grinding 15-mm-diameter balls (18 balls) [9]. In doing so, the total work-load of the mill grinding cartridge (volume of grinding bodies plus the total filling of the cartridge with amorphous carbon) was 10 g, which corresponded to the intensity of grinding 1 : 50. The experiment on mechanoactivation was conducted both in argon atmosphere (by analogy with standard schemes of carbon nanotubes (CNTs) fabrication) and in air. In both cases exterior view, structures, and properties of the synthesized material were the same.

An increase in the specific surface of synthesized from nanotubes nanomaterial up to 550 m²/g makes it possible to enhance its sorption capacity virtually by an order of magnitude compared to the most popular ranks of coal. Specific surface was determined by analyzer “Sorbtometer-M” (Russia, Novosibirsk) using thermal desorption of nitrogen (see Table 3).

Table 3 – Sorption capacity of VNTs and active carbon on metal cations depending on the time of nanotube formation and rank of coal

Carbon material	Sorption capacity, mg/g			
	Ag ⁺	Pb ²⁺	Cd ²⁺	Cu ²⁺
CNTs after 8 h of mechano-chemical processing	59 (70)	51 (57)	47 (52)	37 (40)
CNTs after 10 h of mechano-chemical processing	63 (74)	54 (61)	51 (57)	40 (44)
CNTs after 27 h of mechano-chemical processing	85 (93)	70 (77)	65 (72)	59 (63)
Active coal Silcarbon	6.3 (7.4)	7.3 (8.5)	6.7 (7.4)	5.9 (6.4)
Active coal OAO (OJSC) “Medisorb”	9.2 (10.9)	10.3 (11.7)	8.3 (9.5)	7.3 (8.2)
Active coal OAO (OJSC) “Farmstandart-leksredstva”	9.7 (9.7)	10.2 (12.2)	7.8 (8.8)	7.2 (8.1)
Active coal OAO (OJSC) “Uralbiofarm”	7.9 (8.7)	8.9 (9.3)	7.5 (8.2)	6.9 (7.3)

Footnote: values of metal sorption are given at exposition of 1 h, in brackets – 3 h. Processing temperature in concentrated HNO₃ – 120 °C.

As is seen from Table 3, the experiment determined the sorption of Ag, Cu, Pb, and Cd cations from water solutions. Three series of nanotubes obtained as a result of 8, 10, and 27 h mechanochemical processing of amorphous carbon were studied as sorbents. Before sorption examinations carbon materials were treated with concentrated acid HNO₃ at a temperature of 120 °C in analytical autoclave for 55 min. Then obtained samples were washed with distilled water in ultrasound washer “Elmasonic S15” (Germany) for 45 min before neutral pH was achieved. After that they were processed in centrifuge for 15 min and dried for 75 min at a temperature of 150 °C in desiccator “Binder”. To study sorption of Ag⁺, Pb²⁺, Cd²⁺ и Cu²⁺ ions individual solutions with concentration of 150 mg/l

at a ratio of solid substance and liquid of 1 : 25 (0.1 g of CNTs for 25 ml of solution) during 130 min at a constant shaking were prepared. Mixture was filtered after the achievement of sorption equilibrium. The content of metals in filter was done with flame absorption (atomization in flame) at spectrometer "AAAnalyst 200" (PeikutElmer, USA). Active coals were used as comparison objects of medical purpose fabricated by "Medisorb OAO" (Open Joint-Stock Company, Russia, Perm), "Farmstandart-leksredstva OAO" (OJSC, Russia, Kursk) and "Uralbiofarm OAO" (OJSL, Russia, Ekaterinburg) and activated coal of "Silcaibon Aktivkohle GmbH". Also, another analytical equipment was used. For example, the structure of surface, particle shape and size of modified carbon, and structure of nanofibrous carbon were examined with high resolution scanning electron microscope Hitachi

S5500 with an attachment for transmission electron microscopy.

3. CONCLUSIONS

Thus, it is appropriate to use renewable resources of peat bogs such as peat liquid phase and sphagnum mosses for synthesis of carbon nanomaterials, which find wide use today not only as sorption compounds and dissipaters of excitation energy but also as modifiers of interphase boundaries of composite systems and materials, and also radio- and thermostabilizing additives. Also, we have every reason to believe that synthesized nanotubes form amorphous organic carbon feature high effectiveness as carbon agents for synthesis of metal carbides and power-consuming anode materials for Li-ion batteries.

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