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Water mediated modification of structure and physical chemical properties of nanocarbons

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Abstract

Considerable amount of water incapsulated in native shungite carbon (ShC) and its amphiphilic properties are originated from fullerene-like structure. We report on the study of ShC and its stable aqueous dispersion by high-resolution solid state ^{13}C and ^{1}H MAS NMR, and time-of-flight (TOF) mass spectrometry. ^{13}C NMR spectrum changes substantially as ShC was transformed into aqueous dispersion: a narrow sp^2-carbon signal (at 116 ppm) attributed to the basic structural unit (BSU) in the form of bowls is observed. Distance from carbon atoms in BSU to hydrogen atoms of water was estimated at ~0.8 nm using cross-polarization technique. ^{1}H solid state NMR spectrum consists of two peaks at 0.40 and 3.16 ppm. They were assumed to be related to water complexes on BSU (0.40 ppm) and to adsorbed water (3.16 ppm). TOF mass spectra of the ShC aqueous dispersion showed maximum intensity at ~284 m/z corresponding to the dominant structure of ShC.

Keywords: Nanocarbon; Shungite; Nanotechnology

1. Introduction

Carbon nanoparticles (NP) play an important role in biological and geochemical processes and affect the environmental situation as they provide a building material for soils and sediments and carry organic pollutants. They are used in production of adsorbents and filters for water purification and are considered to be promising elements in biology and pharmacology [1,2]. These applications of NPs propose their conversion into the form of aqueous dispersions. Hence the problems in nanocarbon–water interaction are acute.

Some publications on the molecular-dynamic modelling of water behaviour near the native surface, including carbon nanotubes, have seen the light lately [3]. The latest calculations are valuable because the authors formulate various models of carbon–water force interaction; this interaction is thought to be due to the formation of the donor-acceptor bonds of carbon atoms with water molecules. There is a method for the production of stable aqueous dispersions of fullerenes proposed by G.V. Andrievsky and used to produce aqueous dispersions of shungite [4]. The authors of the above publications have made assumptions regarding the molecular structure of water dispersions of fullerenes, hydration effects in them and the "fullerene–water" interaction pattern. Nevertheless, they are still poorly understood because small concentrations of nanocarbon in water are difficult to identify and NPs are highly active, their activity can manifest itself in low concentrations.

The following mechanisms are considered to explain stability of aqueous dispersions of carbon NPs:

1. Formation of specific polar groups on the surface of NPs.
2. Formation of specific water "cages" around NPs (clathrate or semiclathrate hydration).
3. Presence of relatively small structural units around NPs with dipole momentum (interacting with water dipole) which takes part in oscillation and rising entropy of the system. This entropy compensates an excess of the surface energy of NPs and stabilizes the dispersion.

We suppose the latter to be the most challenging in the case of stabilization of shungite carbon aqueous dispersion.

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Of the known nanocarbon materials, amphiphility has been described for shungite carbon (ShC). Hydrophobic nature of carbons is in contradiction with a considerable amount of water incapsulated in ShC (2–7 wt.%) [5]. However, the source of bipolar structure was not understood. Obviously, to efficiently use shungites on a large scale, the above problems should be solved. First of all, we need to find the source of activity of ShC, which, according to available geological evidence, was formed in water [6,7].

Until recently, the high activity of ShC has been attributed to globules (<6 nm) that exhibit some characteristics of fullerene-like structures [8]. Globular elements aggregate to form durable clusters, thereby decreasing ShC activity, whereas their disaggregation is accompanied by a rise in carbon and shungite rock activity [9].

Separate nanoparticles similar to aggregated giant fullerenes that occur as multi-shelled structures with a distance of 0.35 nm between graphite-like planes have been detected by HRTEM in ShC powder subjected to fine grinding and heat treatment [10]. These particles display globular and polyhedral shapes and size of tens-hundreds nanometers. However, fragments of shells or bent graphene stacks were revealed among 3-dimensional closed shells (globular structural elements) in HRTEM images of ShC [11,12]. The bent stacks (bowls) display a size of 0.5–0.7 nm with thickness of 2–5 nm (5–14 layers) determined by X-ray and electron diffraction. A minimal (basic) structural unit (BSU) of ShC (~0.51 nm) was detected by small-angle-X-ray scattering (SAXS) and were supposed to be the most mobile and active element of ShC [13]. SAXS and atomic force microscopy (AFM) data have led us to assume that two levels of the structural organization of ShC are combinations of BSU [14].

New evidence of ShC structural unit dimension was obtained in SANS study of ShC porosity and during ShC modification with ozone and steam. Pores on the second structural level (with a characteristic radius of ca.10 nm) have an internal fractal structure built by particles whose sizes are beyond SANS resolution, ca.1 nm [15]. Micro- and mesopores were mainly developed under steam treatment, otherwise ultramicropores (dimensions of 0.4–0.7 nm) predominantly increased under ozonization [16].

The first stage in the formation of ShC structure (the formation of clusters smaller than 10 nm) can be traced by analyzing the conditions of formation of fullerene clusters in aqueous and binary solvents and upon clusterization of fullerene-containing soot (FS).

According to [17], elementary particles in powdered fullerenes and FS are 0.45 and 0.6 nm in size, respectively. They combine to form clusters, 30–80 nm in diameter, with a fractal size of 1.8 for fullerene and 1.6 for FS. The structure of soot nanoclusters is not in equilibrium and is changed substantially by various solvents [18]. In addition to fullerenes and carbon particles (ions and atoms), FS products contain fullerene fragments. Comparative analysis of the structures of the BSU of two carbon materials (FS and ShC) would probably provide a better understanding of the basis of the unique properties of both carbons.

X-ray diffraction curves of ShC after arc discharge showed increase in intensity at $2\theta_{\mathrm{Br}} \sim 17.9–18.0$ (for CuK$_\alpha$ radiation), corresponding to BSU of ShC, and similarity of the diffraction pattern with that of FS [19]. The halo in the same region at ca.$2\theta_{\mathrm{Br}} \sim 17^{\circ}$ was reported for ultradisperse diamond of different synthesis [20].

However, ShC disintegration into structural elements is feasible in aqueous media under ultrasonic treatment [21]. Comparative study of aqueous dispersions of fullerenes, ShC, FS and graphite, prepared by ultrasonic treatment, was carried out. Stable dispersions were produced from fullerenes, FS and ShC, whereas graphite powder was not stable in water [22].

It is the hydration of carbon NPs in stable aqueous dispersions that chiefly stabilizes colloid solutions. To prove the statement, the NMR method with an impulse magnetic field gradient was used to measure the partial coefficients of self-diffusion of water molecules in ShC highly concentrated aqueous dispersions [23]. At room temperature and diffusion time $t_d=7$ ms the diffusion coefficients (D_s) and the parts of water fractions (p) calculated from these experiments are $D_{s1}=4.10^{-10}$ m^2/s, $p_1=0.06$ and $D_{s2}=2.1.10^{-9}$ m^2/s, $p_2=0.94$. Obviously, the first component belongs to the water bound to NPs and the second component to the bulk water. The D_{s2} value practically coincides with the coefficient of self-diffusion of pure water ($2.5.10^{-9}$ m^2/s). Exchange between these phases takes place, and exchange time (lifetime) was

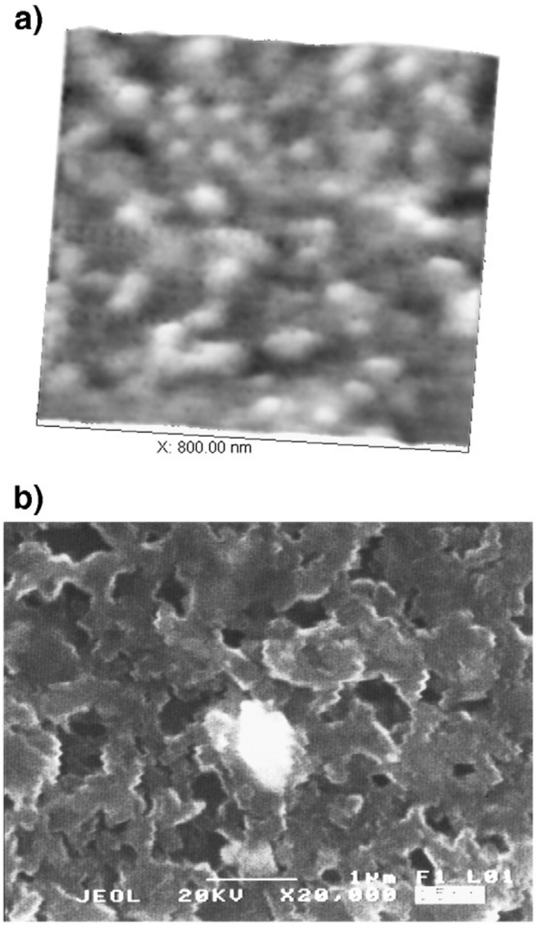

Fig. 1. AFM image of aqueous dispersions of ShC precipitated on a graphite substrate (a), SEM image of the dried aqueous dispersion of ShC. Scale bar is 1 μm (b).

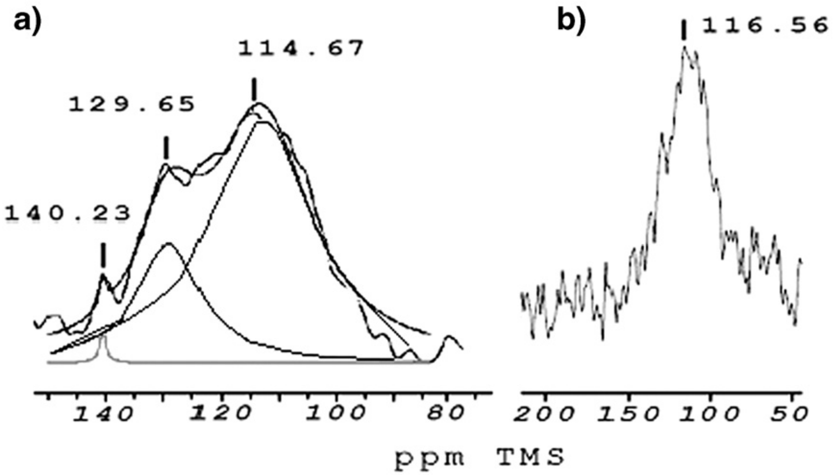

Fig. 2. ^{13}C NMR HR SS spectra (CP/MAS) of untreated shungite powder (a) and ShC precipitated from aqueous dispersion (b).

estimated at 5 ms. Upon addition of water, exchange frequency rises so markedly that at all possible diffusion times uniexponential diffusion damping from which only the average coefficient of self-diffusion of water can be obtained [23].

In the spin probe ESR method, the bulk water problem was solved methodically by freezing nanocarbon dispersions (fullerenes and ShC) with predominant freezing-out of a bulk water fraction in comparison to the water fraction modified by the surface of NPs. The latter is frozen out at lower temperatures, and the spin probe retains recorded mobility in this water phase for a longer time.

The results obtained were interpreted as in a colloid solutions with a low concentration of carbon NPs there exist both hydrophobic cavities filled with water clusters (microphases) showing a distinctive structure. It is assumed that it is these cavities that prevent direct interaction between NPs in a cluster and their coagulation [24].

We assume that it is curved, graphene stacks (bowls), less than 1 nm in size, having dipole moment, that are responsible for ShC interaction with water.

The High Resolution in solid state NMR is the most informative method used to determine the configuration of local bonds in carbon materials and it was employed to throw light on the structural characteristics of ShC, primarily those of its BSU and interaction of BSU with water.

2. Experimental

Aqueous dispersion was prepared from a powder (with particles <40 μm in size) of shungite type I (Shunga deposit, Karelia, Russia) using ultrasonic treatment and characterised thoroughly elsewhere [21]. Initial concentration of carbon in aqueous dispersion after filtration and centrifugation was 0.1 mg/ml. An average radius of particles determined by DLS method was 96 nm [25].

The centrifugated ShC dispersion was dried at room temperature in vacuum until carbon particles precipitated. An average particle size detected by TEM in precipitated ShC dispersion was 10–100 nm in the same range as for fullerenes [26]. The same precipitated dispersion studied by AFM and SEM showed aggregates with an average size 62 nm (Fig. 1a) and a combination of particle aggregates that are connected locally by intersections forming nets fragmentarily (Fig. 1b).

NMR studies of the dried ShC aqueous dispersion were carried out using high-resolution solid state ^{13}C and ^{1}H magic angle scattering (MAS) NMR "Bruker-500" spectrometer.

The mass of nanocarbon fragments stabilized in aqueous dispersions was analyzed using MALDI-TOF mass spectrometer, Reflex IV, Bruker. The radiation power density was 10^6–10^7 W/cm^2.

3. Results and discussion

^{13}C NMR spectra of the initial shungite powder (Fig. 2a) is a complex superposition of many lines; common deconvolution shows that the basic lines are 140, 129 and 114 ppm. The spectrum changed substantially as ShC was transformed to aqueous dispersion and then dried (Fig. 2b). Accent (basic intensity absorption peak) was clearly observed to be shifted to the upfield part of the spectrum (at 116 ppm).

Protons, adjacent to carbon, are known to exert a shielding effect on the carbon nucleus. Using the cross-polarization

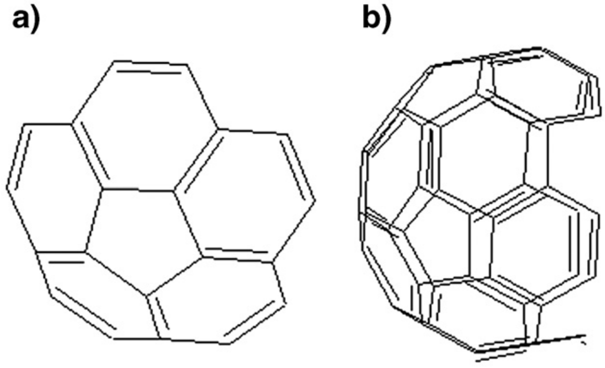

Fig. 3. The models of BSU of ShC aqueous dispersion (a) and untreated shungite powder (b).

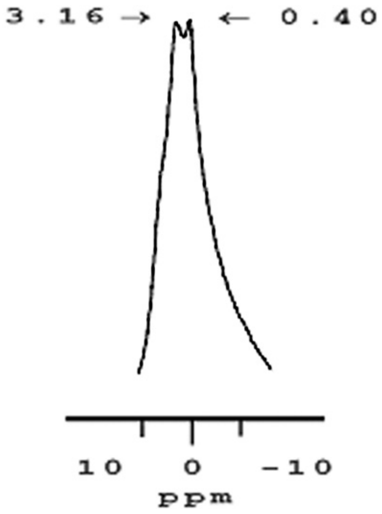

Fig. 4. ^{1}H MAS NMR of ShC aqueous dispersions with spinning at 35 kHz.

technique in our experiment, distance from carbon atoms in BSU to hydrogen atoms of water was estimated at ~0.8 nm.

Based on earlier comparative analysis of the NMR spectra of various carbon materials, primarily structures with the intermediate state between sp^2 and sp^3 hybridization, such as fullerenes, FS, graphite and nanotubes [27], some conclusions regarding the basic structure of ShC can be drawn. The calculated ^{13}C chemical shift for a model structure (Fig. 3a,b) shows a shift to the upfield part of the spectra relative to the planar graphite structure (128 ppm) [27].

Recent paper on MNR investigation of ultrananocrystalline diamond (UNCD) confirms our results [28]. A component (at 119 ppm) ascribing to aromatic carbons (without any hydrogen atoms near by) was suppressed in the ^{1}H–^{13}C CPMAS measurements. Unfortunately, authors did not pay attention to the water incorporated into nanoelements although it is well known that UNCD underwent wet chemistry for purification. A narrow sp^2-carbon signal (at 111 ppm) is seen at the common MAS spectra measured at thermal equilibrium without cross-polarization. This signal was attributed to a fullerene-like shell that covers diamond core of UNCD [28].

A fairly wide spectrum ^{1}H MAS NMR spectrum, obtained from ShC sample dried from aqueous dispersion (Fig. 4), consists of two peaks, the basic peaks being observed at 0.40 and 3.16 ppm. This should obviously be attributed to the water molecules interacted with ShC.

OH-groups grafted to fullerenes were found in fullerols (OH modified fullerenes) at 1.2, 1.5 and 1.8 ppm. The high field chemical shift is typical for the symmetrical grafting of two OH-groups to one C–C bound. Hence it could be concluded that only one OH-group is connected to one C–C bond. The OH-groups, involved in the formation of hydrogen bonds in a water molecule, typically have a stable signal at 7 ppm. A low-field shift of the signal from the OH-group is observed in fullerols at 0.9 ppm and shows their hydrophilic properties. The shifts of OH-signals was estimated for $C_{60}(OH)_2$ and $C_{60}(OH)_3$: 0.68 ppm and 2.65 ppm, respectively [29]. Transformation of fullerenes into fullerols was accompanied by increasing of reference signal of ^{13}C NMR spectra at 112 ppm attributed to restored soot [27].

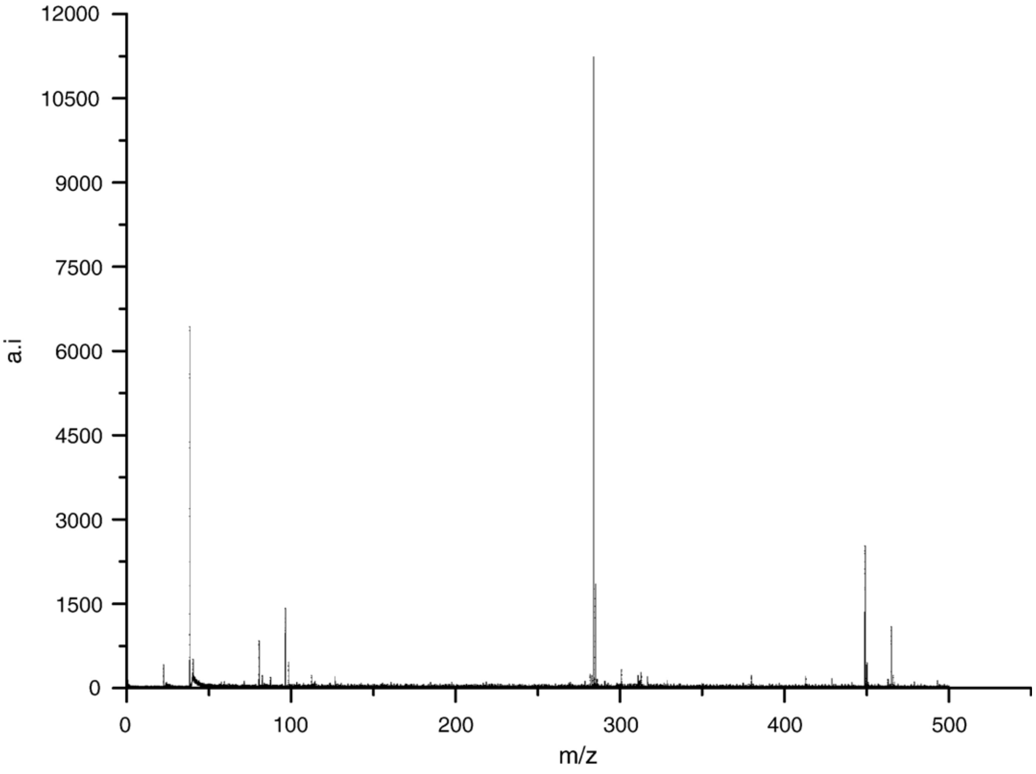

Fig. 5. TOF mass spectrum of shungite carbon aqueous dispersion.

These data are, in general, in good agreement with HR SS proton spectra. The intensity of two peaks in a high-resolution spectrum seems to be the same, but it is not the case. The complex shape of the line suggests the superposition of two signals that differ substantially in intensity. A peak at 0.40 ppm is assumed tentatively to be related to water complexes on BSU and the other peak to adsorbed water.

Our observations agree with the experimental facts reported for fullerenes and SWNT recently. Strained and nonplanar morphology that differ fullerenes and SWNT from those of graphite was shown to predetermine high reactivity of the fullerene structures [30]. At least two types of water adsorbed were detected in SWNT, namely intact water molecules were absorbed inside SWNT and some water molecules reacts at defects of the tube [31].

Fig. 5 showed TOF mass spectra of the ShC aqueous dispersion with the maximum intensity at ∼284 m/z that corresponds to the dominant structure. It was compared with the data carried out on the original shungite using low irradiance ($<10^7$ W/cm^2) laser-desorption mass spectrometry [32]. The most common for ShC was a variety of ions in the vicinity of 200 m/z mass region. Characteristic masses can be found in laser ablation negative ion spectrum of the natural shungite obtained with a laser power of 1.5 MW/cm^2 [33]. The masses presented in the spectra of native shungite and of its aqueous dispersion can be attributed to the basic element easily transformed into water.

4. Conclusion

Analyses of the high resolution ^{13}C and ^{1}H solid state NMR spectra of dried shungite aqueous dispersion, untreated ShC powder, fullerene soot and UNCD spectra has supported the assumption of the identity of their structural constituent.

The basic structural units of shungite carbon in the form of bowls characterizing by nonplanar structure with dimensions of 0.4–0.7 nm are easily transformed into aqueous dispersions and provide polarity sufficient for complexation with water.

The work is in progress to prove that these units due to their size and curvature are playing an important role in stabilization of carbon nanoparticles in water and predetermine specific amphiphilic properties of shungite.

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