Supramolecular Self-assembly of Carbon Structures from Shungite Rock Using Only Water

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ABSTRACT

In spite the fact that any types of carbon are not soluble in water, the main goal of this work is to produce a supramolecular self-assembly of carbon structures from shungite rock using only water. SEM investigations confirm existence of unusual forms of carbon: a fullerene-like quasi-crystal particle with stratified structure, soft spongy-like particle and tensile zeolite-like particle with three-dimensional framework structure. These structures consist of various types of carbon, which conductivity is changed from well conducting up to non-conducting. So the SEM used includes variable pressure technology to investigate elemental analysis of non-conducting specimens in their original conditions without intrusive preparation. Perhaps, discovered pentagonal symmetry in some new carbon structures is an intermediate between animate nature and abiocoen. Moreover, discovered natural fullerene-based self-assembly of supramolecular carbon structures is an intermediate between "intelligent self-assembly" biological structures and other self-assembled materials.

Keywords: self-assembly, natural fullerene, complex molecular center, carbon structure, shungite

1 INTRODUCTION

Shungite (Sh) are the black Precambrian rocks of Karelia (Russia) where the first natural occurrence of fullerenes was demonstrated [1, 2]. Presence of fullerenes and silica-silicate components in such Sh supposes a wide spectrum of catalytic transformations of the substance. In accordance to our model [3], the carbon-rich Sh rocks allow one to consider them as an organized globular matrix, which includes high-concentrated natural fullerene-containing carbon black and mineral component. Our discovery [4] of labile sulfur and CS_2 synthesis during fullerene extraction from Sh treated only with water was found to be the key factor in the possibility of supramolecular self-assembly of unusual carbon structures.

"Intelligent self-assembly" will be based on imitation to living systems and proceeds in a water solution, i.e. in supreme soft conditions with the fair speed, extremely high efficiency and at the minimal cost of energy. So, such technology will be low-temperature, liquid-phased and programmed. We have just attempted to realize some of the mentioned features: materials, produced by nature (Sh rocks aging over billions of years); low-energy synthesis (room temperature); liquid-phase (only water) and self-assembly, which is the key-tool of nanotechnology. As we suppose it was possible due to unique feature of natural fullerenes – self-assembly of fullerene-based complex molecular centers (CMC) [4]. Process of assembling them into large-scale structures was possible thanks to the unusual technology procedures by integrating it into a single whole the methods of extracting, concentrating, purification and crystallization using lower temperature and only water treatment of Sh rocks. Obtained self-assembled macroscopic structures are formed from intermolecular interactions, possibly other than the traditional covalent, ionic, and metallic bonding forces.

2 EXPERIMENTAL DETAILS

All carbon-based structures have been developed through specific pretreated enriched carbon-rich Sh rocks, in which dispersion phase (fullerene-containing Sh carbon ~30 wt. %) was uniformly distributed among dispersion medium (silicates ~70 wt. %, from which ~80 wt. % is silica) in the form of nanoparticles [5].

Obtained supramolecular structures mainly consist of various types of carbon, which conductivity is changed from well conducting up to non-conducting. So options for the equipment used (Digital SEM–106, <SELMI>, Sumy, UKRAINE) include variable pressure technology to investigate elemental analysis of non-conducting specimens in their original conditions without intrusive preparation.

The measurements of temperatures, pH and ORP were carried out by means of HANNA INSTRUMENTS (accuracy: $\pm$ 0.01 pH; $\pm$ 0.5 ^{0}C; $\pm$ 0.2 mV (ISE)). The fast-acting chemical analysis of water-Sh extracts (Total Hardness Test, Ammonium, Chloride, Chlorine, etc.) was verified by means of titrametric method with the help of AQUAMERCK (resolution: ~ 0.01 mg/l). Using the Spectrophotometer UV-vis-CECIL 9000 and Perkin Elmer SPECTRUM BX FT-IR spectrometer we carried out the spectroscopic characterization at first the water-Sh extracts and after that the solutions of fullerene-containing particles in nonpolar solvents, using their reversible dilution.

3 FULLERENE-BASED COMPLEX MOLECULAR CENTERS

While developing optimal methods for extracting fullerenes from Sh [3] we detected the synthesis of core-shell type complex molecular centers (CMC), which equally-spaced location symmetry remained the same as high-symmetrical pristine fullerenes. Usually in such centers the fullerene dimers carry out obligations of core, and the shell is formed from various components of ligands [4].

The next modeling experiments allow determining the molecular catalyst and sorbent properties of a C_{60}, even if the water-carbon disulfide shell surrounds it. In this case a C_{60} can organize the solvent on its own surface and create the conditions for natural fullerene-based self-assemblies. The modeling water-carbon disulfide solution of C_{60} was received by separation of fullerite particles from sediment of water-Sh extracts and following dissolution of these particles in water-carbon disulfide solution. In addition we examined the results of the spectral analysis of the model water-carbon disulfide C_{60} and carbon disulfide CMC solutions.
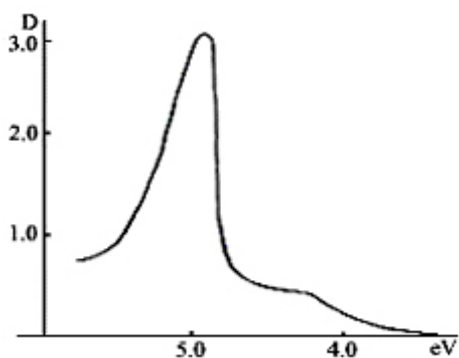

Figure 1: The absorption spectrum of C_{60} in water-carbon disulfide solution (290 K).

In the absorption spectrum of water-carbon disulfide solution of C_{60} (Fig.1) the asymmetric band is dominated ($\Delta\omega = 270\text{-}280$ cm^{-1}) with a peak at ~ 4.97 eV. In the region 4.1-4.56 eV the small peak at ~ 4.29 eV is resolved. The character peak at 3.024 eV for C_{60} in CS_2 is absent. So it is possible to suppose that a peak at 4.97 eV specifies the interaction of exited states of S and C_{60}. The value 4.97 eV is equidistant with respect to values 6.23 eV ($S^0 \rightarrow S^*$) and 3.712 eV (characteristic peak of C_{60} in solution). In addition value 4.97 eV is displaced to 0.150 eV with respect to characteristic π-σ band of C_{60} solution spectra (4.82 eV). This value corresponds within the experimental mistakes to the shift, which is equal to electron-vibrating state. Consequently the peak at 4.97 eV is probably connected with the presence of potential minimum of collective states in CMC. In this case the shift of CS_2 band at 1.02 eV corresponds to the donor-acceptor type of components interaction. Different forms of CS_2 molecules arrangement on the fullerene surface are possible: planar, vertical and mixed. However the planar model is more consistent with experimental data. On a sphere with the diameter of 0.75-0.8 nm (C_{60}) it is possible to arrange 32 balls with the diameter of 0.35-0.36 nm. The 16 regular centers $\{(- C^+ -) - \bar{e}\}$ on the CMC surface take place on account of the shift of electron density from S^- to fullerene and nonlinear geometry of CS_2 molecules. Aggregate of S– and C–atoms may be considered as a nanodrop of low-size carbon solution in C_3S_2 ($\rho = 1.27$ g/cm^3). But if C_3S_2 is not dissolved in water, the water-soluble CMC is possible owing to surface polar groups $\{(- C^+ -) - \bar{e}\}$. Equilibrium state of CMC in water is possible in the composition of ice-like hydrate shell ($\rho = 0.9$ g/cm^3), which includes not less than 200 molecules of H_2O. The condition for equilibrium state of CMC in solution for vertical arrangement of CS_2 molecules is not fulfilled, as in this case the CMC structure allows it to be considered as a nanoparticles with composition of CS ($\rho = 1.66$ g/cm^3) and C_{28} molecule adsorbed on its inside surface.

The mixed geometry of arrangement of CS_2 molecules on the C_{60} surface requires the presence of absorption band in the region of 4.0-5.0 eV. However essentially different intensities of 4.97 and 4.29 eV bands do not correspond to the nature of CS_2 mixed geometry. In accordance with supposed CMC model the interval between three S-atoms and carbon cell has a localization region of low-energy electron states. During adsorption of H_2O molecules at the surface of $(- C^+ -)$ centers, a shift of H-atoms to the region of localization electron density up to dissociation of adsorbate is possible, so that electrostatic potential is very big ($>10^6$ V/cm) and coupling energy relations C–O, S–O, H–O, C–S are significant. If a model of CMC is used to quasi-drop C_3S_2, it is necessary for every S–atom only 2/3 from 32 meV. The total shift of electron density within 32 cm^{-1} coincides with energy shifts of CS_2 band. This corresponds to the collective state of S on the surface of carbon cell. Thus the planar model of 16 CS_2 arrangements on the C_{60} surface shows the best correlation with experimental dates. The 4.97 eV band characterizes the collective electron states of sulfur and fullerene. Hydrosulfide shell $\{(CS_2)_{16} - 32H\}$ is fullerene-like according to atom mass (C_{104}). Fullerene similarity of CMC can be realized also in hydrate shell from 280 molecules H_2O. Hence, the CMC is heterofullerene. Correctness of using fullerene-like molecule shells, which atom masses correspond to macrofullerenes, follows from realization of this feature for aromatic clusters: B_{84}, $(SiO_2)_{20}$, $(BN)_{30}$, T_8C_{12}, Ag_{13}, S_{42}, Si_{42}, $(H_2O)_{80}$ etc.

4 RESULTS AND DISCUSSION

Carbon single bonds are usually sp^3 hybrid bonds pointing in tetrahedral directions, as in silicon. It satisfies its valences with hydrogen rather than with oxygen, as silicon does. This means that carbon can form an extremely wide range of compounds. While it may be owed to the CMC self-assembly into supramolecular structures we can demonstrate the curious and unusual forms of carbon.

4.1 Supramolecular self-assembly of fullerene-like quasi-crystal carbon particles

The presence in water-Sh extracts of the large quantity of thread-like crystals of carbon, sulfur, calcium salt and monosulfide carbon [6] points to existence of two and three-atom molecules. It means that the chemical reaction between Sh and water takes place. In such processes the precipitation of labile sulfur and following CS_2 synthesis from Sh may be of fundamental meaning. Originally, the mineral component of Sh carries the responsibility for a high amount and kinetics of sulfur precipitation from Sh, because the water-soluble substances are concentrated namely in this component. The existence of CS_2 synthesis and multi-stage processes of the natural fullerenes extraction from water-Sh extract was confirmed by C_{60-70} fullerites and fullerene-like quasi-crystal particle self-assemblies. On Fig.2 are shown the results of CMC self-assemble into micrometer-long chess-like fullerite on substrate surface from CS. After some time the separate parts of a red strips become colorless and yellow, this is connected to CS decomposition.
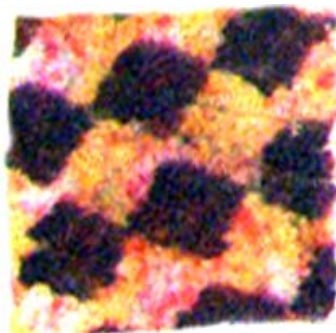

Figure 2: Optical micrograph of supramolecular self-assembly of C_{60-70} chess-like fullerites (black strips with middle size about 40x40 μm) and amorphous CS (red strips) from water-Sh extract.
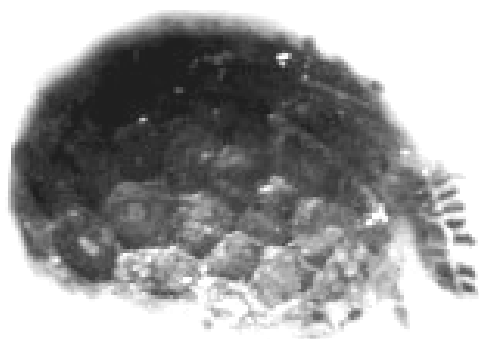

Figure 3: Optical micrograph of supramolecular self-assembly of fullerene-like quasi-crystal carbon particle from water-Sh extract at a final stage origin. The size of particle is the same as on Fig. 4.

The displacement of solvated CS_2 is fixed by induction of the specific splitting band with peak at 314-315 nm. After a time this band may be covered by low-molecular S band. This result is essentially analogous to the separation of a CS_2 drop phase during synthesis of a fullerene-like particle. As shown on Fig.3, the CS thread-like crystal is formed during CS_2 separation out of volume of fullerene-like quasi-crystal carbon particle at a final stage origin. The stress crack is formed and the recrystallization of substance as a tail-like film by account of high concentration CS_2 inside a shell is possible.

An unusual result of supramolecular self-assembly of fullerene-like particle with stratified structure, morphology of which satisfies to a quasi-crystal, is shown on Fig.4. The carbon concentrating inside the crystal edge provides by this way the decoration of crystal sides and angles. The appearance of an impurity in the form of regulated rings located symmetrically on the pentagonal and hexagonal sides corroborates to the presence of the morphological features of long-range order.
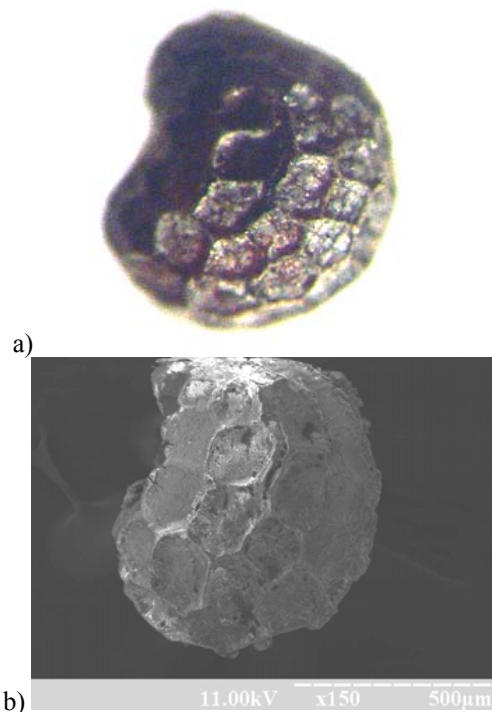

a)

b)

Figure 4: The optical (a) and SEM (b) micrographs of natural fullerene-based supramolecular self-assembled carbon fullerene-like quasi-crystal particle with stratified structure from water-Sh extract. The sizes of both carbon particles are the same.

4.2 Supramolecular self-assembly of carbon soft spongy-like and zeolite-like particles

We demonstrate here (Fig. 5A, c and B) carbon tensile zeolite-like particle with three-dimensional framework structure. The change of their fractal geometry and the

decrease of their volume at polar solvent absorption or carbon layer desorption, allows one to assume that tensile zeolite-like carbon particle with three-dimensional framework structure can attain porosity up to 40-45 %. The soft spongy-like carbon particle has an extremely lightweight structures (Fig. 5A, a). The decoration of pentagonal and hexagonal sides (Fig. 5A, b) of such a particle is feebly marked in comparison with fullerene-like quasi-crystal particles with stratified structure (Fig. 4).
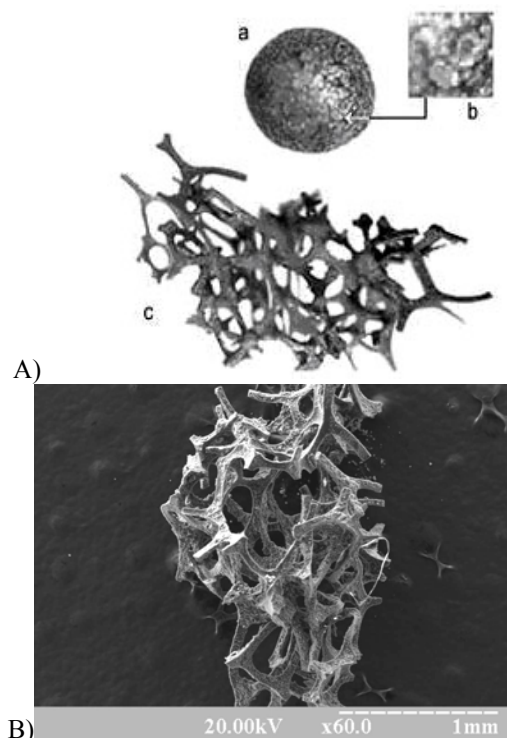

A)

B)

Figure 5: The optical (A) and SEM (B) micrographs of self-assembled carbon structures from water-Sh extract: a soft spongy-like (a) and tensile zeolite-like particles with three-dimensional framework structure (c, B). Enlarged fragment of spongy-like particle surface is (b). The scale of sizes of all carbon particles are the same as in (B).

4.3 SEM elemental analysis of unusual carbon structures

We will see once again how important structure is to properties. Carbon is not black, nor transparent, nor soft, nor hard, nor a conductor, or a nonconductor - it all depends on its structure. SEM elemental analysis detects a few types of carbon (Tab.1): the first one forms fullerene-like carbon particle facets and crystal edges, providing the decoration of crystal sides and angles (Fig.4). Identical sizes of pentagonal and hexagonal sides are morphological features of crystal [3]. The second one forms the largest conductive tensile carbon zeolite-like particles. The third one forms the least conductive soft spongy-like carbon particles.

	Spongy-like carbon particle	Zeolite-like carbon particle	Facet of fullerene-like carbon particle
C, %	91.53±4.04	87.90±3.17	93.62±5.76
O, %	4.34±0.46	7.48±0.68	2.84±0.27
Si, %	2.10±0.17	1.00±0.10	1.81±0.22
Al, %	0.56±0.09	0.67±0.09	
Ca, %		0.19±0.05	0.52±0.13
Cl, %	0.25±0.06	0.94±0.09	0.31±0.09
S, %	0.36±0.07	0.31±0.05	
K, %	0.35±0.07		0.31±0.09

Table 1: Results of SEM elemental analysis of unusual types of carbon particles self-assembled from Sh using only water.

5 CONCLUSIONS

For the first time ever we produced unusual forms of carbon structures from water-insoluble rocks during their water treatment. The ability of natural fullerenes in water-Sh extracts to fabricate large molecular structures through self-assembly has been demonstrated. The presence of the morphological features of long-range order in some self-assembling macroscopic carbon structures, modeling experiments and spectroscopic evidence confirm their synthesis from CMC. Natural fullerenes not only build the CMC, but also create the binding chemical shell. At the same time they don't enter into a chemical reaction.

The uniqueness of the supramolecular carbon structures has provided us with novel approaches to develop new polymeric biomaterials. By understanding the opportunities for self-assembly of macroscopic structures, it may be possible to introduce self-assembly in manufacturing technology for the fabrication of complex structures with minimum cost as well as to shed light on behavior at the molecular level. The present work discusses the fundamental principles that determine the large-scale structural and hierarchical organization of such assemblies.

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