Molecular graphene of shungite

Natalia Rozhkova[1] and Elena Sheka[2]

[1]Institute of Geology Karelian Research Centre RAS, Petrozavodsk 185910, Russia
[2]Peoples' Friendship University of Russia, Moscow 117198, Russia
rozhkovat@krc.karelia.ru

Molecular graphene, consisting of size-restricted graphene sheets, has become a subject of intense theoretical and experimental studies and debates. It was supposed to be one of the most versatile systems in molecular science research that could be easily probed by various scanning probe techniques from mesoscopic down to atomic scales [1]. Such scenario has been realized in the current study of the nanocarbon, produced from natural shungite and consisting of nonplanar nanosize graphene sheets.

Shungite carbon (ShC) can be characterized either as a semiconductor or semimetal and soft matter. Its structural organization has been investigated to disclose the origin of this many-face behavior. It turns out that shungite can be quite easily dispersed. Consecutive processing of shungite powder in water using sonication, filtration and centrifuging results in the formation of a stable aqueous dispersion of ShC nanoclusters [2, 3]. A number of techniques, among which there are MNR C^{13}, SANS and SAXS, Raman scattering and Auger spectroscopy, has been applied to perform a comparative study of ShC with fullerenes (C_{60} and other), graphite and onion-like carbon. The study has convincingly revealed graphene-like features of the matter. Estimated by dynamic light scattering, ShC aqueous dispersion, with the initial carbon concentration of ~0.1 mg/ml, consists of colloidal particles of 50-60 nm in average. High-resolution-TEM visualization has allowed for revealing the finest dispersions of the particles that includes nanosize carbonaceous globules of <6 nm in average, randomly distributed in water. The globules present clusters of curved graphene sheets with linear dimensions of <1 nm, molecular mass <300 m/z and dipole moment ~6.5 D. The condensation of the ShC aqueous dispersion results in the aggregation of the pristine particles followed with the formation of a 3-dimensional net [4]. An example of the globular cluster in the condensed phase is shown in the Figure.

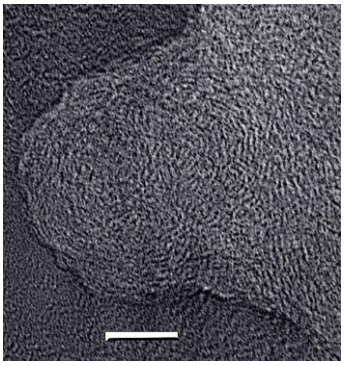

Figure. HRTEM of ShC condensed aqueous dispersion, scale – 5 nm.

Additional evidence of the nanosize-cluster origin of shungite follows from the pore-size distribution that is characteristic for natural shungites as well as the condensate 3-D net. The distribution reveals the predominant pore size within 0.7-5 nm [5]. Small doping of the condensed powders, obtained from the stable aqueous dispersion, enhances nonlinear optical response and substantially influences the photorefractive parameters of the conjugated structures of polyimide matrices [6]. Stable toluene dispersions have revealed the quantum-dot behavior of the graphene globular clusters with respect to

the enhancement of spectral properties of the solutions themselves as well as additionally solved fullerene C_{60} [7].

Canopy- and basket-like shapes of the carbon skeleton of planar pristine graphene membranes subjected to one-side hydrogenation over their basal planes [8] are suggested to explain the origin of the curved graphene molecules of shungite. It was supposed that the shungite formation occurs in due course of the graphitization of the carbon deposits under particular hydrothermal conditions that, according to geological reports [9], are characterized by high temperature and high concentration of water vapors that include atomic hydrogen. Water does not adsorb on the graphite. In contrast, atomic hydrogen willingly makes this, but only from one side. Atomic-hydrogen-one-side adsorption on the top graphite layer causes the irreversible curving of its carbon skeleton that keeps the shape after the adsorbate is removed from the surface due to high temperature. The water, on one hand, promotes splitting this graphene layer one by one from the others and stabilizes the clusterization of individual, curved, one-atom-thick carbon sheets, on the other. A competitive character of the processes, related to graphitization, atomic hydrogen adsorption/desorption, complex water action, results in the finding a compromise, namely in the formation of globular clusters of curved graphenes of nanosize in average.

The curved graphene fragments form globular clusters and stabilize them in dispersion due to their size and specific interaction with water. Water captured in between graphenes is responsible for stabilizing clusters in condensed form. The clusters, compressed into macroscopic blocks during the relevant geological age, were transformed into solid shungite deposits.

References

[1] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, Rev. Mod. Phys. **1**, (2009) 109.
[2] N.N. Rozhkova. Shungite nanocarbon. Petrozavodsk, KRC RAS (2011) 100 p. (in Russian)
[3] N.N. Rozhkova, L.E. Gorlenko, G.I. Emel'yanova, M.V. Korobov, V.V. Lunin, E. Ôsawa, Pure & Appl. Chem. **11** (2009) 2093.
[4] N.N. Rozhkova, A.V. Gribanov, M.A. Khodorkovskii, Diamond & Rel. Mat. **16**, (2007) 2104.
[5] N.N. Rozhkova, G.I. Yemel'yanova, L.E. Gorlenko, A.V. Gribanov, V.V. Lunin, Glass Physics and Chemistry, **6** (2011) 613.
[6] N.N. Kamanina, S.V. Serov, N.A. Shurpo, N.N. Rozhkova, Techn. Phys. Letts., **10 (**2011) 949.
[7] E.F. Sheka, B.S. Razbirin, N.N. Rozhkova, D.K. Nelson, A.N. Starukhin (submitted).
[8] E.F. Sheka, N.A. Popova J. Mol. Mod. Doi: 10.1007/s00894-012-1356-9.
[9] P.R. Buseck,, L.P. Galdobina, V.V. Kovalevski, N.N. Rozhkova, J.W. Valley, A.Z. Zaidenberg, Canadian Mineralogist, **6** (1997)1363.