Raman characterization and X-band EPR studies of multishell nanographites with and without oxygen-sensitive edge-localized spins

Osipov V.Yu.*[1] , Makarova T.L.[1,2], Baranov A.V.[3], Ermakov V.A.[3], Shames A.I.[4], Takai K.[5], Enoki T.[5], Kaburagi Y.[6], Hayashi T.[7], Endo M.[7], Vul' A.Ya.[1]

[1]*Ioffe Physical-Technical Institute, Polytechnicheskaya 26, St. Petersburg 194021, Russia*
[2]*Department of Physics, Umea University, SE-901 87, Umea, Sweden*
[3]*St.Petersburg State University of Information Technologies, Mechanics and Optics, 197101, Russia*
[4]*Department of Physics, Ben-Gurion University of the Negev, Be'er-Sheva 84105, Israel*
[5]*Department of Chemistry, Tokyo Institute of Technology Tokyo 152-8551, Japan*
[6]*Department of Chemistry and Engineering, Tokyo City University, Tokyo 158-8557, Japan*
[7]*Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano-shi 380-8553, Japan*
**e-mail: osipov@mail.ioffe.ru*

Raman scattering spectroscopy is a powerful tool to test nanocarbons having an extended π-electron system combined with electronic states localized at zigzag edges. Nanographite (NG) particles under study were produced by the annealing of detonation nanodiamonds (grain size ~5 nm) in argon flow, as it has been proposed in Ref. [1, 2].

We studied a number of nanographites obtained from nanodiamonds at different heat treatment temperatures: both above 1600°C and below 1550°C. Some of them (group I) synthesized predominantly at elevated temperatures (≥ 1600°C) demonstrate EPR signal associated with zigzag edge-localized states, which linewidth is extremely sensitive to the presence of ambient molecular oxygen. Another samples (group II) demonstrate (surprisingly, irrespective the temperature of synthesis) EPR signals that are completely insensitive to the presence of molecular oxygen. These signals supposed to be (completely or partially) due to sp^3- like defects in the closed defective shells of multishell nanographite. In-plane crystal sizes, obtained by means of Raman spectroscopy via evaluation of D- and G- band intensities ratios (ID/IG), are varied from ~1.6 nm to ~3.5 nm for different nanographites obtained. The enhanced intensity of Raman D-band in the type II nanographites may be associated with possibly large contribution of armchair-type edges.

The armchair edges do not demonstrate paramagnetic edge spin states [2]. From the other angle, particles of smaller (less than 2 nm) sizes are characterized by high number of sp^3- defects and poor crystalline quality of graphene sheets as well as by a corrugated character of graphitic shells. These factors are, in general, the combined reason of the absence of oxygen-sensitive edge localized states in samples with smaller crystalline sizes or higher content of sp3- like defects.

[1] V.Yu. Osipov, et al., *Carbon* **44**, 1225 (2006).
[2] O.E. Andersson et al., *Phys. Rev. B* **58**, 16387 (1998).