

# MULTIFUNCTIONALITY OF GRAPHENE FROM AQUEOUS DISPERSIONS OF HYBRID CARBON-METAL NANOPARTICLES

N.N. Rozhkova<sup>1</sup>, A.A. Kovalchuk<sup>1</sup>, S.S. Rozhkov<sup>1</sup>, A.S. Goryunov<sup>2</sup>

Institute of Geology Karelian Research Center RAS, Petrozavodsk, Russia  
Institute of Biology Karelian Research Center RAS, Petrozavodsk, Russia

## Abstract

Shungite carbon (ShC) nanoparticles in the form of stable aqueous dispersions are promising for optical and biomedical applications. The main role in the stabilization of nanoparticles is played by graphene fragments (~ 1 nm), which display a considerable dipole moment, and the hydrate layers of globular clusters composed of packages of graphene fragments.

Recently the stable dispersions of the hybrid ShC-Ag and ShC-Au nanoparticles have been produced in water dispersions of ShC nanoparticles and corresponding metals under laser impulses of various durations. Raman and UV-Vis spectroscopy allows to monitor structural changes of ShC in its formation of hybrid nanoparticles. Graphene fragments of ShC serve to adjust the size and shape of hybrid nanoparticles in dispersions. Films, occurring as periodic structures that contain metal-graphene hybrids without a hydration constituent, are formed upon condensation of dispersions. Recent results on the new biocompatible hybrid nanoparticles are discussed.

## 1. INTRODUCTION

The most attractive from the perspective of the researchers, the properties of carbon are associated with the ability to form new nanoscale architectonic forms. Recently, one- and two-dimensional carbon layers including graphene and nanoribbons, became a subject of study as promising materials for electronics, spintronics and medicine (1).

Research directions include the development of new approaches to the synthesis of nanostructures and the ability to effect on electronic, chemical, mechanical and magnetic properties of nanostructures by controlling the parameters of defects (2). Defects can play a positive role initiating the creation of new materials and compounds namely for nanoscale structures. It is shown that defects effect on the physico-chemical properties of graphenes and are of decisive importance for the creation of biocompatible materials.

Therefore, the study of shungite carbon (ShC) as a new graphene-like material is of scientific and practical interest (3).

Clustering of non-planar graphenes (basic elements) of ShC is a key process of a multilevel structural organization scenario and of structural transformations in systems of various physico-chemical nature. New data obtained by neutron diffraction and inelastic neutron scattering methods and supported by quantum chemical calculations have proved the role of water in the formation of all structural levels, and, in general, the fractal structure and porosity of the ShC (4). ShC favorably differs from all synthetic objects by fixed lateral dimensions ~ 1 nm of the graphene fragments and their amphiphilicity (5).

Stable aqueous dispersion of ShC nanoparticles (6) is an object of investigation that helps to solve the task of isolation of nanoparticles and their structural constituents. Clusterization of graphene flakes in the stable aqueous dispersion of ShC nanoparticles is well reproducible process (3). Various structural types of ShC nanoclusters and their aggregates have been obtained in aqueous dispersion under normal conditions. ShC nanoparticles are transferred from aqueous dispersions to solvents of different polarity (7).

Recently it was shown that the packing density of nanoclusters in dispersions can be regulated with additives (sucrose, urea, HCl, NaOH, NaCl) that affect boundary water in ShC clusters (8).

The patterns of the spectral behavior of ShC nanoparticles (regardless of the solvent) of UV-excitation, namely, the amplification of luminescent molecules in clusters of graphenes are analogous to the emission of synthetic reduced graphene oxide and metal nanoparticles, which are known as quantum dots (9). The validity of this approach is confirmed by the experimentally determined features of the nonlinear optical properties of ShC nanoparticles dispersions. They exhibit stronger optical limiting in the range of the nanosecond laser pulses in visible and near-IR pulsed radiation (10). Heating of absorbing nanoparticles is an important factor in restricting reuse nanoparticles under the high energy density radiation.

The specific characteristics of graphene-nanoparticle hybrids are widely used in the production of biosensor systems for detection of allergens, toxins, bioactives, and foodborne pathogens. Biosensors that combine graphene with metallic nanoparticles are among the most promising of those obtained on the basis of graphene (11). An important aspect in fabrication of the biosensors is the preservation of biological activity of biomolecules while they are immobilized in the nanoparticle microenvironment. Our results obtained so far have shown the extent to which the interactions with ShC nanoparticles affect the native biological state of some blood proteins, and the conditions that allow maintaining the biological functionality (12).

A stable dispersion of hybrid nanoparticles was prepared under joint treatment by laser pulses of carbon and metal nanoparticles in the aqueous dispersion.

The paper presents results of comparative study of the hybrids and original ShC nanoparticles in aqueous dispersions and films.

## 2. EXPERIMENTAL

Stable aqueous dispersions of ShC nanoparticles were prepared according to (6)[Patent RF. The initial concentration of the dispersions was 0.1 g/l. ShC nanoparticle radius in the dispersion was derived from the size distribution maximum of dynamic light scattering (DLS) intensity. It equals 51 nm with the distribution peak width 20 nm.  $\zeta$ -potential equals -30 mV. The measurements were conducted on a Malvern Zetasizer Nano ZS DLS system equipped with a 633 nm He-Ne laser.

The Raman spectra of ShC nanoparticles aqueous dispersions and films of the condensed dispersions on glass substrates were obtained on a dispersive Nicolet Almega XR spectrometer (Thermo Scientific) with the laser 532 nm - ND-YAG. The spectra were collected at 2  $\text{cm}^{-1}$  spectral resolution. Raman spectral data were determined using OMNIC software.

Parameters of the carbon nanoparticles were detected using absorption spectroscopy methods in UV-Vis ranges (spectrophotometer SF-56).

The scanning electron microscopy (SEM) of the films was carried out using a SU1510 (Hitachi) and VEGA 11 LSH (TESKAN) equipped with an energy dispersive spectroscopy (EDS). EDS-INCA Energy 350.

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The initial colloidal systems are prepared by continuous laser ablation of silver and gold targets in liquid environment (deionized water). As a result, the average particle size of 10 nm is obtained at a concentration of ~1mg/ml (13). Laser irradiation of our ShC nanoparticles dispersion with dispersions of Ag nanoparticles and Au nanoparticles was carried out in Vladimir State University. Dispersions were irradiated using YAG:Nd laser by continues wave (CW), nanosecond (ns) and Ti-Sp femtosecond pulses(fs).

### 3. REUSLTS AND DISCUSSION

Dispersions of ShC nanoparticles and their condensates showed well-resolved D and G peaks with the lower values of the ratio of its intensities ID/IG. Drastic changes in structure could be concluded from the Raman spectra decomposition of the dispersions that underwent nano- and femto- second pulses, namely ID/IG = 0.1-0.2 (Fig.1). The original aqueous dispersion of ShC nanoparticles after condensation is characterized by ID/IG = 1.4.

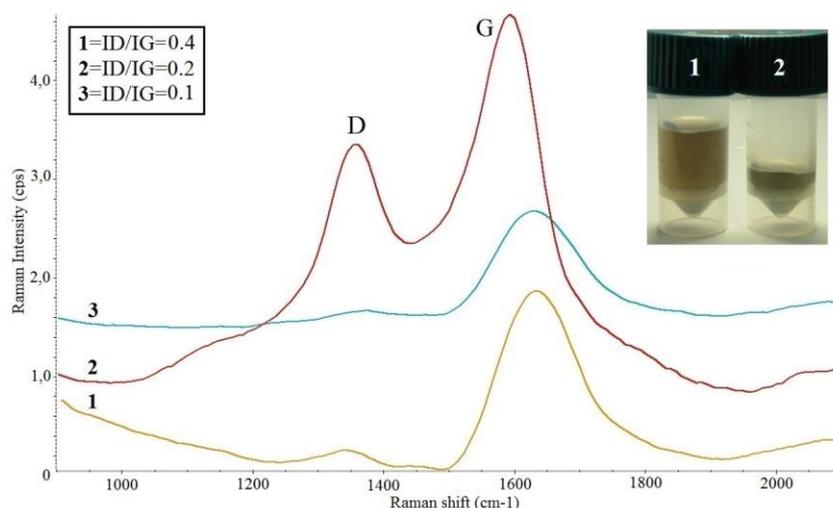


Figure 1. Raman spectra of aqueous dispersions of ShC nanoparticles: 1- original dispersion, 2,3 – after irradiation by ns and fs pulses, respectively. Inclusion: dispersions of ShC nanoparticles after ns (1) and fs (2) pulses irradiation.

Hybrid nanoparticles in dispersions obtained under CW laser irradiation and by laser irradiation of fs duration remained stable Fig. 2. There are no precipitated particles in the test tubes with ShC+Ag dispersions (Fig.2-1,2) and ShC+Au dispersions (Fig.2-3,4).

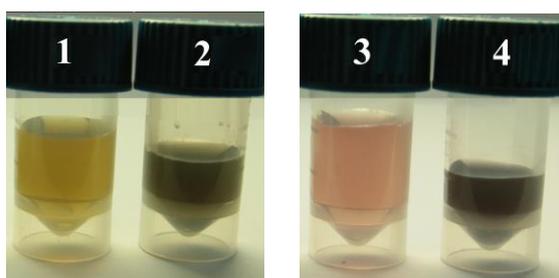


Figure 2. Photos of hybrid nanoparticles in dispersions after laser irradiation: ShC+Ag nanoparticles: 1 – fs duration , 2 – CW; ShC+Au nanoparticles: 3 – fs duration, 4 – CW.

Spectral studies indicate on the interaction of the carbon and metal nanoparticles. The absorption spectra of hybrid nanoparticles in the dispersion in comparison with ShC nanoparticles are shown in Fig.3. The absorption spectrum of ShC nanoparticles dispersion (Fig.3-1) displays a wide peak with a maximum at 256-259 nm, similar to the reported for synthetic reduced graphene oxides (14). When a fs laser impulse affected the dispersion no changes in the spectra were revealed.

In metal-bearing dispersions the wide peak maximum is shifted to 261 and 250 nm for dispersions containing Au and Ag nanoparticles, respectively. The peaks 522 nm for Au and 415 nm for Ag, typical of the nanoparticles of these metals in water, are observed.

The shifting of the absorption band into the Vis range («red shift»), compared with the absorption of Ag sols at 390 nm, indicates a decrease in the electron density of the metal and the increment of the nanoparticle size.

Laser processing by a fs impulse triggers considerable changes in the absorption spectra of dispersions of ShC+Ag nanoparticles: in addition to two main peaks at a frequency of 249 and 415 nm, “a shoulder” at 209 nm appears, that coincides with the characteristic peak of graphene oxide (14). The same additional peak at 208 nm is determined in dispersions of ShC+Au.

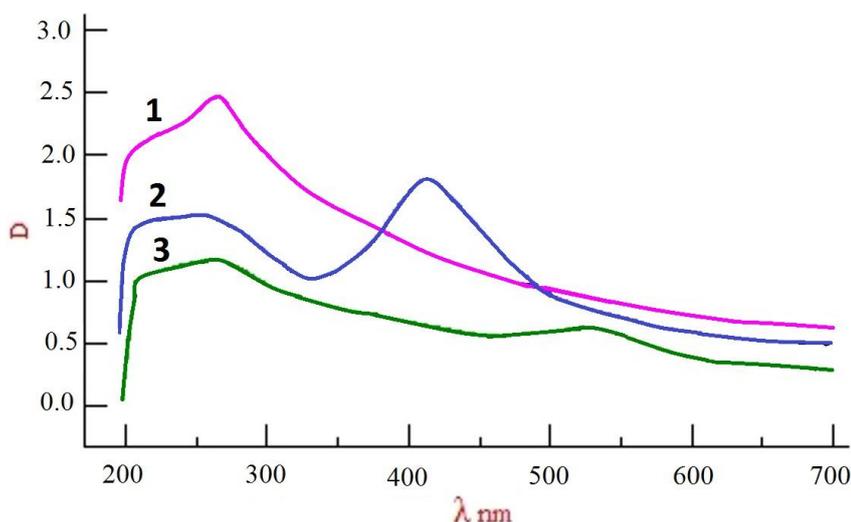


Figure 3 – UV-Visible adsorption spectra: 1- ShC nanoparticles in aqueous dispersion, 2 – ShC+Ag nanoparticles dispersion, 3 – ShC+Au nanoparticles dispersion.

The effect of ns and fs impulses results in bimodal size distribution (DLS data). The fs impulse exerts the same influence on the size distribution of nanoparticles for ShC+Ag and ShC+Au hybrids: 10-25 nm nanoparticles appear.

An average particle size of nanoparticles in dispersion under CW irradiation increased up to  $395 \pm 33$  nm and  $365 \pm 10$  nm for ShC+Ag and Sh+Au, respectively. Nevertheless, the nanoparticles remained stable in the dispersion.

Raman spectra (Fig.4) show doublets, consisting of characteristic G- and D-bands for all the samples. The intensities of Raman spectra of nanoparticles of ShC at the contact with Ag grow 4 and more times (Fig. 4-1). This can be explained by the surface plasma resonance phenomenon associated with the existence of surface electromagnetic waves on the boundary between metal and carbon (15).

Under the influence of ns and fs pulses, the Raman spectra of ShC in hybrid nanoparticles undergo a significant change characteristic of nanoparticles in the dispersion, which is confirmed by the ratio of  $I_D/I_G$ –0.16–0.8.

Raman spectra of the films prepared by condensation of the dispersions on the glass substrates are characterized by low values of  $I_D/I_G$  – 0.5 and D peak shifting to  $1271$ - $1291$   $\text{cm}^{-1}$ . The films can not be converted back into the aqueous dispersion.

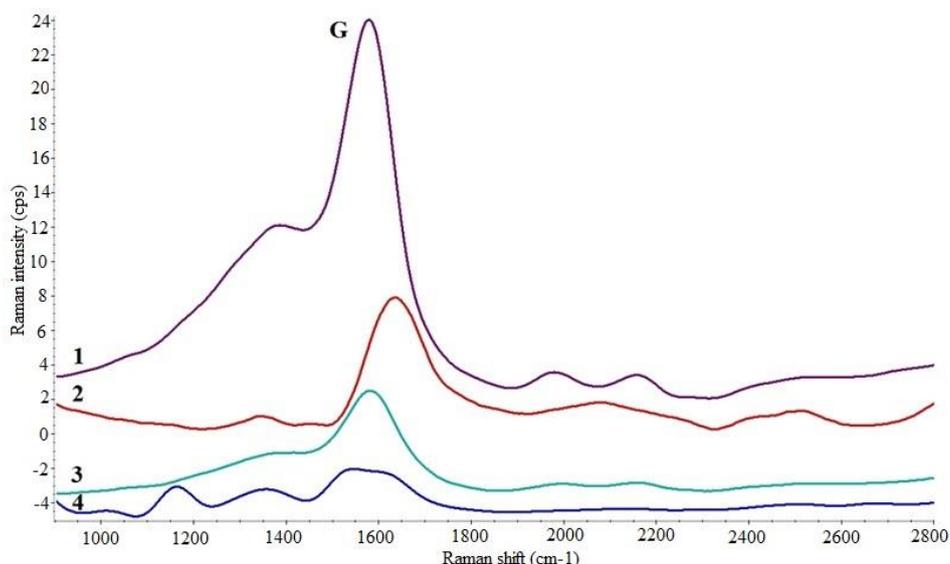


Figure 4. Raman spectra of nanoparticles in aqueous dispersions: 1. ShC+Ag nanoparticles underwent ns pulse; 2. ShC nanoparticles initial dispersion (x 4); 3. ShC +Ag after fs pulse laser irradiation; 4. ShC +Ag CW laser irradiated.

Nanoparticles in the films form mesoporous nets (Fig. 5). An average size of hybrid particles in the nodes of nets is 10-300 nm.

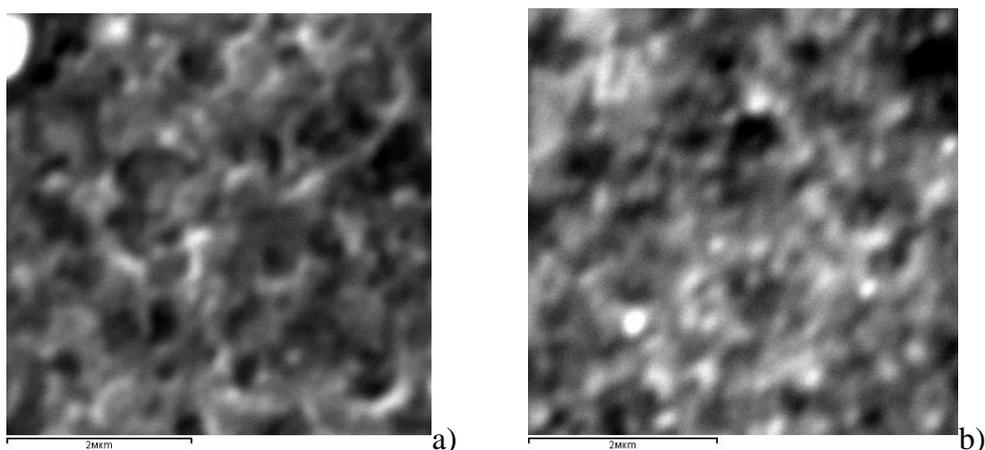


Figure 5. SEM images of films precipitated on glass substrate of the water dispersion treated by CW laser: a) ShC+Ag; b) ShC+Au

## 5. CONCLUSIONS

Stability of ShC nanoparticles in aqueous dispersions under laser irradiation of pulses of different duration (CW, nano- and femto-second) was studied. Thin films of graphene-like carbon could be obtained from the dispersions.

Nanoparticles in the dispersion irradiated by pulses of nanosecond duration showed irreversible changes of ShC nanoparticles structure.

Stable aqueous dispersions of hybrid ShC+Ag, ShC+Au nanoparticles were produced under irradiation by laser pulses of nano- and femto-second durations. The most pronounced changes in nanoparticles dimensions were obtained by femto-second pulse irradiation, namely,

bimodal distribution pattern of ShC+Ag and ShC+Au hybrids with nanoparticles of 10-25 nm in size.

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