# Lamellar structures from graphene nanoparticles produced by anode oxidation

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# Abstract

An effective cheap method for graphene nanoparticles (GNP) production with controlled size distribution was developed based on **anodic** oxidation of condensed exfoliated graphite. As it is shown, under certain condition the GNP could be self-organized into a 3-dimensional structure that could be important for understanding of the GNP interaction with different type of surfaces. Based on this feature, a synthesis method for preparation of composites containing GNP and polychlorotrifluoroethylene (PCTFE) was developed. Raman spectroscopy of GNP and GNP/PCTFE revealed a good crystalline structure of synthesized nanoparticles. Laser correlation spectroscopy and electron microscopy studies show that average size of particles ranges from tens to thousands nanometers and thickness consists ten or more graphene layers. We found that conductivity of GNP is of electronic nature. The real and imaginary parts of complex permittivity in the microwave range and electric conductivity at low frequencies were found to be a nonlinear function of a volume content of GNP in GNP/PCTFE composite. It could be explained by a presence of the percolation threshold equals to 0.5 wt.%. Low percolation threshold of GNP/PCTFE composite as self-organized 3D structure, could be a certificate of high surface energy for the particles strongly interacting with the surrounding media. Copyright © 2017 VBRI Press.

Keywords: Graphene, lamellar structure, synthesis, properties.

# Introduction

Nowadays a lot of research is devoted to finding of the best way of graphene nanostructures (nanoparticles, nanoplatelets. nanoflakes, graphene monolayers) synthesis, and development of GNP-filled composites technology [1-3]. Methods based on the usage of dispersions of compounds containing graphene layers or derived from natural graphite (artificial highly oriented pyrolytic graphite, exfoliated graphite (EG), graphite intercalation compounds, oxide and fluoride graphite, carbon nanotubes, etc) are considered as promising for industrial production as well as for relatively simple modification of the GNP properties [3]. Among these methods an electrochemical anodic oxidation of graphitebased structures is the most attractive to control the synthesis process and the final product properties [1, 4, 5]. The electrochemical intercalation, namely, the anodic oxidation, is an environmental friendly, energy saving method for production of the graphite intercalation compounds in a controlled mode [6]. In this paper we aimed to adjust specific parameters of EG, including structural properties of its volume and physicochemical state of surface, and to apply EG as GNP precursor for industrial development and conductive material usage.

# Experimental

The EG is a cluster nanoscale system containing cylindrical, conical, slit-like defects with a middle crosssection size about 0.7-20 nm (**Fig. 1**). Block size of X-ray coherent scattering from the basal and perpendicular planes of EG is about 20 nm [**7**].–Under EG anodic oxidation, namely, insertion of anions between crystal layers of graphite, intercalation does not take place. In this case a diffusion of the anions to the structure defects dominates; we call this process as a secondary "intercalation". Thus, the GNP has been prepared by the secondary "intercalation" of the electrodes from EG foil (Ukrainian standards TU U 26.8-30969031-002-2002) in the alkaline electrolyte (KOH) of low concentration at an electric current ranging of 6-60 mA/cm<sup>2</sup>.



Fig. 1. TEM (a) and SEM (b, c) images of EG particles.

The secondary "intercalation" of condensed EG "opensup" nanoscale defects in the EG structure results to formation of nanoparticles dispersion in an aqueous electrolyte solution. GNP separation has been provided by polypropylene membranes (**Fig. 2**).



Fig. 2. The scheme of EG anode oxidation: (+) - anode, (-) – cathode, 1 and 2 – polypropylene membranes.

The GNP dispersion was obtained in aqueous electrolyte solution under ultrasonic treatment. A surfactant may be added to electrolyte solution. Then the dispersion was deposited onto the surface of powdered PCTFE, dried and extruded as a rectangle plate with a size of  $10\times23$  mm, and density of 2.1 g/cm<sup>3</sup> at polymer melting temperature (240 °C).

The obtained GNP were analyzed by different physical methods. Raman spectra of GNP were registered with T-64000 Horiba Jobin-Yvon Raman spectrometer in the backscattering geometry at room temperature under excitation with argon laser ( $\lambda = 514.5$  nm, 1 mW). The Si

Raman band at 520 cm<sup>-1</sup> was used as a reference for wave number calibration. The GNP sizes has been estimated by laser correlation spectroscopy (LCS) with spectrometer "Zeta-Sizer 3", Malvern Instrument (UK), with heliumneon laser LH-111 ( $\lambda = 633$  nm, 25 mW) and scanning electron microscopy (SEM) (JSM-35, JEOL). CONTIN software for LCS [8] in the polymodal mode ("polymodal" approach) allows one to define a distribution of particle volumes (in the case of constant density) and a number of particles of a certain size (approach of spherical particles).

Measurements of real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) parts of complex dielectric permittivity of the composites were carried out in the range of 8-12 GHz using an analysis of standing wave ratio and attenuation by R2-60 device (Latvia) with non-contact method via the phase difference interferometer RFK2-18. Electric conductivity at low frequencies (0.1, 1 and 10 kHz) was measured by double contact method with E7-14 [9]. The frequency dependence of complex electric conductivity of the composites was evaluated from calculations of the impedance spectra in the frequency range  $10^{-2}$ - $10^{6}$  Hz obtained by impedance spectrometer Solartron SI 1260.



**Fig. 3.** The particle size distribution in suspension of GNP (sample 1, **Table**): (a) – "mono-modal" mode in different points of the sample; (b) – "poly-modal" mode.

## **Results and discussion**

LCS particle size analysis showed that the GNP sample contains two types of particles - large particles (13 microns), which soon precipitate, and smaller ones of about 450 nm in size being more stable (**Fig. 3**). The size and shape dependencies of the GNP are presented in **Table.** A shape deviation from sphere for the particles is calculated by polydispersity coefficient.

In the approach of spherical particles, minimal sizes for small particles fraction is 8-12 nm, maximum size is 130-300 nm and the dominant size is 35-55 nm depending on the anodic oxidation conditions. For the big size particles fraction these values are 130-300, 3200-70000 and 640-16500 nm, respectively.

Table. The size of the graphene material particles obtained by EG anodic oxidation.

N	Average	1 <sup>st</sup> fraction, nm			2 <sup>nd</sup> fraction, nm			Poly-
	, nm	min	max	dom	min	max	dom	dispersity
1	2162	8	130	40	130	31000	7954	1
2	623	12	300	54	300	25000	4133	1
3	1529	11	200	35	200	68000	16500	1
4	3251	11	280	35	280	70000	16500	1
5	1264	12	300	55	300	43000	10048	1
6	1349	12	200	40	200	3200	642	0.6
7	7049	33	800	42	800	8000	1664	1

According to **Table**, we may conclude about a possibility to adjust the size of GNP by tuning technological conditions during anodic oxidation. The value of polydispersity coefficient shows that a main fracture of the particles is not spherical. To determine the shape of GNP the precipitates of dilute suspension were studied by SEM. The substrates of gold and carbon films on glass plates were used for the experiments. Two types of particles were found mainly in obtained precipitates (**Fig. 4**).



Fig. 4. SEM images of the GNP observed on the carbon/glass surface: plate agglomerates of ordered structure of sticks (a), prisms (b), and c - agglomerate of thin plates - "hedgehog".

The first type of the structure looks like an ordered lamellar structure. The shape of the particles is a pile-like (**Fig. 4** (**a**)) which could be arranged in a hole pentagonal prism (**Fig. 4** (**b**)). The second type of the structure looks like a "hedgehog" that consists of thin plates (**Fig. 4** (**c**)). The difference between the two types of the particles is evident in shape, duration of the formation, and thickness of the building blocks. The first type of the structure was mainly observed at slow drying. The shape of the particles was stable and unchanged. A minimum thickness of the single plates in this type of the particles was about 25-30 nm. The second type of the structures was formed during rapid drying stimulated by substrate heating. This type of particles was found more often on gold substrates (Fig. 5).

The thickness of the second type plates (see Fig. 5) is equal to 5-7 nm that is confirmed by changes in the image brightness along the AB direction (Fig. 5 (c)). We estimated the plate thickness as equal to ten graphene layers. In all experiments we observed the both types of the 3D graphene-type structures as we prove below.



**Fig. 5.** SEM images of GNP on gold surface (the substrate is tilted at an angle of  $60^{\circ}$  to the electronic probe): (a) - GNP; (b, c) – magnification of GNP (a) and (b), respectively (marked with squares).

The Raman spectra of our GNP are typical for GNP or graphene multilayers (Fig. 6). We have registered Gband (so called "graphitic" mode of E<sub>1g</sub> symmetry in Gpoint of Brillouin zone) at 1581 cm<sup>-1</sup> corresponding to tangential vibrations of carbon atoms in the rings of graphene sheet [10]. We also registered so-called D band at 1353 cm<sup>-1</sup> that characterizes a disorder in graphene multilayers and which is absent in our initial EG [11]. This Raman mode is assigned to breathing vibration of rings of graphene layer in the K-point of Brillouin zone. Relative intensity and half-width (FWHM) of D and G bands reflects a degree of material disorder (broadening of the bands corresponds to larger degree of disorder). The second order mode of D vibration (2D band) is registered at 2713 cm<sup>-1</sup> [12] with higher intensity than is usually observed for the second order vibration. The last fact could be an evidence of similarity of carbon nanostructures manifesting a strong electron-phonon interaction and strong dispersion dependence of D-mode. More conductive materials have stronger electron-phonon interaction than semi-conductive ones. A weaker band at 2451 cm-1 named by D" by Vidano [12], consists sum of D and D<sub>1</sub> modes (D<sub>1</sub> – sp<sup>3</sup> at 1060-1080 cm<sup>-1</sup>). In the case of our GNP, the position of G-mode at 1581 cm<sup>-1</sup> does certify good crystalline structure of GNP (its theoretical value for graphite and graphene is 1580 cm<sup>-1</sup>), relative intensity  $I_{2D}/I_G = 1.12$ . The analysis of fitted data for 2D mode suggests that the obtained GNP are of good crystalline structure and metal-like conductive properties (inharmonic 2D mode is about 10 cm<sup>-1</sup>) [13].



Fig. 6. Raman spectra of GNP on glass coverslip measured at different points of the sample (1, 2, 3).

In the case of symmetric uniform 2D band with intensity equaled to G band, the spectrum 1 (Fig. 6) corresponds to multi-graphene layer with weak interlayer interaction. A weak Raman intensity and non-uniform contour of 2D band indicate to a few number graphene layers in the sample (Fig. 6) – (spectra 2, 3). In the spectrum of GNP/PCTFE we recorded additional bands at ~1291, 1415, 1439, 1461, 1611, and 1728 cm<sup>-1</sup> that indicates a contribution from the polymer substrate. It comes from comparing the spectrum of substrate (Fig. 7 (a)) with that for GNP/PCTFE composite (Fig. 7 (b)).



Fig. 7. Raman spectra of polymer (PCTFE) (a) and GNP/PCTFE composite (b): 1- the drop center, 2- the drop border.

**Fig. 6** shows the Raman spectra of GNP on glass coverslip measured from different points of the sample. The results of investigation of dependence of GNP disperse system conductivity on frequency in the region

of  $10^{-2} - 10^5$  Hz is presented on (**Fig. 8** (a)), indicating on its linear increases on frequency. This means a main electron contribution to the conductivity and a lack of ion conductivity component [14].



Fig. 8. Frequency (a) and temperature (b) dependence of GNP conductivity: 1 - heating; 2 - cooling.

The conductivity increases with increasing temperature, which indicates an activation nature of conductivity (**Fig. 8** (b)), while its increase after heating could be connected with a decrease of a resistance contact between the GNP particles that changes a chemical state of the surface. **Fig. 9** shows conductivity at low frequencies, as well as  $\varepsilon'$  and  $\varepsilon''$  at 9 GHz for systems GNP/PCTFE as a function of GNP concentration.

Even with small amounts of GNP, the values of  $\varepsilon'$  and  $\varepsilon''$  drastically increase. The analysis of the results shown in **Fig. 9 (a)** was made using percolation theory equation  $\sigma = \sigma_i (\phi - \phi_c)^t$ , where  $\sigma_i$  – conductivity of filler,  $\phi$  - volumetric content,  $\phi_c$  - the concentrations corresponding to the percolation threshold, *t* - critical code allowed to define threshold values, and critical system indexes are  $\phi_c = 0.0045$ , t = 2.48,  $\sigma_i = 0.17$  Oh m<sup>-1</sup>·cm<sup>-1</sup>.

The growth of PCTFE conductivity (Fig. 9 (a)) is nonmonotonic: the most drastic change of its values is observed in a narrow concentration range (C) of graphene (0 < C < 1 wt.%) indicating that the implementation of the percolation transition.

At the graphene content in the GNP/PCTFE of < 0.5 wt.%, the particles are self-arranged in local clusters. The

increasing of their content increases the average size of clusters. At GNP concentration of 0.5 < C < 1 wt.% the main isolated clusters transfer into an infinite cluster spreading a polymer composite in all directions. Moreover, so-called conductance channel appears which leads to increasing mean of  $\sigma$  in several orders.



Fig. 9. Conductivity (a) of GNP/PCFE at 0.1 kHz; real  $\epsilon'$  (1) and imaginary  $\epsilon''$  (2) parts of permittivity (b) at 9 GHz as a function of GNP content.

Further increase of GNP content (C > 1%) leads to monotonous increase of infinite cluster volume and conductivity in the frequency range of  $10^{-2} - 10^5$  Hz. This is due to the contribution of additional channels to the conductivity, which is significantly smaller than that of the main conductance channels. An increase in total number of dipoles of GNP clusters, together with subsequent increase in their size and number, leads to the formation of 3D net and more effective interaction with electromagnetic radiation (**Fig. 9** (b)). As a result, dielectric permittivity of GNP/PCTFE increases.

Thus, the percolation threshold in the GNP/PCTFE system equals to  $\sim 0.5$  wt.%. This value is rather less compared to literature data (0.7 and 1.4 wt.% for different polymers filled by GNP [13]). Less percolation threshold is a certification of higher homogeneity and better dispersion of 3D GNP structures.

## Conclusion

We developed a cheap technology of GNP production by anodic oxidation of solid EG with controlled parameters and particles size distribution from tens to thousands of nanometers and thickness of ten or more graphene layers. The GNP particles obtained by the developed technology has good graphitic structure and metallic properties. They could be self-organized in 3D structure depending on the surrounding medium. The electric conductivity of GNP/PCTEF composites is determined by electronic contribution. The real and imaginary parts of dielectric permittivity in an extremely high frequency region, as well as electric conductivity in low frequency region have non-linear dependence from volume content of GNP in GNP/PCTFE composite being a result of percolation threshold at C = 0.5% at 1kHz. The prepared composites are of promising technical application as catalysts, supports and semi-conductive materials.

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### Author's contributions

Conceived the plan: M. Kartel, Yu. Sementsov, G. Dovbeshko; Performed the expeirments: S. Makhno, T. Aleksyeyeva, L. Karachevtseva, Yu. Grbel'na, V. Styopkin, Wang Bo, Yu. Stubrov; Data analysis: Yu. Sementsov, G. Dovbeshko; Wrote the paper: M. Kartel, G. Dovbeshko. Authors have no competing financial interests.

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