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Morphology, molecular and electronic structure of the composite material based on graphene oxide and polyaniline

© *T.N. Myasoedova*[1], *O.V. Nedoedkova*[2], *R. Kalusulingam*[1], *A.S. Mikheykin*[2],
A.S. Konstantinov[2], *G.E. Yalovega*[2,¶]

[1] Institute of Nanotechnologies, Electronics and Equipment Engineering, Southern Federal University,
Taganrog, Russia
[2] Faculty of Physics, Southern Federal University,
Rostov-on-Don, Russia
¶ E-mail: yalovega@sfedu.ru

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A composite material based on graphene oxide (GO) and polyaniline (PANI) was synthesized. By methods of scanning electron microscopy, Raman scattering, infrared spectroscopy confirmed the formation of the composite material, which is nanofibers of PANI in protonated state, tightly wrapped around agglomerated multilayered (2−3 layers) GO nanosheets. The optical bandgap width of the GO-PANI composite is reduced compared to that of the pure PANI, which makes it promising to use this material in supercapacitors and optical devices.

Keywords: carbon-containing electrode materials, nanocomposites, supercapacitors, conductive structure.

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1. Introduction

In recent years one of the promising and actively synthesized materials for supercapacitors are composite systems based on polyaniline (PANI) [1] and graphene oxide (GO) [2], which have high electronic conductivity. The ratio of PANI and graphene oxide, as well as the form of existence of composites (dispersion, film, powder, embedding in polymer matrices) are of special importance [3,4]. For applications in electronic devices, conductivity is an important factor. According to the paper [5], in GO-PANI nanocomposites graphene acted as a template for the PANI growth and contributed to the alignment of the polymer chain, thereby improving its conductivity. The paper [6] shows that by nanoplates distribution in PANI matrix, it is possible to avoid graphene aggregation, which makes it possible to increase the number of charge transfer paths and to improve the mobility of charge carriers. The functional groups of GO provide high interaction with PANI through hydrogen and electrostatic interactions. The possibility of synthesis of composites based on PANI and GO as active materials for supercapacitors was confirmed in the papers [7]. It was shown that in such composites the graphene plates can provide conductive paths for PANI degradation products in the electrochemical process, which improves the specific capacitance and stability of the entire electrode [8].

In this paper, composites based on graphene oxide and polyaniline were synthesized, and their morphology, molecular and electronic structure were studied.

2. Samples preparation and characterization methods

Graphene oxide (GO) was prepared by the modified Hummers method by oxidizing graphite [9]. Graphite was mixed with $NaNO_3$ at a temperature of 0°C. $KMnO_4$ was introduced further into the resulting mixture for 4 h, distilled water was added and stirred until the temperature 95°C was reached. Finally, they were treated with 30% hydrogen peroxide solution. Functionalization of graphene oxide with amino groups (GO-NH_2) was carried out by the solvothermal method by heating graphene oxide powder in ethylene glycol at temperature 180°C for 10 h. Polyaniline (PANI) powder was obtained by acid-free method using a technology developed by the authors and described previously in the paper [10]. GO-PANI composites were formed by adding GO-NH_2 powder to a solution of aniline and ammonium persulfate, so that the ratio GO : aniline was 2 : 1 [11].

Images of the samples were obtained using Nova NanoLab 600 (FEI) scanning electron microscope. Measurements of Raman scattering (RS) spectra in the range $0-3500\,\mathrm{cm}^{-1}$ were carried out on Renishaw in Via Reflex spectrometer, using lasers with wavelengths of 325 and 514 nm. Infrared (IR) spectra were obtained in the wavenumber range $350-4250\,\mathrm{cm}^{-1}$ with a resolution of $2\,\mathrm{cm}^{-1}$ using FSM-1202 infrared Fourier spectrophotometer in transmittance mode. Visible ultraviolet (UV) spectra were measured on Unico 2804 (USA) dual-beam spectrophotometer in the wavelength range from 100 to 1000 nm in steps of 1 nm. The optical band gap width (E_g) of the samples under study was determined using the Tauc method [12].

3. Results and discussion

Analysis of scanning electron microscopy (SEM) images showed that graphene oxide has a multilayer structure similar to nanosheets (Figure 1, *a*), and PANI sample

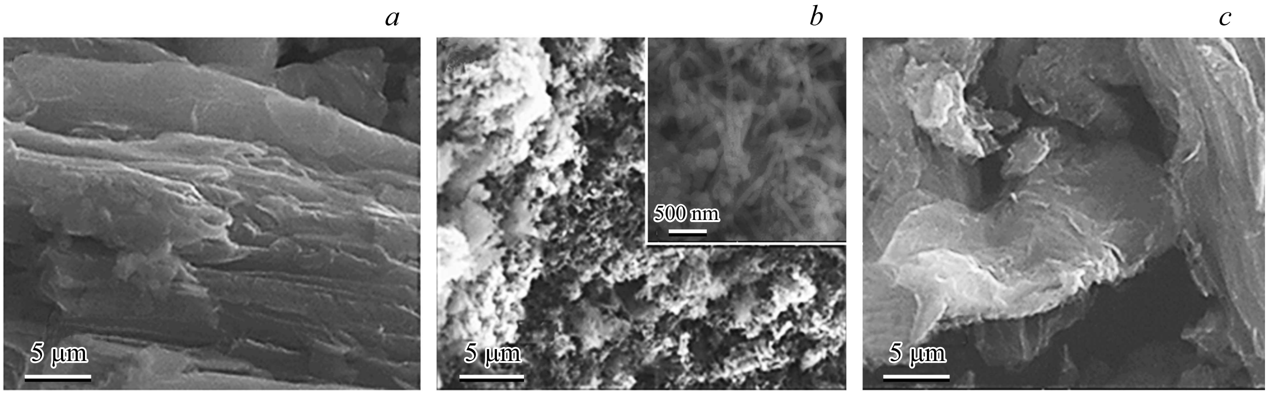

Figure 1. SEM images: *a* — GO, *b* — PANI, *c* — GO-PANI.

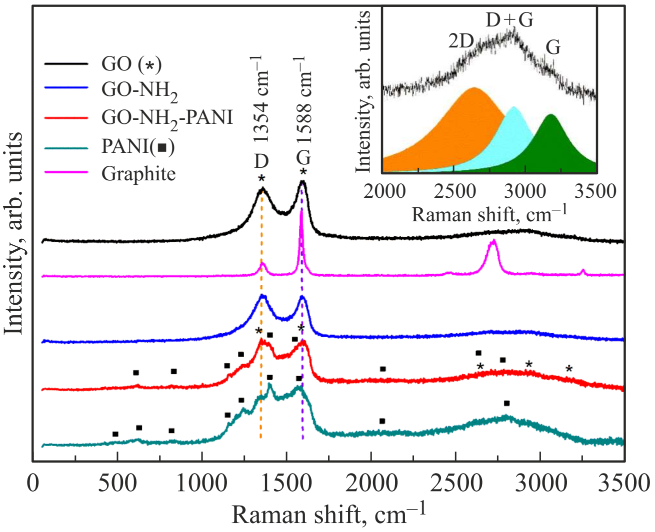

Figure 2. Comparison of RS spectra of GO, GO-NH$_2$, GO-PANI, PANI and graphite. Approximation of CO lines of second order (insert).

has a highly porous structure consisting of nanofibers (Figure 1, *b*). The GO-PANI composite consists of PANI nanofibers tightly wrapped around agglomerated GO nanosheets (Figure 1, *c*).

Studies by RS indicated that the shape of the spectrum of the graphene oxide synthesized in this study coincides with the spectra from the paper [13]. The comparison of GO RS spectrum with the spectrum of graphite showed broadening of the GO lines compared to the lines of graphite (Figure 2), which is associated with high number of defects arising due to oxidation of the graphene plane. The intensity ratio $I_\mathrm{D}/I_\mathrm{G}$ indicates that GO sample [14] is multilayered. Estimation of the number of layers using second-order lines showed the greatest similarity of the approximation with 2–3 layers (Figure 2, insert). In PANI RS spectra the bands at 430, 600 and 813 cm^{-1} are attributed to in-plane and out-of-plane vibrations of the ring of the protonated emeraldine form of polyaniline [15]. A comparison of the RS spectra of GO-PANI at various stages of composite formation with the spectra of GO and PANI showed a redistribution of the intensities of D, G lines and the second-order lines 2D and D + G compared to GO spectrum as a result of the functionalization of GO by groups NH$_2$. The spectrum of GO-PANI composite reflects contributions from graphene oxide and polyaniline, manifested in bifurcation, redistribution of intensity and frequencies of the lines D and G, as well as the shape of the second order lines 2D and D + G. Besides, lines at frequencies 616, 824, 1150, 1241 and 2009 cm^{-1}, characteristic of the spectrum of polyaniline, are observed in the spectrum of the composite material. Thus, RS spectra of the GO-PANI composite are more similar to the spectra of PANI, which indicates the polyaniline presence on the surface of graphene oxide.

The IR spectra of the GO sample showed the presence of a stretching vibration band in O–H group approximately of 3650 to 3050 cm^{-1} (Figure 3, *a*). The presence of the amine functional group in GO-NH$_2$ led to the overlap of bands with the group O–H at 3433, 1726 and 1619 cm^{-1}. The absorption bands between 3285 and 3527 cm^{-1} are due to the stretching of N–H bonds in amino groups, while the band at 1580 cm^{-1} — stretching of N–H bonds in the same plane. During the synthesis of PANI and its GO-PANI composite, bands appear at 1481 and 1293 cm^{-1} and in the range 1235–1022 cm^{-1}, which correspond to C=C vibration of benzene ring, and C–N vibration of benzene ring, and stretching vibration C–N of aromatic amines. On the other hand, the bands at 858 and 1634 cm^{-1} are caused by the vibration of S–O in the composite and the bending vibrations of N–H in the amine, respectively [9].

The visible UV spectra of PANI and GO-PANI have two absorption bands at 330 and 620 nm, characteristic of $\pi \rightarrow \pi^*$ (peak A, A*) transition, and forearm B. characteristic of $n \rightarrow \pi^*$ transition (Figure 3, *b*, insert). The calculated values E_g for GO, PANI and GO-PANI were 2.7, 3.8 and 3.5 eV, respectively (Figure 3, *b*). It can be seen that the addition of GO to the polymer reduces the band gap of GO-PANI compared to pure PANI. This is consistent with the results of the work [16], where it was shown

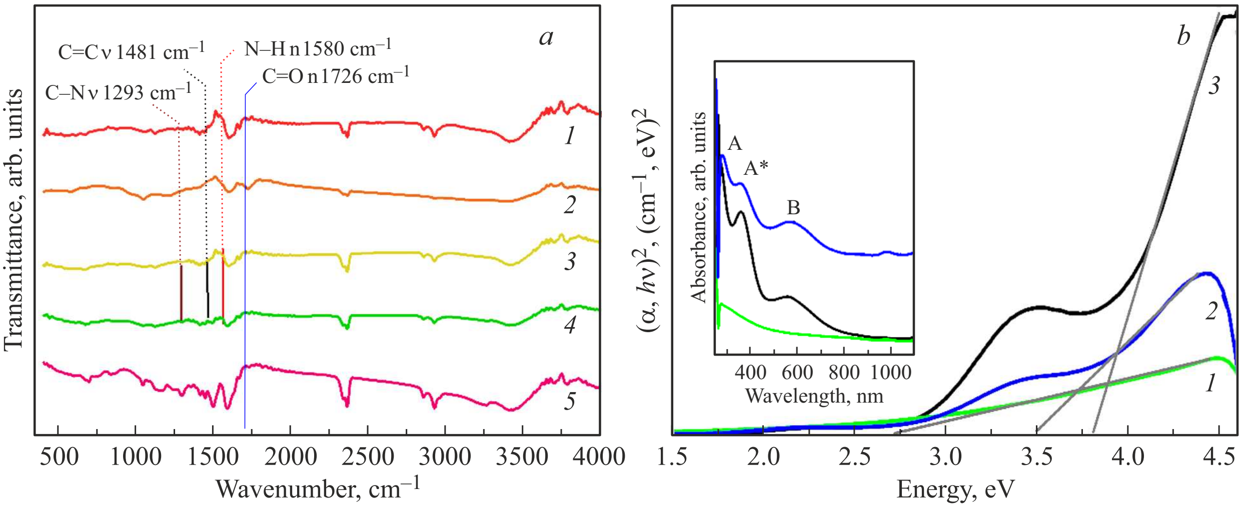

Figure 3. *a* — IR spectra of graphite (curve *1*), GO (curve *2*), GO-NH$_2$ (curve *3*), GO-PANI (curve *4*), PANI (curve *5*); *b* — E_g samples of GO (curve *1*), GO-PANI (curve *2*) and PANI (curve *3*). Visible UV spectra (insert).

that the band gap of GO-PANI decreases with increasing graphene oxide content in the sample. Optical absorption in conjugated polymers can be caused by the charge carriers transition across the band gap. The decrease in band gap is due to the occurrence of new excitation energy levels below the conventional band gap of PANI as a result of charge transfer from GO to PANI.

4. Conclusion

The paper involved the synthesis of composite material based on graphene oxide and polyaniline, obtained by an acid-free method. SEM, RS, and IR methods confirmed the formation of composite material consisting of PANI nanofibers in protonated state, tightly wrapped around agglomerated multilayer (2–3 layers) of OG nanosheets. According to visible UV spectroscopy, the formation of the composite material based on polyaniline and graphene oxide leads to a decrease in the band gap, which makes it possible to use this composite in supercapacitors and optical devices as an electrode material.

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Conflict of interest

The authors declare that they have no conflict of interest.

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