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Electron paramagnetic resonance study of gadoliniumum doped graphene oxide

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The samples obtained by the Hammer method and then doped with 5, 10 and 15 percent gadolinium were studied by the EPR analysis method. The conducted studies were carried out at room temperature. Depending on the degree of addition of gadolinium during the studies an increase in the intensity of the signal and a decrease in the intensity of free radicals were observed. So that, when the amount of gadolinium reaches 15%, the signal of free radicals disappears. The reason for this is that the Gd ion forms a single homogeneous system with the formation of strong bonds between the surface of the graphene oxide sample. In addition, it can be noted that unpaired electrons in the form of free radicals, which are stabilized in the carbon rings in the crystal structure of graphene oxide, cause this connection.

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1. Introduction

Graphene-based samples, which are considered smart materials, are important in terms of creating the cores of modern devices. There are different methods of obtaining these samples. The Hammer method, which has a special place among them, is currently one of the most widely used approaches. [1] in the research work, the paramagnetic centers in the graphene oxide (GO) sample were investigated by means of electron paramagnetic resonance in the temperature range of 4.2-300 K with wave and pulse. During the EPR analysis of the sample, it was observed that the signal reaches the saturation limit. It can be associated with different functional groups present in the sample. Thus, an increase in the spin relaxation times of the paramagnetic centers with the change in temperature was determined and it was suggested that this is related to the water molecules present in the composition [1]. The EPR signal of the GO sample was shown to consist of two Lorentz lines. During the research, it was determined that the integral depends weakly on temperature. When studying the absorption of various functional groups and water molecules GO and reduced graphene oxide suggest that signaling occurs due to localized charge carriers [2]. In situ EPR analysis was based on a three-electrode system using Pt mesh, Ag|AgCl as electrodes respectively [3].

The problem of multiqubit analysis for a diamond sample calculated from allotropic shifts of carbon is quite complicated. Thus, when conducting research in more dimensions, it leads to the installation of a time-remembered phase of the centers [4]. During the EPR analysis of N-rGO/rGO, it was observed that the signal decays over time in 6 M KOH aqueous electrolyte resulting in chemical quenching of radical species [5].

Graphene oxide/sulfur compound obtained by Hammers method was synthesized, composition, quantitative index of functional groups present, degree of wear, number and size of layers, modeling VAC, electrical and structural properties, Raman spectroscopy and SEM analysis were characterized. The VAC of the obtained sample was measured at room temperature. As a

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result of the research, a negative differential resistance was observed at the corresponding voltages, and the reason for this was suggested to be related to the transitions between the localized levels created by the functional groups present in the sample [6-11].

The amount of sulfur present in graphene oxide synthesized by the Hummers method has been discussed in several articles. Raman analyzes of the obtained samples were performed at different temperatures [12].

Graphene oxide samples have very interesting application areas. They also have a wide range of applications such as nanoelectronics, opto-nanoelectronics, catalysis, energy storage and solar cells [9,13-15].

2. Experimental details

Graphene oxide sample obtained by Hammers method and addition of 5%, 10% and 15% of gadolinium was carried out. The samples were analyzed by different analysis methods.

Four samples of graphene-oxide substance with gadolinium metal ion added by EPR method were selected for research purpose. The substances differ from each other by the percentage of gadolinium added to the graphene oxide. If we denote the studied samples with letters a, b, c and d, respectively: the amount of gadolinium in a- sample was 0%, in b- sample 5%, in c-sample 10%, and in d-sample 15%.

The EPR spectra of the samples were recorded at room temperature on a Bruker EMX Plus radio spectrometer. The working frequency of the radio spectrometer was ν~ 9.8 x 109 Hs (wavelength λ~ 3 sm), modulation frequency 100 kHz, modulation amplitude 10 G, wave power~ 2.14 mW. In order to reveal the signals of all possible paramagnetic centers in the studied samples, the spectra were taken in all possible intervals of the magnetic field (0 ÷ 6000 G).

3. Results

EPR spectra were obtained from all samples and those spectra are shown in figure 1.

It can be seen from Figure 1a that a signal consisting of the superposition of two lines is observed in the region corresponding to the value of g - factor g=2,000 of the magnetic field. The first of them is a low-intensity signal with a 6-line fine superstructure (SPR), which originates from the Mn^{2+} ion. Mn^{2+} ions are widely distributed in nature by dissolving in water, and due to the magnetic moment of its nucleus I=5/2, 6 IR lines appear. The second signal is a rather thin symmetric singlet signal, which lies between the 3rd and 4th IR lines of the Mn^{2+} line, and is also shown in Figure 2 at a smaller magnetic field interval (400 G).

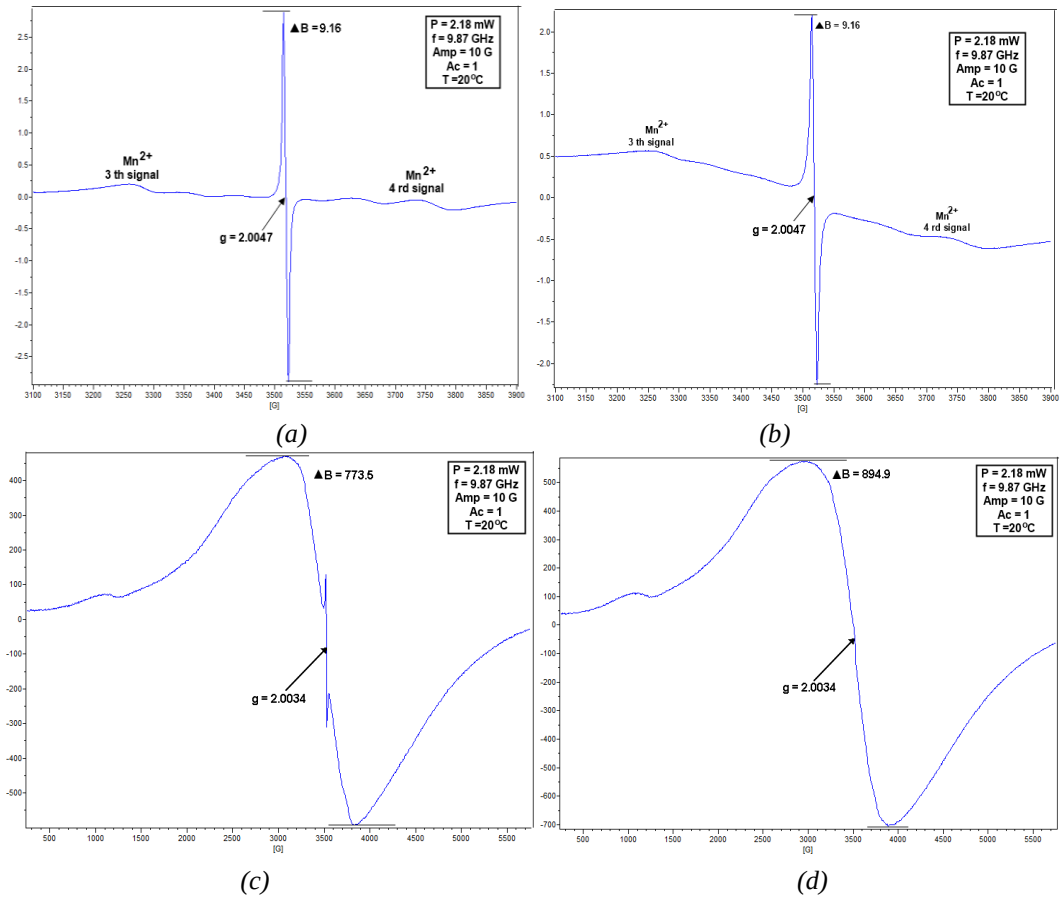

Fig. 1. Electron paramagnetic resonance of graphene oxide and doped gadoliniumum: a) Graphene oxide b) Graphene oxide doped 5% Gd c) Graphene oxide doped 10% Gd d) Graphene oxide doped 15% Gd.

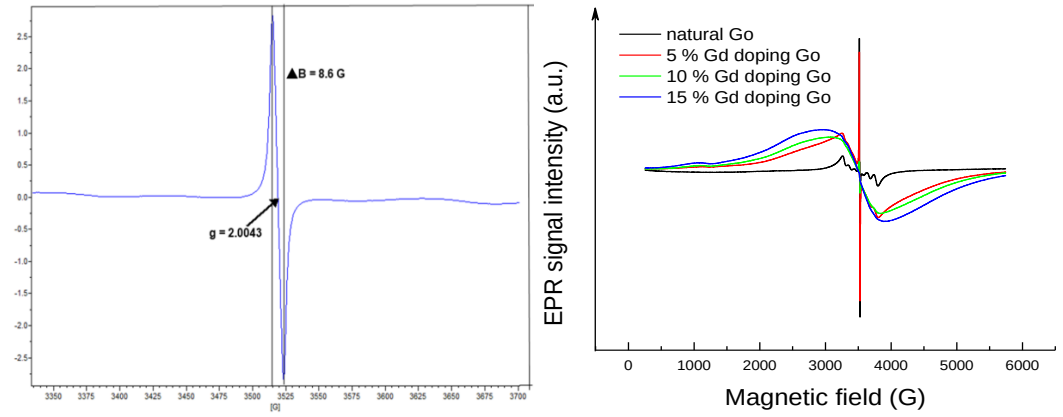

Fig. 2. Thin singlet line observed in graphene oxide.

4. Discussions

The parameters of this line are g = 2.0043 and ΔB = 8.6 G. Figure 1b shows that adding 5% gadolinium to graphene oxide adds a third signal to the two EPR signals. This third signal differs in that its line width is very large. In the spectrum of the sample with 10% Gd -, this third signal is completely detected and its intensity increases several times compared to the previous spectrum. In the middle part of the spectrum, the singlet line remains reduced and the six lines

from the Mn 2+ ion are no longer visible. Finally, when the amount of gadolinium reaches 15%, only the third line remains in the EPR spectrum of the sample, and the other two lines are not observed. The width of this broad line is ΔB = 960 G and the g - factor is g = 2.016. Figure 2a shows the thin singlet line observed in graphene oxide and Figure 2b shows the dependence of the magnetic field on the intensity of the EPR signal. An increase in the signal intensity was observed with the increase in the degree of addition.

5. Conclusions

The analysis of the spectra shows that the second singlet symmetric signal line observed in pure graphene oxide is related to the carbon system that forms the basis of the bulk of graphene oxide. During the synthesis of graphene material, hexagonal rings are formed as a result of the C=C bond breaking during the pyrolysis process, and these rings are joined along one side to form the plane of the carbon ring system of graphene. in the form of a free radical, it gives a signal whose parameters are g = 2.0043 and Δ B = 8.60 G, as can be seen in Figure 2. As a result of the introduction of gadolinium ions into graphene oxide, the third signal appears in the EPR spectrum and the intensity of this signal increases with the increase in the amount of Gd- ion, which suggests that this signal is related to Gd ion. The parameters of this line g = 2.016 and ΔB~960 G, fully detected in the 15% sample, indicate that the chemical source of this signal is the Gd - ion. Because the g-factor of this signal is significantly different from the g-factor of a free electron (g = 2.0023) and the width of the line is very large, it applies only to metal ions with strong spin-orbital interaction.

The fact that the EPR spectrum can be observed from the samples can be an indication of the homogeneous distribution of Gd ion on the surface of the monoatomic layer of graphene oxide in the studied samples. It can be easily seen from Figure 1 that the intensity of the third signal increases and the intensity of free radicals decreases when the percentage of Gd is in excess, and the signal of free radicals disappears when the amount of Gd is 15%. This fact suggests that the Gd ion enters into a complex relationship with the surface of graphene oxide and creates a single homogeneous system. Unpaired electrons in the form of free radicals stabilized in the carbon rings of graphene oxide participate in the creation of this bond. Thus, the free radicals on the surface become very active and participate in the formation of mutual communication in the system with Cd ions entering the surface, and as a result, the EPR signal from free radicals gradually decreases and finally disappears.

References

[1] M. A. Augustyniak-Jabłokow, K. Tadyszak, R. Strzelczyk, R. Fedaruk, R.Carmieli, Carbon 152, pp.98-105 (2019); https://doi.org/10.1016/j.carbon.2019.06.024
[2] M. Kempinski, P. Florczak, S. Jurga, M. Sliwinska-Bartkowiak, W. Kempinski, Appl. Phys. Lett. 111, pp.084102, (2017); https://doi.org/10.1063/1.4996914
[3] B. Wang, A.J. Fielding, R.A.W. Dryfe, Chem. Commun. 54 (31) pp.3827-3830, (2018).
[4] M. E. Trusheim, L. Li, A. Laraoui, E.H. Chen, H. Bakhru, T. Schr€oder, et al., Nano Lett. 14 pp.32-36, (2013); https://doi.org/10.1021/nl402799u
[5] B. Wang, A. J. Fielding, R. A. W. Dryfe, ACS Appl. Nano Mater. 2 pp.19-27, (2018).
[6] W. Hummers, R. Offeman, Preparation of graphitic oxide, J. Am. Chem. Soc. 80, pp.1339-1339, (1958);
[7] R. G. Abaszade, Journal of Optoelectronic and Biomedical Materials, Vol.14, №3, pp.107–114, (2022); https://chalcogen.ro/107_AbaszadeRG.pdf
[8] R. G. Abaszade, S. A. Mamedova, F. H. Agayev, S. I. Budzulyak, O. A. Kapush, M. A. Mamedova, A. M. Nabiyev, V. O. Kotsyubynsky, Physics and Chemistry of Solid State, Vol.22, №.3, pp.595-601, (2021); https://doi.org/10.15330/pcss.22.3.595-601

[9] S. R. Figarova, E. M. Aliyev, R. G. Abaszade, R. I. Alekberov, V. R. Figarov, Journal of Nano Research Submitted, Vol.67, pp.25-31, (2021); http://dx.doi.org/10.4028/www.scientific.net/JNanoR.67.25].
[10] R. G. Abaszade, A. G. Mammadov, V. O. Kotsyubynsky, E. Y. Gur, I. Y. Bayramov, E. A. Khanmamadova, O. A. Kapush, International Journal on Technical and Physical Problems of Engineering, Vol.14, №2, pp.302-306, (2022); http://www.iotpe.com/IJTPE/IJTPE-2022/IJTPE-Issue51-Vol14-No2-Jun2022/37-IJTPE-Issue51-Vol14-No2-Jun2022-pp302-306.pdf
[11] R. G. Abaszade, A. G. Mamedov, I. Y. Bayramov, E. A. Khanmamadova, V. O. Kotsyubynsky, O. A. Kapush, V. M. Boychuk, E. Y. Gur, Physics and Chemistry of Solid State, Vol.23, №2, pp. 256-260, (2022); https://doi.org/10.15330/pcss.23.2.256-260
[12] V. M. Boychuk, R. I. Zapukhlyak, R. G. Abaszade, V. O. Kotsyubynsky, M. A. Hodlevsky, B. I. Rachiy, L. V. Turovska, A. M. Dmytriv, S. V. Fedorchenko, Physics and Chemistry of Solid State, Vol.23, №4, pp. 815-824, (2022); https://doi.org/10.15330/pcss.23.4.815-824
[13] S. R. Figarova, E. M. Aliyev, R. G. Abaszade, V. R. Figarov, Advanced Materials Research, vol.1175, pp.55-62, (2023); https://doi.org/10.4028/p-rppn12
[14] Z. Liu, Z. Chen, F. Yu, Sol. Energy Mater. Sol. Cells 174, pp.453-459, (2018); https://doi.org/10.1016/j. solmat.2017.09.034
[15] A. Singh, A. Sharma, A. Ahmed, A.K. Sundramoorthy, H.Furukawa, S.Arya, A.Khosla, Biosensors, 11, pp.336, 2021; https://doi.org/10.3390/bios11090336