https://doi.org/10.32603/1993-8985-2019-22-3-88-96
УДК 661.666.23

Denis Yu. Kornilov ✉
LLC "AkKo Lab"
65/1, Gilyarovskogo Str., 129110, Moscow, Russia

THE INFLUENCE OF THE THERMAL REDUCTION TEMPERATURE ON THE STRUCTURE AND ELECTROPHYSICAL PROPERTIES OF REDUCED GRAPHENE OXIDE FILMS

Abstract

Introduction. *An incomplete list of the properties of graphene includes its high electrical and thermal conductivity, strength, specific surface area (SSA) and optical light transmittance. Graphene is a very promising material for use in micro- and nano-electronics applications. An additional advantage of graphene is the variety of means by which the material may be obtained, allowing the creation of novel materials with useful physicochemical properties by appropriate technological methods.*

Objective. *The study aims at investigating the influence of thermal reduction temperature on the physicochemical properties of graphene oxide (GO) films.*

Materials and methods. *In the present work, GO films are obtained on the surface of a slide by means of its immersion in a graphene oxide water dispersion (dip coating). Obtained samples are studied using scanning electron microscopy, Raman spectroscopy and elemental CHN analysis methods. The resistance of the graphene sheet is measured using a four-point probe method.*

Results. *A difference in the elemental content (C, H, N) in studied samples, along with an increase in graphene structure defectiveness and decreased sheet resistance, are found to be proportional to an increase in reduction temperature. A decrease in the thickness of GO films following heat treatment is also observed, which may be attributed to the loss of with a functional GO groups during thermal reduction.*

Conclusion. *The research results demonstrate the possibility of obtaining carbon films from reduced graphene oxide (RGO). Such graphene films demonstrate desired physicochemical properties for use in thin-film technologies. The presented research is of potential use in understanding general issues relating to the acquisition and application of GO and RGO.*

Keywords: graphene oxide, reduced graphene oxide, multilayer films

For citation: Kornilov D. Yu. The Influence of the Thermal Reduction Temperature on the Structure and Electrophysical Properties of Reduced Graphene Oxide Films. Journal of the Russian Universities. Radioelectronics. 2019, vol. 22, no. 3, pp. 88–96. doi: 10.32603/1993-8985-2019-22-3-88-96

Acknowledgements. Initiative work.

Conflict of interest. The author declares no conflict of interest.

Submitted 07.04.2019; accepted 20.05.2019; published online 27.06.2019

Д. Ю. Корнилов✉
ООО "АкКо Лаб"
ул. Гиляровского, д. 65, стр. 1, Москва, 129110, Россия

ВЛИЯНИЕ ТЕМПЕРАТУРЫ ТЕРМИЧЕСКОГО ВОССТАНОВЛЕНИЯ НА СТРУКТУРУ И ЭЛЕКТРОФИЗИЧЕСКИЕ СВОЙСТВА ПЛЕНОК ВОССТАНОВЛЕННОГО ОКСИДА ГРАФЕНА

Аннотация

Введение. *Высокая электропроводность, теплопроводность, прочность, большая площадь поверхности, высокий коэффициент светопропускания – это лишь неполный перечень свойств графена – материала, являющегося весьма перспективным с точки зрения применения в микро- и наноэлектронике. Кроме того, к преимуществам графена можно отнести возможность его получения различными способами. Это позволяет, используя соответствующие технологические приемы, создавать материалы с заданными физико-химическими характеристиками.*

Цель работы. *Исследование степени влияния температуры термического восстановления на физико-химические свойства пленок оксида графена (ОГ).*

Материалы и методы. *В описываемой работе пленки ОГ были получены на поверхности предметного стекла посредством его погружения и извлечения из водной дисперсии оксида графена (dip coating). Полученные образцы были охарактеризованы методом сканирующей электронной микроскопии, спектроскопии комбинационного рассеяния света, элементного CHN-анализа. Удельное поверхностное электрическое сопротивление было измерено четырехзондовым методом.*

Результаты. *Установлено отличие содержания элементов (C, H, N) в исследуемых образцах, снижение дефектности в графеновой структуре, а также уменьшение удельного электрического сопротивления пропорционально увеличению температуры восстановления. Также обнаружено уменьшение толщины пленок ОГ при термической обработке, что предположительно связано с потерей функциональных групп в ОГ при его термическом восстановлении.*

Заключение. *Результаты исследований демонстрируют возможность получения углеродных пленок из восстановленного оксида графена (ВОГ) с заданными физико-химическими характеристиками, которые могут найти применение в тонкопленочных технологиях. Представленные материалы также могут быть полезны исследователям в вопросах получения и применения ОГ и ВОГ.*

Ключевые слова: оксид графена, восстановленный оксид графена, тонкослойные пленки

Для цитирования: Корнилов Д. Ю. Влияние температуры термического восстановления на структуру и электрофизические свойства пленок восстановленного оксида графена // Изв. вузов России. Радиоэлектроника. 2019. Т. 22, № 3. С. 88–96. doi: 10.32603/1993-8985-2019-22-3-88-96

Источник финансирования. Инициативная работа.

Конфликт интересов. Авторы заявляют об отсутствии конфликта интересов.

Статья поступила в редакцию 07.04.2019; принята к публикации 20.05.2019; опубликована онлайн 27.06.2019

Introduction. An analysis of literature data reveals a significant number of works (Fig. 1) in the materials science field of graphene-based films, comprising a carbon atom monolayer material joined by σ- and π-bonds into a hexagonal two-dimensional crystal lattice. INTEL considers graphene as one of the possible foundations of future microelectronics [1]. The significant research interest in graphene can be explained in terms of the material's unique, empirically-confirmed properties. For example, a monolayer graphene has the largest possible specific surface area (SSA) of 2640 m^2/g and can withstand high-density currents [2]. With a Young’s modulus of 1TPa, graphene is the strongest material known to science, capable of undergoing significant deformation without crystal lattice disordering [3]. Monolayer graphene is highly conductive with a thermal conductivity of 5000 W/(m·°C) and a maximum car-

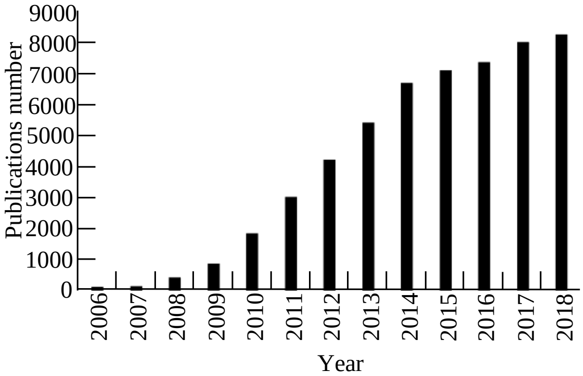


Fig. 1. The number of publications in a graphene applications field in thin-film technologies over a period from 2006 to 2018 (keywords search for "graphene films" by using the EBSCO Discovery Service database)

rier mobility at a room temperature of 200 000 cm^2/(V·s) [4]. The optical transmittance of graphene is 97.7%. Various approaches for the production of graphene include chemical vapour deposition on a metal substrate from a carbon-containing gas mixture, direct graphite dispersion in various solvents in the presence of surface-active agents (surfactants) and epitaxial growth of graphene on a silicon carbide crystal face using thermal decomposition. An additional approach consists in chemical solution-based synthesis method, known as Hummers' method, which consists in a graphite chemical oxidation and its subsequent dispersion in the solution thus allowing formation of oxidised graphene, consisting of graphene flakes with oxygen-containing functional groups on the edges or inside the carbon network, where further thermal or chemical treatment results in recovery of graphene from graphene oxide (GO). According to the International Organisation for Standardisation (ISO) TS80004-13 dictionary [5], graphene materials (graphene and related two-dimensional (2D) materials) include: graphene taking the form of a monolayer of carbon atoms; bilayer graphene (2LG) consisting of two layers of carbon atoms; trilayer graphene (3LG) consisting of three layers of carbon atoms; few-layer graphene (FLG) having three to ten layers of carbon atoms. This classification is in agreement with publications [6]–[8] confirming the unique properties of graphene materials when they consist of no more than 10 layers of carbon atoms.

Consequently, a combination of graphene properties such as high strength, electrical and thermal conductivity, elasticity, optical transmittance, large specific surface area, as well as the possibility of its production using various technological methods indicate graphene as a very promising material from a point of view of its application in micro- and nanoelectronics. For example, it can be used to form electrically conductive coatings on dielectric materials when creating elements used in measuring circuits, detectors, sensor panels, photoelectric converters, photodetectors, heating compositions, as well as when developing shielding and radio wave absorbing materials and planar chemical current sources (CCS) [9]–[14].

The objective of the present work is to study the influence of thermal reduction temperature on the physicochemical properties of GO.

Materials and methods. In order to obtain GO films via Hummers' method, an aqueous dispersion of GO flakes was used, having a concentration of 2.3 mg/ml, lateral size of 0.1–4 μm and thickness of up to 1.5 nm. The results were characterised by modern physicochemical analysis methods [15] as reported in previously published works [16]–[18]. The dispersion method used for obtaining GO was as follows: first, concentrated sulphuric acid was poured into a glass beaker, then ammonium persulfate and phosphorus pentoxide were added under stirring with a magnetic stirrer. The resulting reaction mixture was heated up to 80–85°C until the reagents were completely dissolved. Next, a natural graphite powder (99.9%) was added into the beaker and the mixture was kept at 80°C for 5 hours while stirring. Then, distilled water was slowly poured into the mixture, which had previously been cooled to room temperature. After that, the obtained precipitate was repeatedly filtered with a help of a fritted glass filter to pH=7 followed by drying. The dried powder was then transferred to a beaker containing sulphuric acid that had been cooled in an ice bath. Then, potassium permanganate was added under constant stirring. After that, distilled water was added in a volume equal to the reaction mixture volume keeping mixture temperature below 40 °C. After some time, an equal volume of water was added together with a small amount of 30% hydrogen peroxide. This stage is accompanied by the release of gaseous bubbles and the suspension changing colour to yellow-brown. The obtained solid precipitate was filtered with a large amount of de-ionised water (DIW) and subjected to drying. In order to obtain the GO dispersion, the obtained powder was placed in a cylindrical beaker and distilled water poured over it, followed by ultrasonic treatment (frequency 20.4 kHz, specific power 0.1–1 W/cm^3) for 15 minutes. The resulting dispersion was centrifuged for 10 min at 2000 rpm to remove large and poorly oxidised particles.

The films were obtained on the surface of a glass slide by dipping the glass substrate into an aqueous GO dispersion (dip-coating) followed by drying at a temperature of 40–50 °C. In order to simplify the handling of the studied objects, the film was not removed from the glass.

Preparation and cleaning of glass substrates were carried out in several stages, including the following treatments:

– washing out the surfactants;
– cleaning with DIW;
– keeping in an aqueous solution of 20% NaOH at room temperature for 20 minutes;
– cleaning with DIW;
– keeping in an aqueous solution of 5% HF at room temperature for 5 minutes;
– cleaning with DIW;
– processing in an ultrasonic bath for 10 minutes;
– cleaning with DIW;
– air drying for 1 hour.

In order to study the dependencies of changes in properties of GO film on thermal reduction conditions, test samples were heated in a muffle furnace at a heating rate of 2 °C/min up to 200, 300 and 400 ºC with a holding time of one hour after reaching each predetermined temperature.

A morphology study of the film surface was carried out using a Carl Zeiss SUPRA 40 scanning electron microscope (Germany). When receiving images in secondary and backscattered electrons, the accelerating voltage was 1…10 kV.

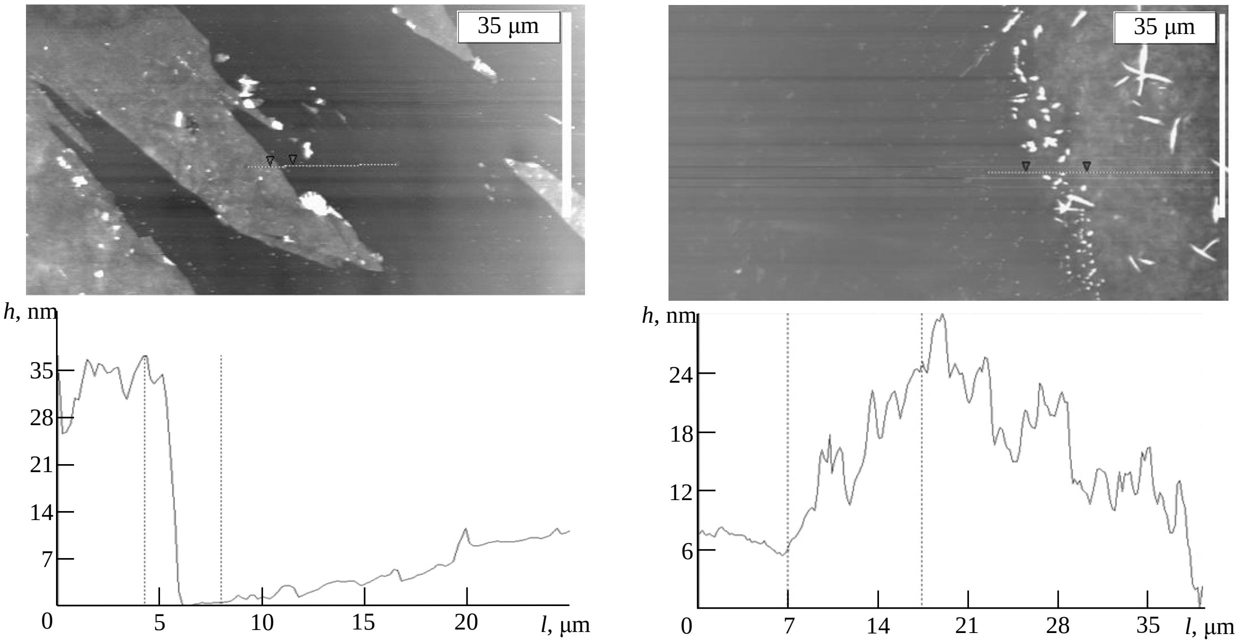
A Raman scattering (RS) method was used to study the atomic bond structure of the films with a Renishaw inVia spectrometer (UK) having a laser excitation wavelength of 514 nm. The spectrometer was calibrated on a standard sample of monocrystalline silicon with a fundamental vibration mode of 520.5 cm^{-1}. The D, G, and D’ band shapes are described by a Gaussian function.

The sheet resistance (R_S) of thin-film samples was measured with an Elins P-30J potentiostat/galvanostat (Russia) using a four-point probe method in a cell with platinum-coated point contacts. The distance between the contacts was 1.6 mm.

The thickness of the studied coatings was determined by atomic force microscopy (AFM) using a NANOSCOPE III scanning probe microscope (USA). The dotted line shown in AFM images (Fig. 2) indicates the studied region used to analyse the surface relief profile. On the AFM images, the locations of triangular markers correspond to the dotted lines on the cross-section plots.

Elemental CHN analysis was performed using a vario Micro cube automatic analyser (Germany). The sample portion was 0.8…1 mg. The sample is burned at a temperature of 950 ºC. The CHN content is calculated automatically by the instrument software. The program considers predetermined calibration coefficients for standard samples, as well as blank run results and sample portion.

Results. The film samples obtained from the GO



a b

Fig. 2. AFM images of the films and their cross-sections along the dotted lines: *a* – GO film; *b* – RGO film after the heat treatment at 400 °C

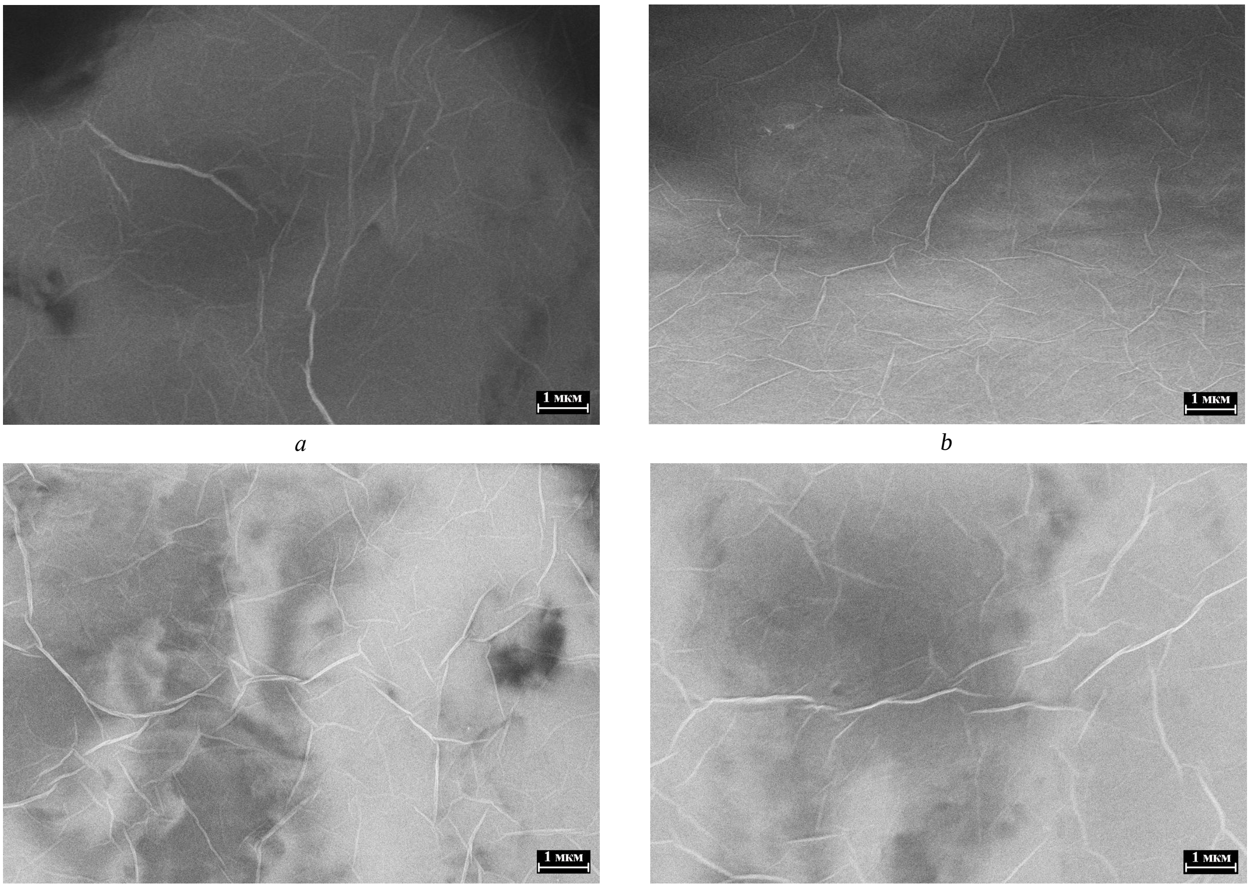
dispersion for the purposes of the experiment had thicknesses of no more than 37 nm (Fig. 2, *a*), as determined by the AFM method. The thickness of the films was unaffected by heating at temperatures of 200 and 300 ºC; however, processing at 400 ºC led to a film thickness decrease not exceeding 19 nm (Fig. 2, *b*), which is possibly due to a height decrease of GO monolayer (0.9…1.2 nm) up to graphene (0.335 nm) due to a thermal reduction and as a result of an oxygen-containing functional groups loss, which is also indicated by CHN analysis results allowing to observe a carbon increase associated with decreasing of hydrogen and presumably oxygen in the total mass [19]–[24]. In addition, it is possible to note the dependence of a films sheet resistance decrease with the thermal reduction temperature increase (see Table) from 75 kΩ/□ for a sample of reduced GO (RGO) obtained at the thermal reduction temperature of 200ºC to 8 kΩ/□ for a rGO sample obtained at the thermal reduction temperature of 400ºC.

By using scanning electron microscopy (SEM) method it was found that studied samples have a folded surface structure (Fig. 3) that remains unchanged regardless of heat treatment conditions.

Physico-chemical characteristics of the films of GO and RGO

Sample	t_{red}, ...°C	R_s, Ω/W	CHN- analysis		
			C, %	H, %	N, %
GO	–	–	45.97	3.25	0.65
RGO 200	200	75	73.48	1.19	1.22
RGO 300	300	9.5	74.09	1.09	1.39
RGO 400	400	8	74.74	1.12	1.79

The samples differences are confirmed by research results obtained by Raman spectroscopy. Fig. 4 shows Raman spectra of RGO films acquired at different reduction temperatures. The main factor characterising the graphene structures in studied samples is a corresponding peaks presence in the Raman spectra. For example, G-lines indicate oscillations of the sp^2-carbon bonds system (1560 cm^{-1}). D-lines (1360 cm^{-1}), while D+G-lines (2940 cm^{-1}) indicate the formation of a defective structure, which decreases in proportion to the thermal reduction temperature increase that is evidenced by the absence of a D+G-line in the Raman spectrum obtained at 400ºC; here, unlike sample spectra obtained at lower temperatures, a 2D-line (2690 cm^{-1}) is clearly observed, consisting in a D-line overtone indicating a



a *b*

c *d*

Fig. 3. SEM micrographs of GO and RGO films surface structure: *a* – GO film; *b* – RGO film following heat treatment at 200 °C; *c* – film following heat treatment at 300 °C; *d* – film following heat treatment at 400 °C

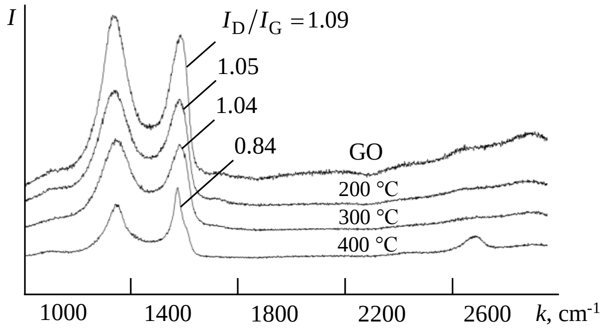


Fig. 4. The results of GO and RGO films studies by using Raman spectroscopy

small number of layers in this graphene structure [25], [26]. According to the estimation of the I_D/I_G ratio, it can be observed that with an increase in the thermal reduction temperature, the I_D/I_G ratio decreases, indicating an increase in the degree of structure ordering [27].

Thus, the resulting conductive RGO thin-films having different hydrogen and oxygen contents can be used to create planar chemical current sources [28] (batteries and supercapacitors) having a high charge density and energy as widely used as components of ultra-dense surface-mount on printed circuit boards for microelectromechanical system power supply, memory blocks and various sensors.

Conductive RGO films can also be used as a conductive base for a subsequent deposition of CCS cathodes and anodes, which function as current leads having minimal thickness and weight [29]. This is very important when developing CCS having high specific power-capacitance characteristics. In addition, using the RGO films on surfaces of traditional current leads (copper and aluminium) of microbatteries and capacitors protects against corrosion by preventing direct contact of a metal with electrolyte decomposition products [30] formed during electrochemical cycling, thus reducing Faraday processes and – consequently – self-discharge and CCS irreversible capacity loss. The use of GO films having different degrees of reduction allows the creation ofg bipolar electrodes of a lithium-ion battery [31], [32], thus eliminating the necessity of cathode materials, which, having a higher density than graphene, greatly increase the weight of CCS structures.

Conclusion. On the basis of conducted studies, the dependency of changes in the physicochemical properties of films, having thicknesses not exceeding 37 nm and obtained from GO dispersion by the dip-coating method, on thermal reduction conditions is established. During heat treatment at 400°C, a change in the film thickness up to 19 nm is observed. This is presumably associated with a decrease in the thickness of GO monolayers due to loss of oxygen-containing functional groups, while thermal reduction, which is confirmed by CHN analysis results and Raman spectroscopy, additionally demonstrates a decrease in graphene structure defectiveness as the temperature of thermal reduction increases; this is also indicated by the peak appearance in Raman spectrum of a small number of graphene layers in a sample obtained by the heat treatment at 400°C. A decrease in the sheet resistance of the RGO films from 75 kΩ/□ to 8 kΩ/□ is proportional to the increase in reduction temperature. The results indicate the possibility of using graphene to form electrically conductive coatings on dielectric materials.

REFERENCES

1. Morozov S. V., Novoselov K. S., Geim A. K. Electronic Transport in Graphene. *Physics-Uspekhi* [Advances in Physical Sciences], 2008, vol. 178, no. 7, pp. 776–780. doi: 10.3367/UFNr.0178.200807i.0776 (In Russ.)

2. Kul'chitskii N. A., Naumov A. V. The Current State of Thin-Film Photovoltaics. Nano- and Microsystems Technology. 2013, no. 9, pp. 29–37. (In Russ.)

3. Kulova T. L., Skundin A. M. Thin-Film Lithium-Ion Batteries. *Elektrokhimicheskaya Energetica* [Electrochemical Energetics]. 2009, vol. 9, no. 2, pp. 57–66. (In Russ.)

4. Kulova T. L., Skundin A. M. Thin-Film Battery Design Issues. *Elektrokhimicheskaya Energetica* [Electrochemical Energetics]. 2011, vol. 11, no. 2, pp. 71–74. (In Russ.)

5. Gubin S. P., Tkachev S. V. *Grafen i rodstvennye nanoformy ugleroda* [Graphene and Related Carbon Nanoforms]. Ed. 4. Moscow, *Lenand*, 2015, 112 p. (In Russ.)

6. Huang G., Hou C., Shao Y., Wang H., Zhang Q., Li Y., Zhu M. Highly strong and elastic graphene fibres prepared from universal graphene oxide precursors. Scientific Reports. 2014, vol. 4, article number: 4248. doi: 10.1038/srep04248

7. Ferrari A. C., Bonaccorso F., Falko V., Novoselov K. S., Roche S., Boggild P., Pugno N. Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. Nanoscale. 2015, vol. 7, pp. 4598–4810. doi: 10.1039/c4nr01600a

8. ISO/TS 80004-13:2017 Nanotechnologies – Vocabulary. Part 13: Graphene and related two-dimensional (2D) materials. 2017. Available at: https://www.iso.org/obp/ui/#iso:std:iso:ts:80004:-13:ed-1:v1:en (accessed 27.09.2018)

9. Bobrinetskii I. I., Komarov I. A., Lavrent'ev K. K., Levin D. D., Simunin M. M., Nevolin V. K., Kvacheva L. D.,

Chervonobrodov S. P., Burian A., Khavelek L., Voznitsa N. Graphenes Integration Features in Microelectronics Technological Processes. Proc. of Universities. Electronics. 2013, no. 3, pp. 33–42. (In Russ.)

10. Svintsov D. A., V'yurkov V. V., Lukichev V. F., Orlikovskii A. A., Burenkov A., Okhsner R. Graphene Tunnel Field Effect Transistors. Semiconductors/Physics of the Solid State. 2013, vol. 47, iss. 2, pp. 244–250. (In Russ.)

11. Sorokin P. B., Chernozatonskii L. A. Graphene-based Semiconductor Nanostructures. *Physics-Uspekhi* [Advances in Physical Sciences]. 2013, vol. 183, no. 2, pp. 113–132. doi: 10.3367/UFNr.0183.201302a.0113(In Russ.)

12. Shakirzyanov F. N. Graphene and Photoresistive Effect. Electricity. 2011, no. 1, pp. 65–66. (In Russ.)

13. Chigirev P. M. Application of Graphene in Electronics. Nano- and Microsystems Technology. 2011, vol. 127, no. 2, pp. 28–30. (In Russ.)

14. Timofeev V. B., Popov V. I., Nikolaev D. V., Timofeeva T. E., Smagulova S. A. Preparation of Transparent Conductive Films from CVD Graphene by Lamination and Their Characterisation. Nanotechnologies in Russia. 2017, vol. 12, no 1–2, pp. 49–52. (In Russ.)

15. Tkachev S. V., Buslaeva E. Yu., Naumkin A. V., Kotova S. L., Laure I. V., Gubin S. P. Graphene Obtained by the Graphene Oxide Reduction.. Inorganic Materials. 2012, vol. 48, no. 8, pp. 909–915. (In Russ.)

16. Rychagov A. Yu., Gubin S. P., Chuprov P. N., Kornilov D. Yu., Karaseva A. S., Krasnova E. S., Voronov V. A., Tkachev S. V. Electrochemical Reduction and Electric Conductivity of Graphene Oxide Films. Russian Journal of Electrochemistry. 2017, vol. 53, no. 7, pp. 813–819. doi: 10.7868/S0424857017070052(In Russ.)

17. Kornilov D. Yu., Gubin S. P., Chuprov P. N., Rychagov A. Yu., Cheglakov A. V., Karaseva A. S., Krasnova E. S., Voronov V. A., Tkachev S. V., Kasharina L. A. Reduced Graphene Oxide as a Protective Layer of the Current Collector of a Lithium-Ion Battery. Russian Journal of Electrochemistry 2017, vol. 53, no. 6, С. 701–705. doi: 10.7868/S0424857017060081(In Russ.)

18. Gubin S. P., Rychagov A. Yu., Chuprov P. N., Tkachev S. V., Kornilov D. Yu., Almazova A. S., Krasnova E. S., Voronov V. A. Supercapacitor Based on Electrochemically Reduced Graphene Oxide. E*lektrokhimicheskaya Energetica* [Electrochemical Energetics]. 2015, vol. 15, no. 2, pp. 57–63. (In Russ.)

19. Tararan A., Zobelli A., Benito A. M., Maser W. K., Stephan O. Revisiting Graphene Oxide Chemistry via Spatially-Resolved Electron Energy Loss Spectroscopy. Chemistry of Materials. 2016, vol. 28, pp. 3741–3748. doi: 10.1021/acs.chemmater.6b00590

20. Dolbin A. V., Khlistuck M. V., Eselson V. B., Gavrilko V. G., Vinnikov N. A., Basnukaeva R. M., Benito A. M. The Effect of the Thermal Reduction on the Kinetics of Low-Temperature 4He Sorption and the Structural Characteristics of Graphene Oxide. Low Temperature Physics. 2017, vol. 43, pp. 383–389. doi: 10.1063/1.4979362

21. Alvarez P., Blanco C., Santamaria R., Blanco P., Gonzalez Z., Fernandez-Garcia L., Menendez R. Tuning Graphene Properties by a Multi-Step Thermal Reduction Process. Carbon. 2015, vol. 90, pp. 160–163. doi: 10.1016/j.carbon.2015.04.022

22. Slobodian O. M., Lytvyn P. M., Nikolenko A. S., Naseka V. M., Khyshun O. Y., Vasin A. V., Nazarov A. N. Low-Temperature Reduction of Graphene Oxide: Electrical Conductance and Scanning Kelvin Probe Force Microscopy. Nanoscale Research Letters. 2018, vol. 13. doi: 10.1186/s11671-018-2536-z

23. Vijayarangamuthu K., Ahn S., Seo H., Yoon S.-H., Park C.-M., Jeon K.-J. Temporospatial Control of Graphene Wettability. Advanced Materials. 2015, vol. 28, iss. 4, pp. 661–667. doi: 10.1002/adma.201503444

24. Qiu Y., Guo F., Hurt R., Kulaots I. Explosive Thermal Reduction of Graphene Oxide-Based Materials: Mechanism and Safety Implications. Carbon. 2015, vol. 72, pp. 215–223. doi: 10.1016/j.carbon.2014.02.005

25. Singh R. K., Kumar R., Singh D. P. Graphene Oxide: Strategies for Synthesis, Reduction and Frontier Applications. RSC Advances. 2016, vol. 6, pp. 64993–65011. doi: 10.1039/c6ra07626b

26. Ferrari A. C. Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects. Solid State Communications. 2007, vol. 143, pp. 47–57. doi: 10.1016/j.ssc.2007.03.052

27. Yang H., Hu H., Wang Y., Yu T. Rapid and Non-Destructive Identification of Graphene Oxide Thickness Using White Light Contrast Spectroscopy. Carbon. 2013, vol. 52, pp. 528–534. doi: 10.1016/j.carbon.2012.10.005

28. Ye M., Zhang Z., Zhao Y., Qu L. Graphene Platforms for Smart Energy Generation and Storage. Joule. 2018, vol. 2, pp. 245–268. doi: 10.1016/j.joule.2017.11.011

29. Wang R., Qian Y., Li W., Zhu S., Liu F., Guo Y., Chen M., Li Q., Liu L. Performance-Enhanced Activated Carbon Electrodes for Supercapacitors Combining Both Graphene-Modified Current Collectors and Graphene Conductive Additive. Materials. 2018, vol. 11, iss. 11, 13 p. doi: 10.3390/ma11050799

30. Prabakar S. J. R., Hwang Y. H., Gyoung E., Dong B., Lee K., Pyo M. Graphene oxide as a corrosion inhibitor for the aluminum current collector in lithium ion batteries. Carbon. 2013, vol. 52, pp. 128–136. doi: 10.1016/j.carbon.2012.09.013

31. Wu Z., Parvez K., Feng X., Mullen K. Graphene-Based In-Plane Micro-Supercapacitors with High Power and Energy Densities. Nature communications. 2013, no. 4, article number: 2487. doi: 10.1038/ncomms3487

32. El-Kady M., Kaner R. Scalable Fabrication of High-Power Graphene Micro-Supercapacitors for flexible and On-Chip Energy Storage. Nature communications. 2013, no. 4, article number: 1475. doi: 10.1038/ncomms2446

Denis Yu. Kornilov – Cand. of Sci. (Engineering) (2008), Head of laboratory of LLC "AkKo Lab". The author of 36 scientific publications. Area of expertise: inorganic chemistry and electrochemistry.
E-mail: kornilovdenis@rambler.ru
https://orcid.org/0000-0002-4881-3209

СПИСОК ЛИТЕРАТУРЫ

1. Морозов С. В., Новоселов К. С., Гейм А. К. Электронный транспорт в графене // УФН. 2008. Т. 178, № 7. С. 776–780. doi: 10.3367/UFNr.0178.200807i.0776

2. Кульчицкий Н. А., Наумов А. В. Современное состояние тонкопленочной солнечной энергетики // Нано- и микросистемная техника. 2013. №. 9. С. 29–37.

3. Кулова Т. Л., Скундин А. М. Тонкопленочные литий-ионные аккумуляторы // Электрохимическая энергетика. 2009. Т. 9, № 2. С. 57–66.

4. Кулова Т. Л., Скундин А. М. Проблемы конструкции тонкопленочных аккумуляторов // Электрохимическая энергетика. 2011. Т. 11, № 2. С. 71–74.

5. Губин С. П., Ткачев С. В. Графен и родственные наноформы углерода. 4-е изд., доп. М.: ЛЕНАНД, 2015. 112 с.

6. Highly strong and elastic graphene fibres prepared from universal graphene oxide precursors / G. Huang, C. Hou, Y. Shao, H. Wang, Q. Zhang, Y. Li, M. Zhu // Scientific Reports. 2014. Vol. 4. Article number: 4248. doi: 10.1038/srep04248

7. Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems / A. C. Ferrari, F. Bonaccorso, V. Falko, K. S. Novoselov, S. Roche, P. Boggild, N. Pugno // Nanoscale. 2015. Vol. 7. P. 4598–4810. doi: 10.1039/c4nr01600a

8. ISO/TS 80004-13:2017 Nanotechnologies – Vocabulary. Part 13: Graphene and related two-dimensional (2D) materials. 2017. URL: https://www.iso.org/obp/ui/#iso:std:iso:ts:80004:-13:ed-1:v1:en (дата обращения 27.09.2018)

9. Особенности интеграции графенов в технологические процессы микроэлектроники / И. И. Бобринецкий, И. А. Комаров, К. К. Лаврентьев, Д. Д. Левин, М. М. Симунин, В. К. Неволин, Л. Д. Квачева, С. П. Червонобродов, А. Буриан, Л. Хавелек, Н. Возница // Изв. вузов. Электроника. 2013. № 3. С. 33–42.

10. Туннельные полевые транзисторы на основе графена / Д. А. Свинцов, В. В. Вьюрков, В. Ф. Лукичев, А. А. Орликовский, А. Буренков, Р. Охснер // Физика и техника полупроводников. 2013. Т. 47, вып. 2. С. 244–250.

11. Сорокин П. Б., Чернозатонский Л. А. Полупроводниковые наноструктуры на основе графена // Успехи физических наук. 2013. Т. 183, № 2. С. 113–132. doi: 10.3367/UFNr.0183.201302a.0113

12. Шакирзянов Ф. Н. Графен и фоторезистивный эффект // Электричество. 2011. № 1. С. 65–66.

13. Чигирев П. М. Применение графена в электронной технике // Нано- и микросистемная техника. 2011. Т. 127, № 2. С. 28–30.

14. Получение прозрачных проводящих пленок из CVD-графена методом ламинирования и их характеризация / В. Б. Тимофеев, В. И. Попов, Д. В. Николаев, Т. Е. Тимофеева, С. А. Смагулова // Российские нанотехнологии. 2017. Т. 12, № 1–2. С. 49–52.

15. Графен, полученный восстановлением оксида графена / С. В. Ткачев, Е. Ю. Буслаева, А. В. Наумкин, С. Л. Котова, И. В. Лауре, С. П. Губин // Неорганические материалы. 2012. Т. 48, № 8. С. 909–915.

16. Электрохимическое восстановление и особенности электропроводности пленок оксида графена / А. Ю. Рычагов, С. П. Губин, П. Н. Чупров, Д. Ю. Корнилов, А. С. Карасева, Е. С. Краснова, В. А. Воронов, С. В. Ткачев // Электрохимия. 2017. Т. 53, № 7. С. 813–819. doi: 10.7868/S0424857017070052

17. Восстановленный оксид графена в качестве защитного слоя токового коллектора катода литий-ионного аккумулятора / Д. Ю. Корнилов, С. П. Губин, П. Н. Чупров, А. Ю. Рычагов, А. В. Чеглаков, А. С. Карасева, Е. С. Краснова, В. А. Воронов, С. В. Ткачев, Л. А. Кашарина // Электрохимия. 2017. Т. 53, № 6. С. 701–705. doi: 10.7868/S0424857017060081

18. Суперконденсатор на основе электрохимически восстановленного оксида графена / С. П. Губин, А. Ю. Рычагов, П. Н. Чупров, С. В. Ткачев, Д. Ю. Корнилов, А. С. Алмазова, Е. С. Краснова, В. А. Воронов // Электрохимическая энергетика. 2015. Т. 15, № 2. С. 57–63.

19. Revisiting Graphene Oxide Chemistry via Spatially-Resolved Electron Energy Loss Spectroscopy / A. Tararan, A. Zobelli, A. M. Benito, W. K. Maser, O. Stephan // Chemistry of Materials. 2016. Vol. 28. P. 3741–3748. doi: 10.1021/acs.chemmater.6b00590

20. The effect of the thermal reduction on the kinetics of low-temperature 4He sorption and the structural characteristics of graphene oxide / A. V. Dolbin, M. V. Khlistuck, V. B. Eselson, V. G. Gavrilko, N. A. Vinnikov, R. M. Basnukaeva, A. M. Benito // Low Temperature Physics. 2017. Vol. 43. P. 383–389. doi: 10.1063/1.4979362

21. Tuning graphene properties by a multi-step thermal reduction process / P. Alvarez, C. Blanco, R. Santamaria, P. Blanco, Z. Gonzalez, L. Fernandez-Garcia, R. Menendez // Carbon. 2015. Vol. 90. P. 160–163. doi: 10.1016/j.carbon.2015.04.022

22. Low-temperature reduction of graphene oxide: electrical conductance and scanning kelvin probe force microscopy / O. M. Slobodian, P. M. Lytvyn, A. S. Nikolenko, V. M. Naseka, O. Y. Khyshun, A. V. Vasin, A. N. Nazarov // Nanoscale Research Letters. 2018. Vol. 13. doi: 10.1186/s11671-018-2536-z

23. Temporospatial Control of Graphene Wettability / K. Vijayarangamuthu, S. Ahn, H. Seo, S.-H. Yoon, C.-M. Park, K.-J. Jeon // Advanced Materials. 2015. Vol. 28, iss. 4. P. 661–667. doi: 10.1002/adma.201503444

24. Explosive thermal reduction of graphene oxide-based materials: Mechanism and safety implications / Y. Qiu, F. Guo, R. Hurt, I. Kulaots // Carbon. 2015. Vol. 72. P. 215–223. doi: 10.1016/j.carbon.2014.02.005

25. Singh R. K., Kumar R., Singh D. P. Graphene oxide: strategies for synthesis, reduction and frontier applications // RSC Advances. 2016. Vol. 6. P. 64993–65011. doi: 10.1039/c6ra07626b

26. Ferrari A. C. Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects // Solid State Communications. 2007. Vol. 143. P. 47–57. doi: 10.1016/j.ssc.2007.03.052

27. Rapid and non-destructive identification of graphene oxide thickness using white light contrast spectroscopy / H. Yang, H. Hu, Y. Wang, T. Yu // Carbon. 2013. Vol. 52. P. 528–534. doi: 10.1016/j.carbon.2012.10.005

28. Graphene Platforms for Smart Energy Generation and Storage / M. Ye, Z. Zhang, Y. Zhao, L. Qu // Joule. 2018. Vol. 2. P. 245–268 doi: 10.1016/j.joule.2017.11.011

29. Performance-Enhanced Activated Carbon Electrodes for Supercapacitors Combining Both Graphene-Modified Current Collectors and Graphene Conductive Additive / R. Wang, Y. Qian, W. Li, S. Zhu, F. Liu, Y. Guo, M. Chen, Q. Li, L. Liu // Materials. 2018. Vol. 11, iss. 11. 13 p. doi: 10.3390/ma11050799

30. Graphene oxide as a corrosion inhibitor for the aluminum current collector in lithium ion batteries / S. J. R. Prabakar, Y. H. Hwang, E. Gyoung, B. Dong, K. Lee, M. Pyo // Carbon. 2013. Vol. 52. P. 128–136. doi: 10.1016/j.carbon.2012.09.013

31. Graphene-based in-plane micro-supercapacitors with high power and energy densities / Z. Wu, K. Parvez, X. Feng, K. Mullen // Nature communications. 2013. № 4. Article number: 2487, doi: 10.1038/ncomms3487

32. El-Kady M., Kaner R. Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage // Nature communications. 2013. № 4. Article number: 1475. doi: 10.1038/ncomms2446

Корнилов Денис Юрьевич – кандидат технических наук (2008), заведующий лабораторией ООО "АкКо Лаб". Автор 36 научных публикаций. Сфера научных интересов – неорганическая химия и электрохимия.
E-mail: kornilovdenis@rambler.ru
https://orcid.org/0000-0002-4881-3209