REVIEW

of official reviewer for a doctoral thesis of
Kuanyshbekov Tilek Kuanyshbekuly
on the topic «Researching the properties of functionalized few-layer graphene nanostructures», submitted for the degree of Doctoral of Philosophy (PhD) in specialty 6D071000 – «Materials science and technology of new materials»

1. The relevance of the topic and its connection with general scientific and national programs (the requirements of practice and the development of science and technology).

Graphene, functionalized graphene, and its related structures remain to this day an object of increased interest in various fields of science and technology due to its unique mechanical, electrical and optical characteristics. In addition, graphene and its related structures are considered as promising materials in the production of various gas sensors, humidity sensors, electronic devices, and electrical sources, in particular, lithium-ion batteries, which can be used in various fields of production, such as nanoelectronics, aviation, military technology, and medicine. One of the main directions in the study of graphene is the study of its modifications, for example, GO, which may be referred to as functionalized few-layer graphene (FFLGN). Graphene oxide (FFLGN) is an oxide form of graphene, which is atomic-thin sheet-like material dispersed in water, which has numerous oxygen-containing groups, where oxygen is introduced into graphene by chemical oxidation. On the other hand, the most urgent task is to reduce such sheets of functionalized graphene by removing oxygen-containing groups. Reduced sheets of functionalized graphene are usually considered as one of the types of chemically produced graphene and have a number of other names such as functionalized few-layer graphene (FFLGN), chemically modified graphene, transformed graphene, or reduced GO.

The most attractive property of FFLGN is the change in its electrical and optical characteristics, which is realized by removing functional oxygen-containing groups using thermal reduction of FFLGN films and membranes in air and hydrogen atmosphere at optimum temperature conditions. Also, thermal reduction contributes to the production of graphene and graphene-like materials in a large-scale quantity, which is still an actual problem and to this day researchers are trying to achieve a large-scale and more affordable production technology.

Thesis work of Kuanyshbekov T.K. on the topic "Researching the properties of functionalized few-layer graphene nanostructures" is devoted to the synthesis and computer simulation of FFLGN, obtaining of FFLGN films and membranes and investigation of their physicochemical properties after thermal reduction at various temperatures as well as the creation of a humidity sensor based on a FFLGN membrane, and the study of its electrophysical characteristics.

Thus, the development of technology for producing FFLGN, films and membranes based on them, the study of the optical, electrical properties of FFLGN films with optimal thermal annealing, the study of the influence of temperature on the structure and composition of the FFLGN membrane after reduction, and the use

of the FFLGN membrane as a humidity sensor are an actual task in the field of materials science.

The relevance of the research topic is confirmed by its implementation in accordance of the scientific project "Development of technology in creation of protective coatings based on functionalized graphene nanostructures and investigation of their properties", funded under the financing grant of project, № AP05130413 from the Science Committee of the Ministry of Education and Science of Republic of Kazakhstan.

2. Scientific results in the framework of the requirements for dissertations (paragraphs 2, 5, 6 of the "Rules for the award of scientific degrees")

The scientific results obtained by the applicant are characterized by internal unity. The author's intention corresponds to a thought-out structure of the study. The purpose, tasks, and plan of the dissertation work correspond to its main content. Each subsequent result is based on its previous one. The thesis consists of an introduction, 3 sections, conclusion, list of used sources. The following are the main scientific results obtained by the author during the course of this work:

1. Computer simulations of some possible stable structures of graphene and few-layer graphene functionalized by Ga, FFLGN, reduced FFLGN and calculating their energy and structural characteristics were performed;

2. The technology of synthesis FFLGN by the functionalization of graphene with strong oxidizing agents such as H_2SO_4, $NaNO_3$, $KMnO_4$, and obtaining FFLGN films were optimized, and their optimal heat treatment conditions in the air at next temperatures 80 °C, 120 °C, 160 °C, 200 °C, 240 °C, 280 °C were determined, at which functional oxygen-containing groups were removed, in the result of which the optical and electrical characteristics of the films are changed;

3. It was experimentally established that with increasing of reduction temperature the significant changes of visible light transmission are observed between temperatures of 25 °C and 160 °C, as well as 200 °C and 280 °C, where the percentage of transmission decreases approximately by 20-30%, also sheet resistance decreased from 5 to 2.5 MΩ/square at temperatures of 200 °C – 280 °C, and sheet resistance of the pure FFLGN at 280 °C is more than 5 times lower than the sheet resistance of the impure FFLGN and is equal to 13 MΩ/square, also the average thickness decreased by 50 % from the initial sample thickness at 280 °C, which is explained by the removal of unstable and stable oxygen-containing groups;

4. TGA of FFLGN membrane was shown that the main mass leaves at temperatures from 150-300 °C, from 300-900 °C much weaker, also the elemental analysis by the EDS method showed changes in the C/O ratio from 4.18 to 45.08 with increasing temperature, as well as a decreasing in the interplanar distance d from 1,07 to 0.37 nm and the thickness decreased by ~37% (from 22 to 14 μm), that is explained by removal of oxygen-containing functional groups, and are presumably associated with the binding energies of the groups;

5. A simple and low-cost method was developed for creating of a humidity

sensor based on FFLGN membrane, operating in a wide range of relative humidity (5-100%), with a symmetric signal response and recovery time (360 seconds), with high stability (+/- 2%).

3. Degree of validity and reliability of each scientific result (scientific provision) and conclusion of the applicant, formulated in the thesis.

The validity and reliability of scientific results ensured by the correctness, accuracy and originality of the tasks set, the application of well-tested experimental methods and research methods.

Degree of validity and reliability of each scientific result are confirmed by a large amount of own research performed using a complex of physicochemical methods of analysis, the logical interrelation of the experimental results obtained and their consistency with generally accepted scientific principles.

The main results of the thesis were published in publications recommended by the Committee for the Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, as well as in peer-reviewed foreign scientific journals included in the Web of Science and Scopus databases and in collections of materials of international and foreign conferences.

4. The degree of novelty of each scientific result (scientific provision), conclusions of the applicant, formulated in the thesis.

The results of theoretical and experimental research presented in the dissertation are new.

1. On the basis of computer simulation of graphene nanostructures configuration with functional groups -O and -OH, the length and energies of chemical bonds are calculated using the density functional theory (DFT) considering the surface (C – O = 1.45 Å) and edge (C – O = 1.2 Å) of carbon atoms, and also to determine the energetically favorable position of the Ga atom between the graphene layers.

2. The interplanar distance of functionalized graphene nanostructures can be efficiently controlled from 1.07 to 0.37 nm with retention of highly oriented structure by thermal reduction in a hydrogen atmosphere in the temperature range from 150 to 900 ^{O}C.

3. A low sheet resistivity value of thermally reduced graphene from few-layer functionalized graphene is achieved by purifying the residual impurity chlorine atoms (Cl) and sulfur (S) at a concentration not exceeding 0.5 at.%.

4. Functionalized graphene nanostructures at a low concentration of residual chlorine (Cl) and sulfur (S) impurities are a sensitive material for absorption of water molecules and allow recording relative humidity with a symmetric time response in a wide range (from 5-100%).

5. The practical and theoretical significance of the obtained results.

- computer simulation of possible stable structures of FFLGN has been created, which can be used to better understanding the unforeseen physical and

chemical properties of FFLGN. A technology has been optimized for the production of films and membranes of FFLGN;

- the possibility of changing the electrical and optical properties of FFLGN films by removal functional oxygen-containing groups at various temperatures of thermal reduction in air is shown. Thermally reduced thin films of FFLGN can be potentially used in optoelectronics and as a conductive coating for a wide range of applications;

- thermally reduced FFLGN membranes have a developed surface, which allows them to be considered as promising materials in the manufacture of electronic devices, electrical sources and also in gas sensors;

- obtaining free-standing FFLGN membranes by the vacuum filtration method enable to use it as a humidity sensitive sensor. Dependences of the sensor's electrophysical characteristics (resistance, capacitance) on the relative humidity in a wide range were experimentally demonstrated. The results of study demonstrated the same response and recovery times, as well as stability at various levels of relative humidity.

6. Confirmation of sufficient completeness of publications of the main provisions, results and the conclusion of the dissertation

According to the materials of the thesis 9 articles were published, including 4 articles published in journals recommended by the Committee for Control in the field of Education and Science of the Ministry of Education and science of the Republic of Kazakhstan. Two articles were published in journals with impact factor Sensors & Transducers, 2019 (IF 0.3); Journal of Computational and Theoretical Nanoscience, 2019 (IF 0.45) and 3 abstracts are published in national and international conferences. All of these publications were made during the Ph.D. program.

7. Remarks, suggestions on the content and design of the dissertation.

The content of the work has the following suggestions and remarks:

1) In section 3.2.2, in Figure 32, the transmittance spectrum of the FFLGN films at different temperatures of thermal reduction (p. 60), the author designated the 100 % calibration curve as zero calibration;

2) In section 3.2.8 creation a humidity sensor based on the FFLGN membrane does not describe the influence of humidity and temperature on contact properties when determining the electrical resistance of the FFLGN membrane, and it would also be correct to indicate the voltage value applied to the contacts;

3) Some photographs showing the synthesis steps of FFLGN were small in size, which did not allow a sufficiently good view of the details of the synthesis.

4) In the work it is possible to note the presence of minor grammatical and stylistic mistakes.

8. Compliance of the dissertation with the requirements of section 2 of the "Rules for the award of scientific degrees".

The above comments are not of fundamental importance and do not reduce the scientific significance of the work. The thesis work fully meets all modern requirements for the dissertations of PhDs. Thesis "Researching the properties of functionalized few-layer graphene nanostructures", meets the requirements of section 2 of "Rules for the award of scientific degrees" to dissertations.

All experiments are well arranged and measurements techniques and methods are correctly applied. The explanations are suitable and focused on relevant topics. The combination of new scientifically based theoretical and experimental results is an important achievement in the development of materials science and technology of new materials.

Based on the above, I believe that the applicant, Kuanyshbekov T.K., deserves to be awarded the degree of Doctor of Philosophy in the specialty 6D071000 – «Materials science and technology of new materials».

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